

On the Synthesis of Potential Ferrocene Liquid Crystals

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Condensation products of ferrocenecarbaldehyde and 1,1'-ferrocenedicarbaldehyde with 4-(*N'*-alkylpiperazinyl)anilines were prepared, and their liquid crystalline (LC) properties were examined. None of the prepared ferrocene derivatives possesses the LC properties.

The first review on liquid crystal substances was published in 1957 by *Brown and Shaw* [1]. Since that time synthesis of substances possessing liquid crystalline properties attracts the great attention of the chemists [2–6]. It was found, in contradiction with the first hypothesis, that cyclohexane [7–9] as well as piperazine [10, 11] moiety can be present along the main axis of such molecules. Synthesis of ferrocene derivatives with liquid crystalline properties became a very active field of research, documented in *Deschenaux* review [12]. In the most ferrocene liquid crystals there is a long unit attached to the ferrocene *via* carboxy or carboxyalkyl group. The main goal of this work was to examine liquid crystalline properties of such ferrocene derivatives, which have a long unit including piperazine moiety attached to ferrocene *via* imino group.

The crucial intermediates for the synthesis of final compounds were ferrocenecarbaldehyde, 1,1'-ferrocenedicarbaldehyde, and 4-(*N'*-alkylpiperazinyl)anilines. Ferrocene carbaldehydes were prepared according to [13, 14], *N*-(1-octyl)piperazine was prepared analogously to [15], and 4-(*N'*-alkylpiperazinyl)anilines were prepared by modification of the procedure given in [16] (Scheme 1).

Condensations of substituted anilines with ferrocenecarbaldehydes proceeded smoothly and according to TLC practically quantitatively (Scheme 2).

However, the yields of the isolated products were much lower, which was caused by the problems connected with their chromatographic separation. To our surprise the purification of *N'*-octyl derivatives was simpler than that of *N'*-methyl derivatives. No attention has been paid to the optimization of the reaction procedures. The liquid crystalline behaviour of the prepared derivatives was checked by DTA and by measuring their melting points under polarizing microscope, but unfortunately they melted into isotropic fluids.

EXPERIMENTAL

¹H NMR spectra were recorded in CDCl₃ on a Tesla BS 487 (80 MHz) instrument with tetramethylsilane as internal standard. Melting points were measured on a Kofler hot plate apparatus. Solvents were purified according to published methods. Ferrocenecarbaldehyde and 1,1'-ferrocenedicarbaldehyde were prepared according to Refs. [13] and [14], respectively. *N*-Methylpiperazine (Aldrich) was used without purification.

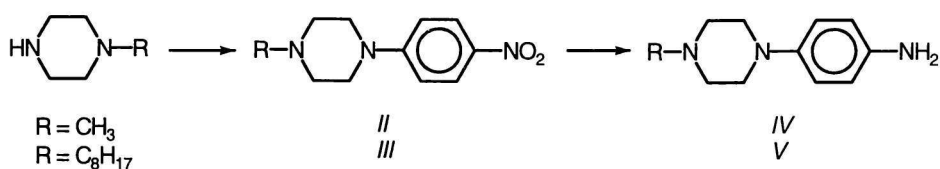
N-(1-Octyl)piperazine (I)

The solution of piperazine (50 mmol) and 1-iodooctane (20 mmol) in methanol (12 cm³) was stirred for three days at room temperature. The precipitated piperazinium iodide was filtered off and the residue was poured into 2 M sodium hydroxide. Product was extracted into diethyl ether, ethereal solution was dried over sodium sulfate. The residue left after evaporation of the solvent was vacuum-distilled, b.p. = 143–145 °C (2 kPa). *N*-(1-Octyl)piperazine was isolated in 50 % yield as a clear liquid. For C₁₂H₂₆N₂ (*M*_r = 198.4) *w*_i(calc.): 72.66 % C, 13.21 % H, 14.13 % N; *w*_i(found): 72.56 % C, 13.17 % H, 14.05 % N. ¹H NMR spectrum, δ: 0.88 (t, 3H, CH₃), 1.28 (m, 12H, (CH₂)₆), 1.68 (s, 1H, NH), 2.33 (t, 2H, CH₂), 2.39 (t, 4H, CH₂), 2.91 (t, 4H, CH₂).

