

Preparation and thermal properties of 4-alkoxy-4'-cyanobiphenyl esters of ferrocene dicarboxylic acid *

J. Bhatt, B.M. Fung and Kenneth M. Nicholas *

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019 (USA)

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Abstract

A series of new mesogenic ferrocenyl-1,1'-diesters **2a–e** incorporating variable length alkoxy-cyanobiphenyl units have been prepared and their melting behavior has been examined. Whereas **2a, b, d** ($n = 3, 4, 8$, respectively) display normal melting properties, **2c** ($n = 6$) and **2e** ($n = 10$) both exhibit polymorphism in the solid state and **2e** has a smectic phase between 85 and 88°C.

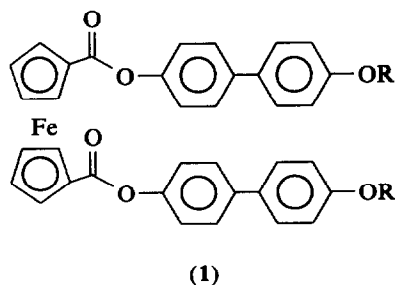
Introduction

In recent years, there has been increasing interest in the synthesis and potential applications of liquid crystalline compounds incorporating transition metals [1–9], stimulated by the prospects of imparting new optical, electrical, and magnetic properties as well as enforcing various well-defined and unique molecular geometries.

Amongst purely organic liquid crystalline compounds, a linear rod-like or a disc-like core with long flexible alkyl chains are the common structural features considered essential for mesomorphic behavior. Much of the work in transition metal-containing liquid crystalline compounds has been directed towards coupling mesogenic ligands to the metal without losing structural features essential for retaining the liquid crystalline character. Only few examples are known where the ligand by itself does not exhibit liquid crystalline behavior but its transition metal complex does.

Recently we reported the synthesis, characterization and liquid crystalline properties of a series of ferrocene-containing diesters of type **1** in which the metallocene core is substituted with two mesogenic units [10]. X-ray diffraction studies in the crystalline as well as in the liquid crystalline state were indicative of an "S"-shaped molecular conformation in both phases [11]. In an effort to provide more stable and wider liquid crystal phase temperature ranges we have sought new ferrocene-based

* Dedicated to Professor Peter Pauson on the occasion of his retirement.

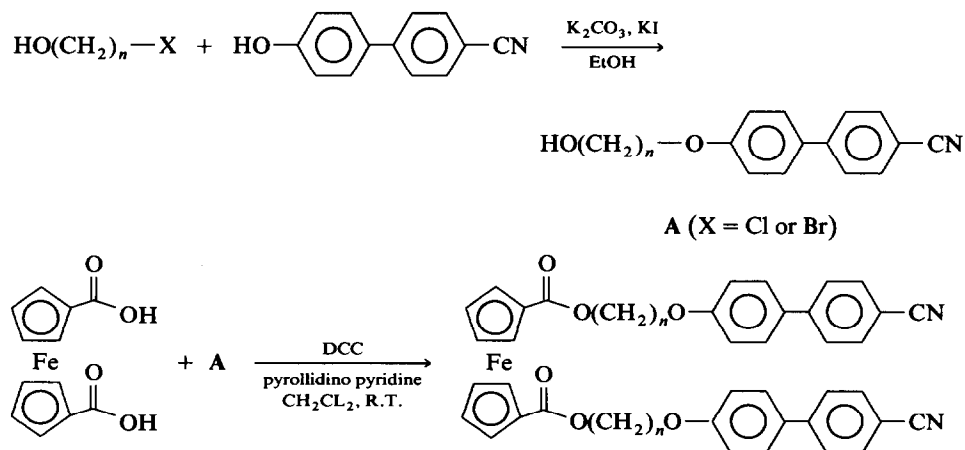


materials which incorporate the 4-alkoxy-4'-cyanobiphenyl unit, organic derivatives of which are liquid crystalline at room temperature [12]. By introducing the alkoxy cyanobiphenyl units as 1,1'-substituents on ferrocene as in **2** we anticipated a twin liquid crystalline behavior with well defined molecular geometry. We report herein the synthesis, characterization and thermal properties of several ferrocene diesters of type **2**.

