

Note

Synthesis and physico-analytical studies of some novel ferrocenyl Schiff base derivatives

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Abstract

A series of ferrocenyl Schiff base derivatives was synthesized by condensation reactions of 1,1'-ferrocenedicarboxaldehyde and aromatic amines containing long chain alkyl groups as free ends which were characterized by their physical properties, elemental, FTIR, ^1H NMR, ^{13}C NMR spectral and thermal analysis. The thermal behaviour of the synthesized compounds was studied by differential scanning calorimetry (DSC) which revealed that these compounds may exhibit mesomorphic properties. The DSC results of aromatic amines and ferrocenyl Schiff bases were compared to study the effects of structure, i.e. rigid core and terminal chain length, on the phase transition behaviour.

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1. Introduction

Ferrocene derivatives with good donor abilities (i.e.; nitrogen, sulfur, oxygen, phosphorus, etc.) have attracted much interest, as the coordination of a metal to these heteroatoms generates multicenter molecules which have potential in many different areas. Amongst these *N*-substituted ligands ferrocenyl Schiff bases play pivotal role in the field of catalysis [1–9]. Another important and widely studied property is the mesogenic behaviour of these compounds. Ferrocene has a favourable balance of structure and properties and is useful for incorporating a metal atom into a molecule that requires certain degree of structural rigidity such as liquid crystals. The ferrocenyl unit is not only useful for modifying the shape of a molecule but also the metal atom with its considerable electron density can be used to modify physical properties such as colour, polarisability and magnetism [10]. Liquid crystalline ferrocene based Schiff bases show interesting magnetic [11] (paramagnetic liquid crystals, control of the molecular orientation in a magnetic field), electrical [12] (one dimen-

sional conductors), strong optical [13] (birefringence, dichroism, and nonlinear optical behaviour) and electro-optical [14] (photoelectric behaviour, ferroelectric electro-optical responses) properties. Many ferrocenyl Schiff base derivatives have been studied for their biological activity and found to be active against microbes and bacteria [15,16]. In our research project, we have synthesized a series of ferrocenyl Schiff bases as materials with great potentials in the field of metallomesogens. In addition to a large no of mesogenic ferrocenyl Schiff bases reported so far, it is a novel series of compounds expected to exhibit the thermotropic liquid crystalline behaviour.

2. Experimental

FTIR spectra (KBr pellets, 4000–400 cm^{-1}) were recorded on Bio-Rad Excalibur FTIR, Model FTS 3000 MX. Elemental analysis was conducted on Perkin Elmer CHNS/02400, America. DSC curves were recorded on DSC 404C (2 $^\circ\text{C}/\text{min}$), Netzsch. ^1H and ^{13}C NMR spectra were obtained in CDCl_3 and $\text{DMSO}-d_6$ solution on a Varian Mercury 300 NMR spectrometer at 300 (^1H) and 75.5 (^{13}C) MHz.

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2.1. Procedure for the synthesis of (4-aminophenyl)-*N*-phenethylamide (**1b**)

4-Nitrobenzoic acid (5 g, 30 mmol) was refluxed for 5 h in the presence of distilled thionyl chloride (2.18 mL, 30 mmol) and reacted with 2-phenethylamine (2.42 mL, 21 mmol) in anhydrous toluene. An equimolar amount of Et₃N (3 mL, 21 mmol) was also added to catalyze the reaction and refluxed with stirring for 3 h. After cooling to room temperature, the reaction mixture was allowed to stand for 16 h. The resulting crude solid was filtered off, washed with water and recrystallized from ethanol. The product **1a** (3 g, 0.012 mmol) with (30 mL, 0.618 mmol) of hydrazine monohydrate, 80 mL of ethanol and 0.1 g of 5% Pd-C were charged in a flask for reduction. This mixture was refluxed with stirring for 16 h and then filtered in hot state to remove Pd-C. White semi-crystalline solid **1b** was obtained on cooling the filtrate to room temperature which was filtered and dried (Scheme 1).