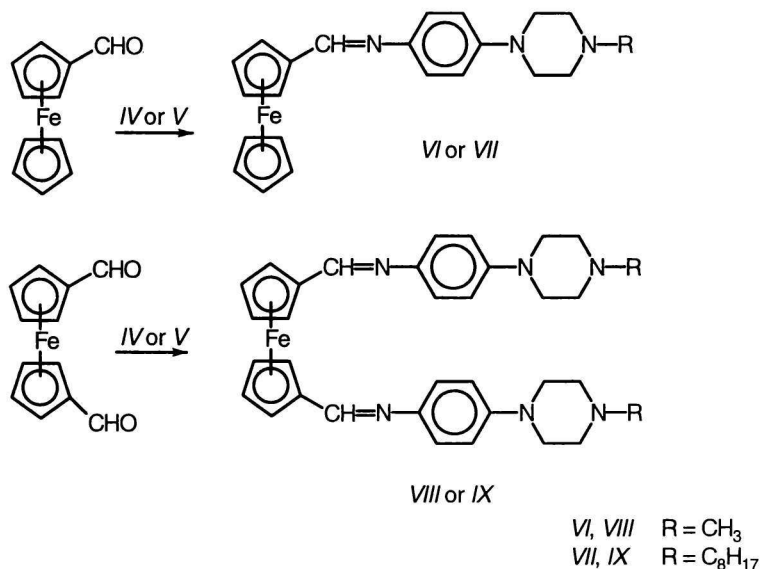
4-(4-Methylpiperazino)nitrobenzene (II)

Anhydrous potassium carbonate (13 mmol) was added to the stirred solution of 4-chloronitrobenzene (10 mmol) and *N*-methylpiperazine (11 mmol) in DMSO (10 cm³) and the reaction mixture was stirred at 100 °C for 3 h. Water (75 cm³) was then added and the precipitated product was filtered off and dried. The material was then purified by col-

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Scheme 1



Scheme 2

umn chromatography on silica gel. The unreacted 4-chloronitrobenzene was eluted by ethyl acetate and the product was eluted using the ethyl acetate—triethylamine ($\varphi_r = 10:1$) mixture. The product was isolated as yellowish powder, m.p. = 108–110°C, in 50 % yield. For $\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_2$ ($M_r = 221.3$) $w_i(\text{calc.})$: 59.71 % C, 6.83 % H, 18.99 % N; $w_i(\text{found})$: 59.30 % C, 6.83 % H, 18.88 % N. ^1H NMR spectrum, δ : 2.35 (s, 3H, CH_3), 2.55 (t, 4H, CH_2), 3.44 (t, 4H, CH_2), 6.81 (d, 2H, $J_{\text{AB}} = 9.52$ Hz, H_{arom}), 8.10 (d, 2H, $J_{\text{AB}} = 9.52$ Hz, H_{arom}).

4-(4-Octylpiperazino)nitrobenzene (III)

The reaction was performed as described above, just *N*-octylpiperazine (11 mmol) was used instead of *N*-methylpiperazine. The product, yellow crystals, m.p. = 68–70°C, was isolated in 33 % yield. For $\text{C}_{18}\text{H}_{29}\text{N}_3\text{O}_2$ ($M_r = 319.5$) $w_i(\text{calc.})$: 67.68 % C, 9.15 % H, 13.15 % N; $w_i(\text{found})$: 67.36 % C, 9.19 % H, 13.28 % N. ^1H NMR spectrum, δ : 0.89 (t, 3H, CH_3), 1.30 (m, 12H, $(\text{CH}_2)_6$), 2.40 (t, 2H, CH_2), 2.58 (t, 4H, CH_2), 6.81 (d, 2H, $J_{\text{AB}} = 9.46$ Hz, H_{arom}), 8.11 (d, 2H, $J_{\text{AB}} = 9.46$ Hz, H_{arom}).