Result and discussion

In order to prepare the desired compounds **2** 1,1'-ferrocene dicarboxylic acid [13] was condensed with a series of 4-(ω -hydroxyalkoxy)-4'-cyanobiphenyls as shown in Scheme 1. The latter were prepared by standard etherification methods. The ferrocene derivatives **2** were isolated in 40–60% yield as orange solids after flash chromatography and were thoroughly characterized by IR, ^1H and ^{13}C NMR, MS spectroscopy and elemental analysis.

The thermal behavior of compounds **2a–e** was studied under a polarizing microscope fitted with a heating stage. Compounds **2a**, **2b** and **2d** displayed typical melting behavior with sharp melting points of 192°C, 123°C and 99°C respectively with no evidence of LC phase. These melting points are much higher than those of



(**2a** ($n = 3$), **2b** ($n = 4$), **2c** ($n = 6$), **2d** ($n = 8$), **2e** ($n = 10$))

Scheme 1

the corresponding 4-alkoxy-4'-cyanobiphenyl derivatives but exhibit the characteristic lowering of melting points with increasing carbon chain length.

Compounds **2c** and **2e** exhibited more unusual thermal properties. Virgin crystals of **2c** melt initially at 108–120 °C and then crystallize only after standing at room temperature for 2–3 days. The crystallized material is polymorphic with one portion melting at 30–32 °C and another portion melting at 98–100 °C. Compound **2e** also exhibits a wide melting range between 70–95 °C upon first melting. After cooling the melt to room temperature for 3–4 days, this compound also crystallizes into two different forms, each exhibiting a sharp melting behavior. Thus a melt after cooling to room temperature for 3–5 days when reheated has one portion melting sharply at 53 °C; the second portion, upon further heating, exhibits a smectic phase between 85 and 88 °C (Fig. 1). Above this temperature it converts to the isotropic liquid. We have not yet determined with certainty the type of smectic phase thus produced from **2e**. This unusual behavior of **2e** is quite reproducible. Unfortunately, various attempts to obtain X-ray quality crystals of either of the two crystalline forms has only resulted in the formation of an inseparable mixture of the two with a wide melting range. Such double melting behavior has been reported for some Cu^{II} chelates [14]. According to the terminology introduced by Ohta and coworkers [15], compound **2c** exhibits “usual” double melting behavior (no liquid crystal phase) whereas **2e** exhibits “unusual” double melting behavior (i.e. with a l.c. phase).

Although one of the alkoxy-cyanobiphenyl-containing ferrocene diesters (**2e**) exhibited polymorphic behavior with one crystalline form passing through a 3° C smectic phase, it appears that insertion of the ferrocene group between the two mesogenic alkoxy-cyanobiphenyl units significantly attenuates liquid crystalline properties. This may reflect the “kinking” effect of the ferrocene unit on the

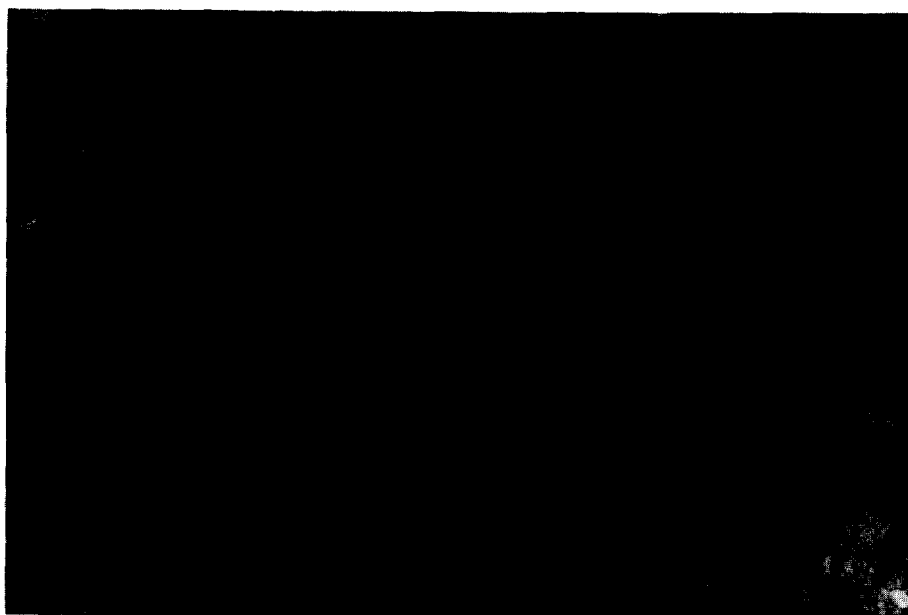


Fig. 1. Smectic phase exhibited by **2e**.