White semi-crystalline solid, yield (82%), m.p. 135–145 °C. DSC melting range 137–148 °C. *Anal. Calc.* for C₁₅H₁₆ON₂: C, 74.97; H, 6.71; N, 11.66. Found: C, 73.86; H, 5.89; N, 10.87%. IR (cm⁻¹) 1604, 3221, 3326. ¹H NMR (DMSO-*d*₆, δ ppm): δ (ph-) = 6.60^d (2–2', 1H), 7.63^d (3–3', 1H); 7.23^m. δ (-NHCO-) = 8.18^s; (-CH₂-) = 3.45^m, 2.85^m; δ (-NH₂-) = 5.65^s.

2.2. General procedure for the synthesis of aromatic amines (**3b**, **4b**, **5b**)

4-[4-Nitrophenyloxy]aniline **2** was synthesized by reported method [17] and condensed with different acid chlorides to get the desired products. A mixture of 4-[4-nitrophenyloxy]aniline (5 g, 210 mmol), acid chloride (210 mmol) and triethylamine (210 mmol) was stirred in dried toluene and refluxed for 3 h. The reaction mixture was allowed to stand at room temperature for 16 h. The resulting solid (**3a**, **4a**, and **5a**) was filtered off, washed several times with water to remove any salt impurities and recrystallized from dichloromethane:toluene (1:1) mixture. The products obtained were then reduced to get **3b**, **4b** and **5b** following the standard procedure as already described (Scheme 2).

2.2.1. 4-[4-Aminophenyloxy]dodecanamide (**3b**)

White solid, yield (85%), m.p. 115–130 °C. DSC melting range 115–134 °C. *Anal. Calc.* for C₂₄H₃₄N₂O₂: C, 75.39; H, 8.91; 7.32. Found: C, 74.68; H, 7.96; N, 6.86%. IR (cm⁻¹) 1655, 3281, 3387. ¹H NMR (DMSO-*d*₆, δ ppm): δ (ph-) = 6.58^d (2–2', 1H), 6.75^d (3–3', 1H), 6.85^d (6–6', 1H), 7.52^d (7–7', 1H); δ(-NHCO-) = 9.80^s; δ (-CH₂-) = 1.3^s, δ(-CH₂CO-) = 2.35^s; δ (-NH₂-) = 5.65^s, δ (-CH₃) = 0.90^t.

2.2.2. 4-[4-Aminophenyloxy]hexadecanamide (**4b**)

White solid, yield (84%), m.p. 111–120 °C. DSC melting range 110–122 °C. *Anal. Calc.* for C₂₈H₄₂N₂O₂: C, 76.71; H, 9.58; N, 6.39. Found: C, 75.48; H, 8.43; N, 6.54%. IR (cm⁻¹) 1655, 3285, 3386. ¹H NMR (DMSO-*d*₆, δ ppm): δ

(ph-) = 6.55^d (2–2', 1H), 6.70^d (3–3', 1H), 6.80^d (6–6', 1H), 7.50^d (7–7', 1H); δ(-NHCO-) = 9.80^s; δ(-CH₂-) = 1.24^s, δ(-CH₂CO-) = 2.40^t; δ (-NH₂-) = 4.98^s, δ (-CH₃) = 0.90^t.

2.2.3. 4-[4-Aminophenyloxy]octadecanamide (**5b**)

White solid, yield (85%), m.p. 95–115 °C. DSC melting range 101–120 °C. *Anal. Calc.* for C₃₀H₄₆N₂O₂: C, 77.25; H, 9.44; N, 6.01. Found: C, 78.37; H, 8.96; N, 6.43%. IR (cm⁻¹) 1655, 3287, 3314. ¹H NMR (DMSO-*d*₆, δ ppm): δ (ph-) = 6.48^d (2–2', 1H), 6.65^d (3–3', 1H), 6.80^d (6–6', 1H), 7.45^d (7–7', 1H); δ(-NHCO-) = 9.80^s; δ (-CH₂-) = 1.26^s, δ(-CH₂CO-) = 2.40^t; δ (-NH₂-) = 5.0^s, δ(-CH₃) = 0.90^t.