4-(4-Methylpiperazino)aniline (IV)

The solution of *II* (2.85 mmol) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (17.1 mmol) in concentrated hydrochloric acid (17 cm^3) was refluxed for 30 min. Reaction mixture was then poured on crushed ice, alkalized by addition of Na_2CO_3 and organic material was extracted into diethyl ether. Ethereal solution was dried over anhydrous sodium sulfate, solvent was evaporated and the residue was chromatographed on silica gel using the mixture ethyl acetate—triethylamine ($\varphi_r = 10:1$) as the eluent. The yellow crystals of the product, m.p. = 82–85°C, were isolated in 27 % yield. For $\text{C}_{11}\text{H}_{17}\text{N}_3$ ($M_r = 221.3$) $w_i(\text{calc.})$: 69.07 % C, 8.96 % H, 21.97 % N; $w_i(\text{found})$: 69.07 % C, 8.97 % H, 21.92 % N. ^1H NMR spectrum, δ : 2.34 (s, 3H, CH_3), 2.57 (t, 4H, CH_2), 3.08 (t, 4H, CH_2), 3.25 (bs, 2H, NH_2), 6.65 (d, 2H, $J_{\text{AB}} = 9.22$ Hz, H_{arom}), 6.88 (d, 2H, $J_{\text{AB}} = 9.22$ Hz, H_{arom}).

4-(4-Octylpiperazino)aniline (V)

The reaction was performed as described above, just *III* (2.85 mmol) was used instead of *II*. The yellow crystals of the product, m.p. = 69–73°C, were

isolated in 64 % yield. For $C_{18}H_{31}N_3$ ($M_r = 289.5$) w_i (calc.): 74.69 % C, 10.79 % H, 14.52 % N; w_i (found): 74.21 % C, 10.74 % H, 14.30 % N. 1H NMR spectrum, δ : 0.89 (t, 3H, CH_3), 1.30 (m, 12H, $(CH_2)_6$), 2.40 (t, 2H, CH_2), 2.57 (t, 4H, CH_2), 3.09 (t, 4H, CH_2), 3.24 (bs, 2H, NH_2), 6.62 (d, 2H, $J_{AB} = 9.16$ Hz, H_{arom}), 6.82 (d, 2H, $J_{AB} = 9.16$ Hz, H_{arom}).

**(4-(*N'*-Methylpiperazinyl)phenyl)-
iminomethylferrocene (VI)**

Solution of ferrocenecarbaldehyde (1 mmol) and 1 mmol of IV in ethanol (10 cm^3) was heated under reflux for 15 min. Water was then added to the reaction mixture and precipitated product VI was filtered off, washed with cold ethanol and recrystallized from the same solvent. Product was isolated in 35 % yield as orange crystals, m.p. = 158–160 °C. For $C_{22}H_{25}FeN_3$ ($M_r = 387.3$) w_i (calc.): 68.22 % C, 6.51 % H, 10.85 % N; w_i (found): 68.29 % C, 6.48 % H, 10.64 % N. 1H NMR spectrum, δ : 2.36 (s, 3H, CH_3), 2.58 (t, 4H, CH_2), 3.29 (t, 4H, CH_2), 4.22 (s, 5H, Cp), 4.45 (t, 2H, H_β), 4.78 (t, 2H, H_α), 6.92 (d, 2H, $J_{AB} = 9.03$ Hz, H_{arom}), 7.15 (d, 2H, $J_{AB} = 9.03$ Hz, H_{arom}), 8.34 (s, 1H, $CH=N$).

