A Liquid Crystalline [3]Ferrocenophane

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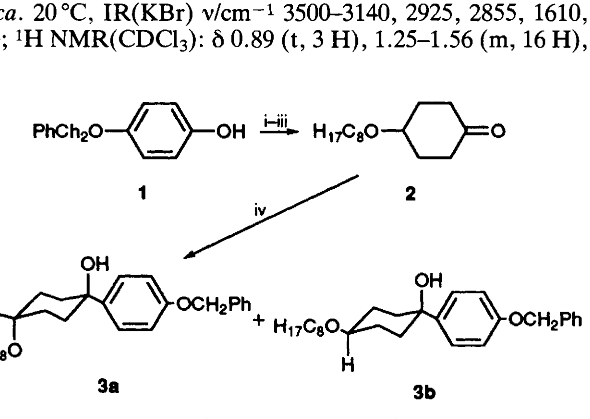
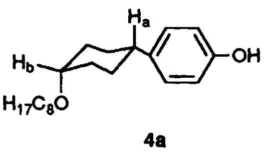
The first example of a liquid crystal with a ferrocenophane unit is described.

In recent years organometallic liquid crystals have attracted considerable interest because of their unique properties and their potential technological applications.[1] Ferrocene derivatives have been investigated quite intensively in this respect.[2–10] The conformation of the molecules in the liquid crystal (LC) phase is not always known with certainty, but due to a recent report[11] the mesogenic 1,1′-*bis*(4′-*p*-propoxybenzoyl-4″-methylidenephenoxyazinomethyl)ferrocene exhibits a *cis*-conformation in the crystalline state. These findings, which are not unexpected, prompt us to report our results concerning a [3]ferrocenophane as building block for a novel LC compound with a fixed U-shaped (*cis*) structure. Here we describe the first bridged ferrocene with LC properties **6b**.