2.3. General procedure for the synthesis of Schiff base derivatives (**6**, **7**, **8**, **9**)

A pre-baked two-neck round bottom flask equipped with condenser and magnetic stirrer was charged with the corresponding amine (1.6 mmol) in absolute ethanol (20 mL) and treated with 1,1'-ferrocene dicarboxaldehyde (0.8 mmol). Concentrated hydrochloric acid (2–3 drops) was added to the reaction mixture as a catalyst and refluxed for 6 h. After cooling to room temperature, the precipitates were collected by filtration and purified by flash chromatography (eluent; hexane:acetone; 5:1) and recrystallized from petroleum ether (Scheme 3). All the reactions involved in the synthesis of Schiff bases were carried out in inert atmosphere, using absolute ethanol as solvent. Water is liberated as a byproduct during the synthesis of all Schiff bases, which is removed continuously by using Dean and Stark apparatus. Otherwise the reaction is reversed to backward direction resulting in the hydrolysis of C=N bond. To avoid the further hydrolysis of the Schiff bases, the solvent is evaporated on vacuum as soon as the product is formed and dried in vacuum dessicator on CaCl₂. The dried product can be stored in dessicator for longer times. All the synthesized ferrocene Schiff base derivatives were obtained in excellent yields (≈85%).

2.3.1. 1,1'-Bis[*N*-phenethylbenzamidoimine]ferrocene (**6**)

Brown solid, semi-crystalline; yield (82.5%), m.p. 160–186 °C. DSC melting range 161–202 °C. *Anal. Calc.* for C₄₂H₃₆FeN₄O₂: C, 73.68; H, 5.26; N, 8.18. Found: C, 72.66; H, 5.34; N, 8.14%. IR (cm⁻¹) 1557, 1639, 500. ¹H NMR (DMSO-*d*₆, δ ppm): δ (ph-) = 6.70^d (2–2', 1H), 7.65^d (3–3', 1H), 7.20^m; δ(-NHCO-) = 8.50^s; δ (-CH₂-) = 3.42^m, 2.80^m; δ(-CH=N-) = 7.62^s; δ (Fe-cp) = 4.95^s (α-α', 1H), 4.60^s (β, β', 1H).

