The Synthesis and Characterization of New Schiff Bases: 4-[(Pyridin-4-ylmethylene)amino]phenylalkanoates

1Sie-Tiong Ha, 2Lay-Khoon Ong, 1Yip-Foo Win, 3Yasodha Sivasothy, 4Guan-Yeow Yeap and 4Peng-Lim Boey

1Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, Jln Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
2Department of Science, Faculty of Engineering & Science, Universiti Tunku Abdul Rahman, Jln Genting Klang, Setapak, 53300 Kuala Lumpur, Malaysia
3Chemistry Department, Faculty of Science, Universiti Malaya, 50603, Kuala Lumpur, Malaysia
4Liquid Crystal Research Laboratory, School of Chemical Science, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

Abstract: Four new heterocyclic Schiff bases were synthesized from the reaction between 4-[(pyridin-4-ylmethylene)amino]phenol and fatty acids with even number alkyl chains ranging from twelve to eighteen carbons. Their structures were elucidated using spectroscopic techniques such as FT-IR, EI-MS and NMR. Phase-transition temperatures and the thermal parameters were obtained from differential scanning calorimetry (DSC). The texture observation was carried out with a polarizing optical microscope (POM) over heating and cooling cycles. All of the title compounds exhibited direct isotropization process.

Key words: 4-[(pyridin-4-ylmethylene)amino]phenylalkanoate, Schiff bases, synthesis, phase transition

INTRODUCTION

Compounds consisting of \( \text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5 \) as the core system are commonly referred to as \( N \)-benzylideneaniline Schiff bases. This system has received a considerable amount of attention from many researchers owing to its importance in exhibiting thermochromism and photochromism (Hadjoudis et al., 1987). A series of studies on photochromic compounds have been undertaken with an attempt to explore the applications of these photochromic materials in various fields such as the control and measurement of radiation intensity, optical computers and display systems. In view of the importance and usefulness of these compounds, chemists are prompted to generate the derivatives by introducing different substituents into the existing skeleton of the molecule. The presence of a long alkyl chain at the \( \text{para} \) position of the aldehyde and aniline fragments of Schiff bases has been regarded as one of the important elements which favours the existence of liquid crystal phases (Yeap et al., 2004, 2006a, 2006b, 2006c).

Subsequent to the concerted effort in studying Schiff bases, an attempt to study Schiff base esters consisting of a pyridine moiety was carried out by preparing a new series of 4-[(pyridin-4-ylmethylene)amino]phenylalkanoate (\( \text{C}_6\text{H}_4\text{NCH}=\text{NC}_6\text{H}_4\text{R} \), where \( \text{R} = \text{C}_11\text{H}_{23}\text{COO}^-, \text{C}_13\text{H}_{27}\text{COO}^-, \text{C}_15\text{H}_{31}\text{COO}^- \) and \( \text{C}_17\text{H}_{35}\text{COO}^- \)). The structures of the title compounds were confirmed using microelemental analysis and spectroscopic techniques (EIMS, FTIR and NMR). Differential scanning calorimetry and polarizing optical microscope were used to study phase behavior and optical textures of the title compounds.

MATERIALS AND METHODS

Materials:

4-Pyridinecarbaldehyde, 4-aminophenol and 4-dimethylaminopyridine (DMAP) were obtained from Merck (Germany). Dicyclohexylcarbodiimide (DCC) was obtained from Acros Organics (USA). Lauric, myristic, palmitic and stearic acids were supplied by Natural Oleochemicals Sdn. Bhd. (Malaysia). The purity of the fatty acids is approximately 99 %.

Corresponding Author: Sie-Tiong Ha, Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, Jln Universiti, Bandar Barat, Kampar, 31900 Perak, Malaysia.

Email: hast@utar.edu.my or hast_utar@yahoo.com
Techniques:

Electron impact mass spectrum (EI-MS) was recorded by a Finnigan MAT95XL-T mass spectrometer operating at 70 eV ionizing energy. Samples were introduced using a direct inlet system with a source temperature of 200°C. Microanalyses were carried out on Perkin Elmer 2400 LS Series CHNS/O analyser. FT-IR data were acquired on Perkin Elmer 2000-FTIR spectrophotometer in the frequency range of 4000–400 cm⁻¹ with samples embedded in KBr discs. ¹H and ¹³C NMR spectra were recorded in CDCl₃ by utilizing JEOL 400MHz NMR Spectrometer with TMS as internal standard. Thin layer chromatography analyses were performed using aluminum backed silica gel plates (Merck 60 F254) and were examined under shortwave UV light. The phase transition temperatures were measured by Mettler Toledo DSC823 differential scanning calorimeter (DSC) at a scanning rate of 10°C min⁻¹.

Synthesis of Schiff Bases:

Synthetic scheme of the title compounds is shown in Scheme 1.

Synthesis of 4-[(pyridin-4-ylmethylene)amino]phenol (1):

4-[(Pyridin-4-ylmethylene)amino]phenol was prepared by mixing equimolar amounts (0.02 mole) of 4-pyridinecarbaldehyde and 4-aminophenol, both dissolved in 40 mL absolute ethanol. The reaction mixture was heated under reflux for three hours and the precipitate thus formed upon cooling to room temperature was filtered. The solid thus obtained was recrystallized from absolute ethanol.