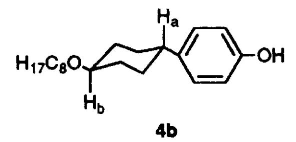
The cycloaliphatic moiety of **6b** was prepared as follows. Treatment of the sodium salt of 4-benzyloxyphenol **1** with 1-bromooctane in the presence of a small amount of potassium iodide gave 1-benzyloxy-4-octyloxybenzene [71%, crystals from diethyl ether–pentane, mp 68–69 °C; ^{1}H NMR($CDCl_3$) δ 0.85 (t, 3 H), 0.99–1.89 (m, 12 H), 3.82 (t, 2 H), 4.93 (s, 2 H), 6.69–6.96 (m, 4 H), 7.17–7.48 (m, 5 H)], which was reduced with Raney nickel (180 atm, 160 °C, 7 h) to 4-octyloxycyclohexanol obtained as a mixture of stereoisomers (93%, oil). The oxidation of this mixture with pyridinium dichromate (PDC)–pyridinium trifluoracetate (CH_2Cl_2, room temp., 3 h) yielded **2** [colourless oil, 95% IR(film) ν/cm^{-1} 1715; ^{1}H NMR($CDCl_3$) δ 0.87 (t, 3 H), 1.03–2.80 (m, 20 H), 3.47 (t, 2 H), 3.58–3.76 (m, 1 H)]. Treatment of **2** with the Grignard reagent prepared from 4-benzyloxy-1-bromobenzene gave **3a** {colourless oil, 11%, IR(film) ν/cm^{-1} 3500–3300, 3080–3030, 2920, 2850, 1605, 1240, 1105; ^{1}H NMR($CDCl_3$) δ 0.88 (t, 3 H), 1.24–1.61 (t, 15 H), 1.78–1.96 (m, 4 H), 2.14–2.24 (m, 2 H), 3.41 (t, 2 H), 3.58 (q, 1 H), 5.07 (s, 2 H), 6.97 (dd, 2 H), 7.31–7.47 (m, 7 H); MS (*m*/*z*) 410.2820 [M$^+$(calc) for $C_{27}H_{38}O_3$], 410.2819 [M$^+$(obs)]} and **3b** {colourless crystals from diethyl ether–pentane, 35%, mp 54–55 °C, IR(KBr) ν/cm^{-1} 3490–3300, 3060–3030, 2920, 2850, 1608, 1242, 1105; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.20–1.44 (m, 10 H), 1.55–1.67 (m, 3 H), 1.69–1.96 (m, 8 H), 3.30 (tt, 1 H), 3.48 (t, 2 H), 5.05 (s, 2 H), 6.94 (dd, 2 H), 7.29–7.45 (m, 7 H); MS (*m*/*z*) 410.2820 [M$^+$(calc) for $C_{27}H_{38}O_3$], 410.2821 [M$^+$(obs)]}, which could be separated by flash chromatography. The removal of the protective group and the reduction of the hydroxy group was accomplished both with Pd and Raney nickel. Whereas treatment of **3a** with Pd (MeOH, room temp., 2.5 h) yielded **4a** exclusively {colourless crystals, 92%, mp *ca.* 20 °C, IR(KBr) ν/cm^{-1} 3500–3140, 2925, 2855, 1610, 1080; ^{1}H NMR($CDCl_3$): δ 0.89 (t, 3 H), 1.25–1.56 (m, 16 H), 1.78 (dq, 2 H), 2.02 (dq, 2 H), 2.47 (tt, $^3J_{aa}$ 11.7, $^3J_{ae}$ 3.0 Hz, 1 H), 3.41 (t, 2 H), 3.59 (m, $^3J_{ae}$ $^3J_{ee}$ 3.0 Hz, 1 H), 6.77 (dd, 2 H), 7.11 (dd, 2 H); MS(*m*/*z*) 304.2394 [M$^+$(calc)] for $C_{20}H_{32}O_2$], 304.2396 [M$^+$ (obs)]}, the reduction of **3b** with Raney nickel (ethanol, reflux, 6.5 h) gave a mixture of **4a** (55%) and **4b** {colourless crystals, 19%, mp 80–81 °C, IR(KBr) ν/cm^{-1} 3500–3240, 2950, 2920, 2850, 1608, 1103; ^{1}H NMR($CDCl_3$) δ 0.88 (t, 3 H), 1.25–1.66 (m, 16 H), 1.89 (dq, 2 H), 2.16 (dq, 2 H), 2.45 (tt, $^3J_{aa}$ 11.7, $^3J_{ae}$ 3.4 Hz, 1 H), 3.28 (tt, $^3J_{aa}$ 10.3, $^3J_{ae}$ 3.2 Hz, 1 H), 3.50 (t, 2 H), 6.77 (dd, 2 H), 7.08 (dd, 2 H); MS (*m*/*z*) 304.2394 [M$^+$(calc) for $C_{20}H_{32}O_2$], 304.2402 [M$^+$(obs)]}.† The structures of **4a** and **b** have been clarified unambiguously by their ^{1}H NMR spectra: for **4a** (only one conformer is observed) H_a shows the coupling constants $^3J_{aa}$ 11.7 and $^3J_{ae}$ 3 Hz, whereas for H_b the values $^3J_{ea}$ 3.0 and $^3J_{ee}$ 3.0 Hz are found; for **4b** similar values for H_a are observed as for **4a** ($^3J_{aa}$ 11.7, $^3J_{ae}$ 3.4 Hz), but the coupling constants for H_b are quite different ($^3J_{aa}$ 10.3, $^3J_{ae}$ 3.2 Hz).[12] Esterification of **5a**,**b** then gave **6a**,**b**. The mixture of **5a**,**b** was obtained[13] by treatment of [3]ferrocenophane[14] with Bu^{n}Li/CO_2; it is well known, that this reaction yields the 2,2′- and 3,3′-isomers exclusively.[13] Without separation the acid chlorides (CH_2Cl_2, oxalyl chloride, small amount of pyridine, 12 h room temp., 6 h reflux; dark-red crystals, 58%, mp 155–157 °C) were treated with the lithium salt of **4b** (Bu^{n}Li, THF) to give **6a**,**b** (THF, reflux, 1 h), which could be separated by chromatography (silica gel, pentane–diethyl ether = 9/1) {**6a**: orange-brown needles, 29%, mp 135.5 °C, UV(MeCN) λ_{max} (log ε) 208 (4.70), 248 (4.10), 290 (3.35), 410 (2.47); IR(KBr) ν/cm^{-1} 3100, 3080, 2950, 2925, 2850, 1728, 1720, 1600, 1285, 1106; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 6 H), 1.19–1.62 (m, 32 H), 1.81–2.23