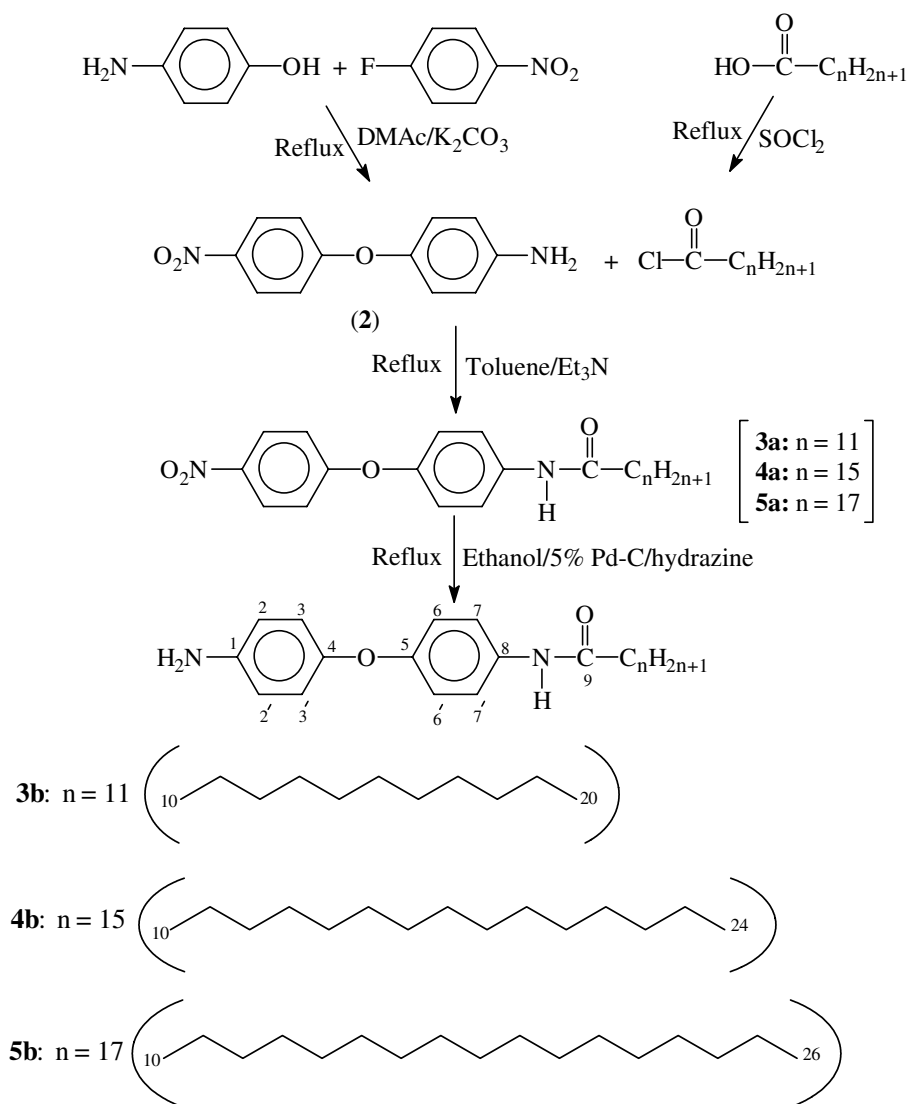
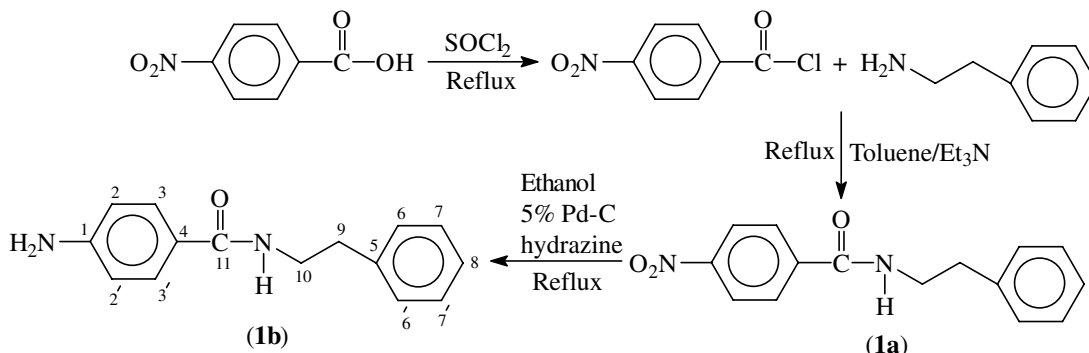
2.3.2. 1,1'-Bis[4,4'-dodecanamido-*N*-phenyloxybenzimine]ferrocene (**7**)

Brown solid, semi-crystalline; yield (85%), m.p. 210–220 °C. DSC melting range 185–224 °C. *Anal. Calc.* for C₆₀H₇₂FeN₄O₄: C, 74.38; H, 7.43; N, 5.78. Found: C, 75.07; H, 6.95; N, 6.12%. IR (cm⁻¹) 1655, 1619, 489.