Synthesis of 4-[(pyridin-4-ylmethylene)amino]phenylundecanoate (2):

This compound was synthesized according to the method described in earlier work (Yeap et al., 2004, 2006a, 2006b, 2006c). Compound 1 (0.01 mole) was first dissolved in 2 mL dimethylformamide, then, was added into 70 mL dichloromethane together with lauric acid (0.01 mole) and DMAP (0.001 mole). The resulting mixture was stirred in an ice bath. To this solution, 0.01 mole of DCC dissolved in 20 mL dichloromethane was added dropwise while stirring in the ice bath for an hour. The resulting mixture was subsequently stirred at room temperature for another three hours. Then, the reaction mixture was filtered and the excess solvent was removed from the filtrate by evaporation. The solid thus obtained was recrystallized several times with absolute ethanol whereupon a pure compound was isolated. Yield: 52%. Anal. calc. for C₂₄H₃₂N₂O₂: C 75.75; H 8.48; N 7.36; Found: C 75.63; H 8.55; N 7.38%; EIMS m/z (rel. int %): 380.3 (3) (M)⁺; 198.1(100); FTIR (KBr), 2920, 2850 cm⁻¹ (C-H aliphatic); 1752 cm⁻¹ (C=O ester); 1622 cm⁻¹ (C=N); 1471 cm⁻¹ (C=C aromatic).

Synthesis of 4-[(pyridin-4-ylmethylene)amino]phenyltetradecanoate (3):

This compound was prepared by using the similar experimental procedure as described for compound 2 in which the lauric acid was replaced by myristic acid (C₁₄H₂₇COOH). Yield: 46 %. Anal. calc. for C₂₆H₃₄N₂O₂: C, 76.43; H, 8.88; N, 6.86; Found: C, 76.57; H, 8.81; N, 6.80%; EIMS m/z (rel. int %): 408.3(3) (M)⁺; 198.1(100); IR (KBr), 2918, 2850 cm⁻¹ (C-H aliphatic); 1752 cm⁻¹ (C=O ester); 1622 cm⁻¹ (C=N); 1594, 1476 cm⁻¹ (C=C aromatic).

Synthesis of 4-[(pyridin-4-ylmethylene)amino]phenylhexadecanoate (4):

This compound was prepared by using the similar experimental procedure as described for compound 2 in which the lauric acid was replaced by palmitic acid (C₁₅H₃₁COOH). Yield: 57%. Anal. Calc. for C₂₈H₄₀N₂O₂: C, 77.02; H, 9.23; N, 6.42; Found: C, 77.93; H, 9.29; N, 6.43%; EIMS m/z (rel. int %): 436.4(4) (M)⁺; 198.1(100); FTIR (KBr), 2916, 2850 cm⁻¹ (C-H aliphatic); 1752 cm⁻¹ (C=O ester); 1625 cm⁻¹ (C=N); 1596, 1474 cm⁻¹ (C=C aromatic).

Synthesis of 4-[(pyridin-4-ylmethylene)amino]phenyloctadecanoate (5):

This compound was prepared by using the similar experimental procedure as described for compound 2 in which the lauric acid was replaced by stearic acid (C₁₇H₃₅COOH). Yield: 65 %. Anal. Calc. for C₃₀H₄₄N₂O₂: C, 77.54; H, 9.54; N, 6.03; Found: C, 77.67; H, 9.47; N, 6.01%; EIMS m/z (rel. int %): 464.4 (5) (M)⁺; 198.1 (100); IR (KBr), 2916, 2850 cm⁻¹ (C-H aliphatic); 1752 cm⁻¹ (C=O ester); 1625 cm⁻¹ (C=N); 1471 cm⁻¹ (C=C aromatic). Representative NMR data is given for compound 5 as below.
RESULTS AND DISCUSSION

Mass Spectroscopy:

In the EIMS spectrum of compound 5, the peak at \( m/z = 464.4 \) was assigned to the molecular ion (M⁺) which is in accordance with the compound having a molecular formula \( C_{30}H_{44}N_2O_2 \). Similarly, the peaks at 380.3, 408.3 and 436.4, attributed to the M⁺ of compounds 2, 3 and 4 confirmed those compounds to have a molecular formula \( C_{24}H_{32}N_2O_2 \), \( C_{26}H_{34}N_2O_2 \) and \( C_{28}H_{40}N_2O_2 \) respectively. A difference in the value of \( m/z \) by a margin of 28 units was observed when we proceed from compound 2 to 3, 3 to 4 and 4 to 5 due to the addition of an ethylene group \((CH_2)_{14}^-\) in each interval.