otherwise grossly linear molecular geometry. It is noteworthy that compounds containing a butadiene iron tricarbonyl unit at one end of the extended mesomorphic moiety have recently been shown to exhibit liquid crystalline behavior [16]. Similarly, the first reported ferrocene-containing liquid crystalline compounds [17] had the ferrocene unit located at the end of the mesomorphic molecule. Perhaps the distance between the two cyclopentadienyl rings in ferrocene is too large, thereby adversely affecting the symmetry and the packing of molecules. Thus in order to enhance the mesogenic properties of metallocene compounds, it may be necessary to have more highly extended mesogenic units which would help in increasing the l/w (length to width) ratio.

Experimental

General

^1H and ^{13}C NMR spectra were obtained at 300 and 75.4 MHz, respectively. IR spectra were recorded either as KBr pellets or as solutions in dichloromethane on a Perkin Elmer 1420 ratio-recording IR spectrophotometer. Elemental analysis on compounds **2c**, **d**, **e** were carried out by Midwest Microlabs, Ltd. The polarizing microscope studies were performed using an Olympus BH-2 polarizing microscope fitted with a Linkam PR600 heating stage and photographs were taken using an Olympus OM camera using Ektachrome 160 slide film.

Glassware was oven dried at 120 °C overnight followed by flame drying of the reaction setup. All reactions were carried out under a nitrogen atmosphere. Dichloromethane was freshly distilled over calcium hydride just prior to use. Flash column chromatography was carried out with E. Merck silica gel (230–400 mesh) under nitrogen pressure (10–15 psi). TLC aluminum plates with 0.2 mm silica gel 60 F₂₅₄ coating were obtained from EM Science. 4-Hydroxy-4'-cyanobiphenyl (BDH Chemicals), ω -halo-1-alcohols (Aldrich Chemical Co.), dicyclohexylcarbodiimide (DCC) (Aldrich), pyrrolidino pyridine (Aldrich), and ferrocene (Pressure Chemical Co.) were used without further purification.

The melting behavior of the compounds were studied using a Linkam TH600/PR600 heating stage mounted on Olympus BH-2 polarizing microscope fitted with an Olympus OM-2S camera.

4-(ω -Hydroxyalkoxy)-4'-cyanobiphenyls

An aqueous ethanolic solution (70% ethanol:30% water; 8–10 mL) containing 1.1 g (7.7 mmol) of K_2CO_3 and 1.28 g (7.7 mmol) of KI was added dropwise over two days to a stirred mixture of 4-hydroxy-4'-cyanobiphenyl (5.1 mmol) and the appropriate halo alcohol ($n = 3, 4, 6$ and 10 , $\text{X} = \text{Cl}$; $n = 8$, $\text{X} = \text{Br}$, 5.1 mmol) in ethanol at reflux. The mixture was neutralized by addition of 10% HCl solution and extracted into dichloromethane. The organic extract is washed with 50 mL distilled water, dried over Na_2SO_4 , and evaporated. The 4-(ω -hydroxyalkoxy)-4'-cyanobiphenyls were isolated by chromatography using 10% EtOAc: CH_2Cl_2 as eluant (55–65% yield).

4-(3-Hydroxypropyloxy)-4'-cyanobiphenyl. ^1H NMR (300 MHz, CDCl_3) δ 7.7 (d, 8.2 Hz, 2H), 7.6 (d, 8.3 Hz, 2H), 7.5 (d, 8.9 Hz, 2H), 7.0 (d, 8.7 Hz, 2H), 4.2 (t, 5.9 Hz, 2H), 3.9 (bt, 2H, OH), 2.1 (q, 5.9 Hz, 2H); IR (KBr) 3300–3500, 3080, 2890

and 2950, 2230, 1600, 1490 cm^{-1} ; HRMS m/e calc. for $\text{C}_{16}\text{H}_{15}\text{NO}_2$: 253.1103, found 253.1114.