^1H NMR (DMSO- d_6 , δ ppm): δ (ph-) = 6.72^d (2–2', 1H), 6.58^d (3–3', 1H), 6.85^d (6–6', 1H), 7.50^d (7–7', 1H); δ (-NHCO-) = 9.85^s; δ (-CH₂-) = 1.28^s, δ (-CH₂CO-) = 2.25^t; δ (-CH₃) = 0.85^t; (-CH=N-) = 7.60^s; δ (Fe-cp) = 4.90^s (α - α' , 1H), 4.75^s (β , β' , 1H).

2.3.3. 1,1'-Bis[4,4'-hexadecanamido-N-phenyloxybenzimine]ferrocene (**8**)

Dark brown solid, semi-crystalline; yield (86%), m.p. 205–213 °C. DSC melting range 185–210 °C. *Anal. Calc.* for C₆₈H₈₈FeN₄O₄: C, 75.55, H, 8.14; N, 5.18. Found: C,



74.67; H, 8.74; N, 4.89%. IR (cm^{-1}) 1655, 1618, 489. ^1H NMR ($\text{DMSO}-d_6$, δ ppm): δ (ph-) = 6.75^d (2–2', 1H), 6.55^d (3–3', 1H), 6.82^d (6–6', 1H), 7.52^d (7–7', 1H); δ (–NHCO–) = 9.80^s; δ (–CH₂–) = 1.25^s, δ (–CH₂CO–) = 2.24^t; δ (–CH₃) = 0.85^t; (–CH=N–) = 7.65^s; δ (Fe-cp) = 4.85^s (α – α' , 1H), 4.72^s (β , β' , 1H).

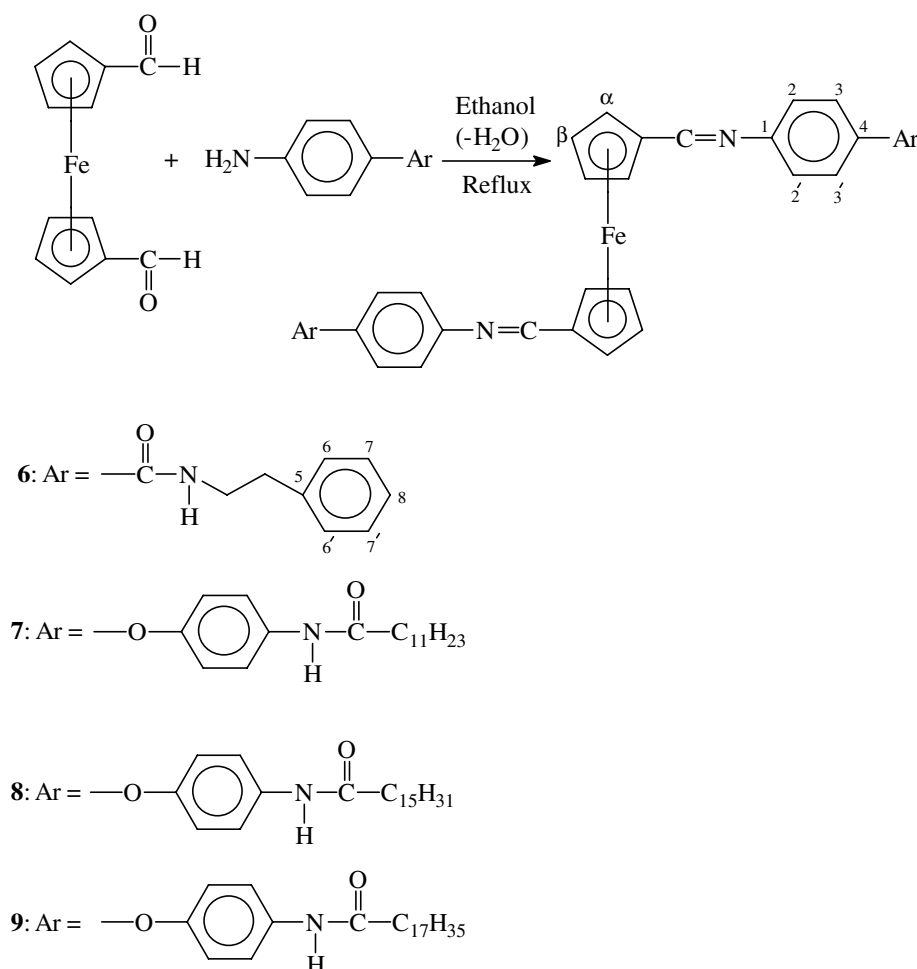
2.3.4. 1,1'-bis[4,4'-Octadecanamido-N-phenyloxybenzimine]ferrocene (**9**)