**(4-(*N'*-Octylpiperazinyl)phenyl)-
iminomethylferrocene (VII)**

Solution of ferrocenecarbaldehyde (0.35 mmol) and 0.35 mmol of V in ethanol (3.5 cm^3) was heated under reflux for 20 min. The reaction mixture was cooled down and precipitated product VII was filtered off, washed with cold diethyl ether and recrystallized from dichloromethane–diethyl ether mixture. Product was isolated in 71 % yield as orange crystals, m.p. = 110–113 °C. For $C_{29}H_{39}FeN_3$ ($M_r = 485.5$) w_i (calc.): 71.75 % C, 8.10 % H, 8.66 % N; w_i (found): 71.95 % C, 8.11 % H, 8.63 % N. 1H NMR spectrum, δ : 0.89 (t, 3H, CH_3), 1.30 (m, 12H, $(CH_2)_6$), 2.41 (t, 2H, CH_2), 2.61 (t, 4H, CH_2), 3.23 (t, 4H, CH_2), 4.23 (s, 5H, Cp), 4.45 (t, 2H, H_β), 4.78 (t, 2H, H_α), 6.92 (d, 2H, $J_{AB} = 9.16$ Hz, H_{arom}), 7.14 (d, 2H, $J_{AB} = 9.16$ Hz, H_{arom}), 8.34 (s, 1H, $CH=N$).

**1,1'-Bis-((4-(*N'*-methylpiperazinyl)phenyl)-
iminomethyl)ferrocene (VIII)**

Solution of 1,1'-ferrocenedicarbaldehyde (0.5 mmol) and 1 mmol of IV in ethanol (10 cm^3) was heated under reflux for 15 min. Water was then added to the reaction mixture and precipitated product VIII was filtered off, washed with cold ethanol and recrystallized from the same solvent. Product was isolated in 34 % yield as red crystals, m.p. = 205–209 °C. For $C_{34}H_{40}FeN_6$ ($M_r = 588.6$) w_i (calc.): 69.38 % C, 6.59 % H, 14.28 % N; w_i (found): 69.44 % C, 6.65 % H, 14.31 % N. 1H NMR spectrum, δ : 2.42 (s, 6H, CH_3), 2.67 (t,

8H, CH_2), 4.49 (t, 4H, H_β), 4.84 (t, 4H, H_α), 6.87 (d, 4H, $J_{AB} = 7.11$ Hz, H_{arom}), 7.11 (d, 4H, $J_{AB} = 7.11$ Hz, H_{arom}), 8.29 (s, 2H, $CH=N$).

**1,1'-Bis-((4-(*N'*-octylpiperazinyl)phenyl)-
iminomethyl)ferrocene (IX)**

Solution of 1,1'-ferrocenedicarbaldehyde (0.17 mmol) and 0.35 mmol of V in ethanol (3.5 cm^3) was heated under reflux for 20 min. The reaction mixture was cooled down and precipitated product IX was filtered off, washed with cold diethyl ether and recrystallized from dichloromethane–diethyl ether mixture. Product was isolated in 62 % yield as red crystals, m.p. = 197–200 °C. For $C_{48}H_{68}FeN_6$ ($M_r = 784.9$) w_i (calc.): 73.45 % C, 8.73 % H, 10.71 % N; w_i (found): 73.29 % C, 8.71 % H, 10.62 % N. 1H NMR spectrum, δ : 0.89 (t, 6H, CH_3), 1.26 (m, 24H, $(CH_2)_6$), 2.41 (t, 4H, CH_2), 2.68 (t, 8H, CH_2), 3.23 (t, 8H, CH_2), 4.50 (t, 4H, H_β), 4.84 (t, 4H, H_α), 6.85 (d, 4H, $J_{AB} = 7.94$ Hz, H_{arom}), 7.10 (d, 4H, $J_{AB} = 7.94$ Hz, H_{arom}), 8.29 (s, 2H, $CH=N$).

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