4-(6-Hydroxyhexyloxy)-4'-cyanobiphenyl. ^1H NMR (300 MHz, CDCl_3) δ 7.7 (d, 8.5 Hz, 2H), 7.6 (d, 8.4 Hz, 2H), 7.5 (d, 8.6 Hz, 2H), 6.9 (d, 8.6 Hz, 2H), 4.0 (t, 6.5 Hz, 2H), 3.7 (t, 6.5 Hz, 2H), 1.8–1.3 (m, 8H); IR (KBr) 3200–3400, 3080, 2860 and 2940, 2240, 1610, 1495 cm^{-1} .

4-(8-Hydroxyoctyloxy)-4'-cyanobiphenyl. ^1H NMR (300 MHz, CDCl_3) δ 7.7 (d, 8.6 Hz, 2H), 7.6 (d, 8.6 Hz, 2H), 7.5 (d, 8.8 Hz, 2H), 7.0 (d, 8.8 Hz, 2H), 4.0 (t, 6.5 Hz, 2H), 3.6 (t, 6.6 Hz, 2H), 1.8 (m, 2H), 1.6–1.4 (m, 10H); IR (KBr) 3200–3400, 3080, 2860 and 2940, 2240, 1610, 1495 cm^{-1} ; HRMS m/e calc. for $\text{C}_{21}\text{H}_{29}\text{NO}_2$: 323.1885, found 323.1897.

4-(4-Hydroxybutoxy)-4'-cyanobiphenyl could not be prepared directly from 4-chloro-1-butanol because of extensive conversion of 4-chloro-1-butanol to tetrahydrofuran. A tetrahydropyranyl protection–deprotection sequence was utilized according to the procedure given in ref. 18.

4-(4-Hydroxybutoxy)-4'-cyanobiphenyl. ^1H NMR (300 MHz, CDCl_3) δ 7.7 (d, 8.4 Hz, 2H), 7.6 (d, 8.4 Hz, 2H), 7.5 (d, 8.7 Hz, 2H), 7.0 (d, 8.7 Hz, 2H), 4.1 (t, 6.1 Hz, 2H), 3.8 (t, 6.3 Hz, 2H), 1.9 (m, 2H), 1.8 (m, 2H); IR (KBr) 3300–3500, 3080, 2895 and 2950, 2240, 1610, 1495 cm^{-1} .

Synthesis of ferrocene diesters, 2

One equivalent of ferrocene-1,1'-dicarboxylic acid was stirred with 2 equiv. of the 4-(ω -hydroxyalkoxy)-4'-cyanobiphenyl and 2 equiv. of dicyclohexylcarbodiimide in CH_2Cl_2 (dried over CaH_2) under an N_2 atmosphere. Pyrrolidinopyridine (0.1 equiv.) was added as a catalyst. The mixture was then stirred at room temperature for 48 h, after which it was filtered through Celite and the CH_2Cl_2 evaporated. The compounds **2** were isolated as orange powders following chromatography over flash silica gel using 10% EtOAc : CH_2Cl_2 as eluant (40–60% yields). Spectroscopic and analytical data are summarized below.

2a. M.p. 192 °C; R_f 0.85 (5% ethyl acetate : 95% dichloromethane); ^1H NMR (300 MHz, CDCl_3) δ 2.25 (q, 4H), 4.18 (t, 6.2 Hz, 4H), 4.39 (t, 1.9 Hz, 4H), 4.44 (t, 6.3 Hz, 4H), 4.81 (t, 1.9 Hz, 4H), 7.04 (d, 8.8 Hz, 4H), 7.54 (d, 8.7 Hz, 4H), 7.63 (d, 8.4 Hz, 4H), 7.69 (d, 8.5 Hz, 4H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 30.1, 63.0, 66.1, 73.0, 74.0, 74.5, 112.0, 116.5, 121.0, 129.0, 130.0, 134.0, 134.5, 147.0, 161.5, 172.0; IR (KBr) 3120–3040, 3000–2900, 2240, 1715, 1610, 1500, 1285, 1255 cm^{-1} ; HRMS m/e calc. for $\text{C}_{44}\text{H}_{36}\text{N}_2\text{O}_6\text{Fe}$: 744.1875, found 744.1923.