Dark brown solid, semi-crystalline; yield (84.5%), m.p. 195–205 °C. DSC melting range 183–207 °C. Anal. Calc. for $\text{C}_{72}\text{H}_{96}\text{FeN}_4\text{O}_4$: C, 76.05; H, 8.45; N, 4.92. Found: C, 77.13; H, 7.64; N, 4.54%. IR (cm^{-1}) 1655, 1619, 490. ^1H NMR ($\text{DMSO}-d_6$, δ ppm): δ (ph-) = 6.70^d (2–2', 1H), 6.55^d (3–3', 1H), 6.85^d (6–6', 1H), 7.52^d (7–7', 1H); δ (–NHCO–) = 9.82^s; δ (–CH₂–) = 1.35^s, δ (–CH₂CO–) = 2.25; δ (–CH₃) = 0.85^t; (–CH=N–) = 7.62^s; δ (Fe-cp) = 4.90^s (α – α' , 1H), 4.80^s (β , β' , 1H).

3. Results and discussion

The FTIR, ^1H NMR, and ^{13}C NMR spectral data for the synthesized compounds is self explanatory with few

exceptions. The IR spectra of the compounds **1b**, **2**, **3b**, **4b**, and **5b** confirm the presence of different functional groups along with the appearance of two absorption bands at 3221 cm^{-1} and 3366 cm^{-1} characteristics of aromatic amines. These bands are absent in the respective Schiff base derivatives **6**, **7**, **8**, **9**, and **10** and a strong peak appeared at 1620 cm^{-1} due to C=N stretch. These compounds also show characteristic absorption peaks of the Fe-Cp stretching vibrations at 483 cm^{-1} or above. In ^1H NMR, all the aromatic amines give broad signals in the range of 5–5.6 ppm, which are shifted upfield at about 7.6 ppm in case of their Schiff base derivatives, characteristics of the proton attached with imine group. They have also shown two different values for the chemical shift of ring protons that confirm the chemical equivalence of the proton atomic pairs present at α - and β -positions and hence its 1,1'-disubstituted structures. The results of DSC provide some useful information about the mesomorphic nature of these compounds due to wide range of melting and clearing temperatures of the compounds **3b**, **4b** and **5b**. There is reduction in melting and clearing temperatures as the terminal chain length increases which is most probably due to the high entropic contribution of the long terminal chains on the



Scheme 3.

melt state. This type of behaviour has been observed previously [18]. Furthermore, this trend coincides with the principal of liquid crystal, i.e. mesomorphism depends on the length ratio of rigid core and terminal chain. It is also explained by the comparison of the ferrocenyl Schiff base derivatives (**7**, **8**, and **9**) with their respective amines (**3b**, **4b**, and **5b**). When rigid core becomes longer due to incorporation of a ferrocene unit, the ratio of the rigid core and flexible chain length is changed resulting in the wider temperature range of phase transition. The stability of the mesophases also increases by the introduction of the ferrocene molecule [19]. The compound **1b** has surprisingly exhibited the liquid crystalline phase which is further stabilized by incorporating the ferrocene moiety. These type of anomalies have been reported earlier [20]. Moreover, the melting points of these compounds provide a supportive evidence towards the mesogenic behaviour as a turbid phase appears during melting.

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