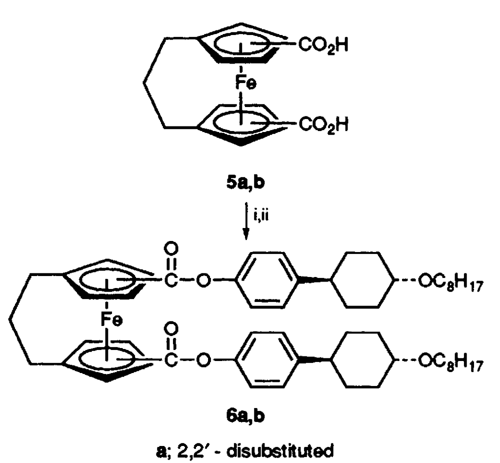
Scheme 1 *Reagents and conditions*: i, NaOEt, EtOH, 1-bromooctane, KI; ii, H_2/Ni, 160 °C, 180 bar; iii, PDC, pyridine, CF_3CO_2H, CH_2Cl_2; iv, Mg, 1-BrC_6H_4-4-CH_2Ph; NH_4Cl, H_2O



4a



4b



6a,b

a; 2,2′-disubstituted
b; 3,3′-disubstituted

$$\boxed{\textbf{6b};\ \mathrm{C}\xrightarrow{100\,^{\circ}\mathrm{C}}\mathrm{SmC}\xrightarrow{139.5\,^{\circ}\mathrm{C}}\mathrm{N}\xrightarrow{158\,^{\circ}\mathrm{C}}\mathrm{I}}$$

Scheme 2 *Reagents and conditions*: i, oxalyl chloride, CH_2Cl_2, reflux; ii, **4b**–Bu^{n}Li, THF, room temp., reflux (m, 11 H), 2.46 (tt, 2 H), 2.65–2.84 (m, 3 H), 3.26 (tt, 2 H), 3.49 (dd, 4 H), 4.29 (dd, 2 H), 4.33 (dd, 2 H), 5.02 (dd, 2 H), 6.96 (dd, 4 H), 7.00 (dd, 4 H); MS (m/z) 886.4815 [M$^+$(calc)] for $C_{55}H_{74}O_6Fe$], 886.4793 [M$^+$(obs)]; **6b**: orange–brown needles, 24%, mp 100 °C, UV(MeCN) λ_{max} (log ε) 208 (4.48), 245 (3.88), 300 (3.34), 420 (2.53); IR (KBr) ν/cm^{-1} 3090, 3040, 2920, 2850, 1721, 1600, 1290, 1101; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 6 H), 1.24–1.65 (m, 34 H), 1.87–2.21 (m, 12 H), 2.46 (tt, 2 H), 3.25 (tt, 2 H), 3.48 (t, 4 H), 4.27 (dd, 2 H), 5.03 (dd, 4 H), 6.92 (dd, 4 H), 6.98 (dd, 4 H); MS (m/z) 886.4815 (M$^+$[calc.] for $C_{55}H_{74}O_6Fe$), 886.4811 (M$^+$[obs])}.

The isomers **6a** (2,2′) and **6b** (3,3′) can be identified by the different coupling schemes in the cyclopentadienyl rings; the ^3J constants are in the region of 2.5 Hz, whereas the values for ^4J are near 2 Hz. In accordance with these findings **6a** (2,2′) shows the following values for the chemical shifts and coupling constants: δ 4.29 (dd, 2 H, $^3J_{3,4}$ $^3J_{4,5}$ 2.6 Hz, 4,4′-H), δ 4.33 (dd, 2 H, $^3J_{3,4}$ 2.6, $^4J_{3,5}$ 1.5 Hz, 3,3′-H), and δ 5.02 (dd, 2 H, $^3J_{4,5}$ 2.6 Hz, $^4J_{3,5}$ 1.5 Hz, 5,5′-H). The values of ^3J and ^4J for **6b** are nearly identical: δ 4.27 (dd, 2 H, $^3J_{4,5}$ $^4J_{2,4}$ 2.0 Hz, 4,4′-H) and δ 5.03 (dd, 4 H, $^3J_{4,5}$ $^4J_{2,4}$ $^4J_{2,5}$ 2.0 Hz, 2,2′-H, 5,5′-H). The thermal behaviour of **6a** and **b** was investigated by optical microscopy. Whereas **6a** showed normal behaviour with a sharp mp at 135.5 °C, a detailed investigation of **6b** revealed a phase transition at 100 °C giving a SmC phase;[15] at 139.5 °C a nematic phase was formed. The transition to the isotropic state occurred at 158 °C. As **6b** is thermally stable this cycle could be observed several times. Compound **6b** constitutes the first member in the family of liquid crystals with a ferrocenophane structure unit.

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Footnote

† A similar result was obtained with Pd in MeOH (80% **4a**, 11% **4b**).

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