2b. M.p. 123 °C; R_f 0.85 (5% ethyl acetate : CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 1.95–2.05 (m, 8H), 4.09 (t, 5.1 Hz, 4H), 4.32 (t, 5.7 Hz, 4H), 4.41 (4H), 4.84 (4H), 7.00 (d, 8.8 Hz, 4H), 7.54 (d, 8.8 Hz, 4H), 7.64 (d, 8.4 Hz, 4H), 7.70 (d, 8.5 Hz, 4H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 27.2, 27.8, 66.0, 69.5, 73.0, 74.5, 74.8, 121.0, 112.0, 116.5, 129.0, 130.0, 133.4, 134.2, 147.0, 161.5, 172.0; IR (KBr) 3040–3020, 2960, 2240, 1715, 1610, 1500, 1280, 1255 cm^{-1} ; HRMS m/e calc. for $\text{C}_{46}\text{H}_{40}\text{N}_2\text{O}_6\text{Fe}$: 772.2236, found 772.2294.

2c. M.p. 31 and 99 °C; R_f 0.85 (5% ethyl acetate : CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 1.51–1.6 (m, 8H), 1.76–1.89 (m, 8H), 4.03 (t, 6.4 Hz, 4H), 4.25 (t, 6.6 Hz, 4H), 4.39 (t, 1.9 Hz, 4H), 4.83 (t, 1.9 Hz, 4H), 7.00 (d, 8.8 Hz, 4H), 7.56 (d, 8.7 Hz, 4H), 7.64 (d, 8.5 Hz, 4H), 7.70 (d, 8.5 Hz, 4H); ^{13}C NMR (CDCl_3) δ 27.0, 30.0, 30.5, 66.0, 69.5, 73.0, 74.0, 74.5, 111.5, 116.0, 121.0, 128.0, 129.5, 133.0, 134.0, 146.5,

161.0, 172.0; IR (KBr) 3100, 2940–2880, 2240, 1715, 1610, 1500, 1300–1250 cm^{-1} ; HRMS m/e calc. for $\text{C}_{50}\text{H}_{48}\text{N}_2\text{O}_6\text{Fe}$: 828.2862, found 828.2905; elemental analysis. calc. (found): C 71.2 (72.48); H 5.93 (5.8), N 3.75 (3.38)%.

2d. M.p. 99°C; R_f 0.85 (5% ethyl acetate : dichloromethane); ^1H NMR (300 MHz, CDCl_3) δ 7.7 (d, 8.4 Hz, 4H), 7.5 (d, 8.7 Hz, 4H), 7.6 (d, 8.5 Hz, 4H), 7.0 (d, 8.8 Hz, 4H), 4.8 (t, 3.8 Hz, 4H), 4.4 (t, 3.8 Hz, 4H), 4.2 (t, 6.7 Hz, 4H), 4.0 (t, 6.5 Hz, 4H), 1.8–1.7 (m, 8H), 1.6–1.3 (m, 16H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 172, 161.5, 147, 134, 133, 130, 129, 121, 117, 112, 74.8, 74.5, 73.2, 69.8, 66.2, 31, 30.9, 30.55, 27.7; IR (KBr) 3040–3110, 2860–2940, 2240, 1720, 1610, 1500, 1285, 1260 cm^{-1} ; HRMS m/e calc. for $\text{C}_{54}\text{H}_{56}\text{N}_2\text{O}_6\text{Fe}$: 884.3488, found 884.3564; elemental analysis. calc. (found): C 72.81 (72.33), H 6.34 (6.34), N 3.75 (3.38)%.

2e. M.p. 53 and 86°C; R_F 0.8 (5% ethyl acetate : dichloromethane); ^1H NMR (300 MHz, CDCl_3) δ 7.7 (d, 8.4 Hz, 4H), 7.6 (d, 8.4 Hz, 4H), 7.5 (d, 8.5 Hz, 4H), 6.9 (d, 8.6 Hz, 4H), 4.8 (bs, 4H), 4.4 (bs, 4H), 4.2 (t, 6.7 Hz, 4H), 3.9 (t, 6.5 Hz, 4H), 1.8–1.7 (m, 8H), 1.2–1.5 (m, 24H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 172, 162, 147, 134, 133, 130, 129, 121, 117, 112, 75, 74.6, 73.5, 70, 66.5, 31.25, 31.1, 31, 30.5, 27.6; IR (KBr) 3040–3120, 2860–2940, 2240, 1710, 1610, 1500, 1260, 1280 cm^{-1} ; HRMS m/e calc. for $\text{C}_{58}\text{H}_{64}\text{N}_2\text{O}_6\text{Fe}$: 940.4114, found 940.4150; elemental analysis. calc. (found): C 74.03 (74.05), H 6.84 (6.81), N 3.04 (2.98)%.

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