The diagnostic base peak at \( m/z = 198.1 \) corresponding to fragment ion, 6 (Figure 1), resulted from the McLafferty rearrangement in the parent ion of compound 5 followed by the elimination of the neutral ketene molecule \( CH_3(CH_2)_{15}-C=C=O \) (Figure 1), consistent with the loss of 266 mass units (Pavia et al., 2001). The proposed fragmentation was different from that reported for the unsubstituted salicylideneaniline and 1-hydroxy-2-naphthylidene-4'-subsituted-aniline of which either the M⁺ or \((M-1)^+\) peak was the base peak for these compounds (Salman and Kamounah, 2002). The presence of the long alkyl chain favoured the proposed fragmentation. The similar feature \([m/z = 198 (100\%)]\) was observed in the EIMS spectra of compounds 2, 3 and 4.

The EIMS spectra of compounds 2, 3, 4 and 5 share a common feature, the diagnostic base peak being at \( m/z = 198.0 \). This fragment ion, 6 (Figure 1), resulted from the McLafferty rearrangement in the parent ion of compounds 2-5 followed by the subsequent loss of the neutral ketene molecule \( R=CH_3(CH_2)_n-C=C=O \) (where \( R=CH_3(CH_2)_n \), \( n = 9, 11, 13 \) and 15) as reported for benzyl esters (Pavia et al., 2001). As representative illustration, Figure 1 shows the fragmentation of compound 5 leading to fragment ion 6 as the base peak. The proposed fragmentation has been found to be different from that reported for the unsubstituted salicylideneaniline and 1-hydroxy-2-naphthylidene-4'-substituted-aniline of which either the M⁺ or \((M-1)^+\) peak was the base peak for these compounds (Salman and Kamounah, 2002). This is due to the presence of long alkyl ester structure in the current Schiff bases 2-5 which is favorable to undergo McLafferty rearrangement (Pavia et al., 2001).

Infrared Spectroscopy:

Evidence which supports the fact that the title compounds were well isolated were indicated by the absence of the terminal hydroxyl group (OH) which was originally attached to the \( \text{para} \) position of the aniline fragment and now has been substituted by \( R= CH_3(CH_2)_n-COO \) and \( n = 12, 14, 16 \) and 18, respectively. The presence of the alkyl groups was confirmed by the occurrence of the absorption bands within the frequency range 2848-2954 cm⁻¹ as reported by Wiberley and his coworkers (1960). The intense peaks observed around 1752 cm⁻¹ in the IR spectra of the title compounds substantiated the presence of the C=O group in the ester bond located between the aniline fragment and the aliphatic chain (Scheme 1). The absorption bands assignable to the stretching of the C=N bond in compounds 2-5 were observed at 1622-1625 cm⁻¹ and these values conform with those reported for \( \text{para} \) substituted 2-hydroxy-3-methoxybenzalideneanilines (Yeap et al., 2003).

NMR spectroscopy:

In \(^1\)H NMR spectrum of compound 5, two triplets were observed at \( \delta = 0.88 \) ppm and \( \delta = 2.57 \) ppm, which can be ascribed to the methyl and methylene protons \((-CH_2COO-Ar)\). The chemical shifts at \( \delta = 1.26 \) ppm can be assigned to methylene protons of long alkyl chain \((-CH_2)_n\). The four distinct double doublets were detected at \( \delta = 7.13, 7.26, 7.75, 8.76 \) ppm can be assigned to eight aromatic protons. A singlet was observed at \( \delta = 8.45 \) ppm is due to proton of imine linking group (Ha et al., 2009). The molecular structure of compound 5 was further verified by using \(^{13}\)C NMR spectroscopy. A peak at \( \delta = 14.08 \) ppm is attributed to the methyl carbon and peaks at \( \delta = 22.65-34.37 \) ppm is contributed by the methylene carbons of long alkyl chain.

chain. Peaks at $\delta = 115.69-150.58$ ppm is assigned to twelve aromatic carbons in compound 5. The peak at $\delta = 157.87$ ppm due to existence of azomethine carbon. The most downfield peak in the spectrum, $\delta = 172.26$ ppm, is ascribed to carbon of ester group.

**Phase Transition Behaviors and Optical Texture Studies:**

The phase transition temperatures and their associated enthalpy obtained from DSC analysis over heating and cooling cycles are tabulated in Table 1. The DSC thermograms for all compounds during heating cycles show only one peak that can be ascribed to direct isotropization process (Cr-to-I). Representative DSC thermogram of compound 5 is shown in Figure 2. Under polarizing optical microscope studies, crystal phase texture was observed to change to dark region isotropic during heating run. No liquid crystal texture was observed during cooling process.

A further examination of DSC data also illustrates the evolution of the Cr-I transition with the lengthening of terminal chains. A plot of the melting and recrystallization temperatures against the number of carbons in the alkanoyloxy chain during the heating and cooling cycles is shown in Figure 3. The melting temperatures for compounds 2 to 4 increases as the alkyl chain of $C_{n-1}H_{2n-1}COO^-$ elongates in the range of $n = 12-16$. This observation could be attributed to the increase of van der Waals attraction when the alkyl chains of the title compounds ($C_{n-1}H_{2n-1}COO^-$) varied from 12 to 14 and 16. However, the melting temperature of compound 5 is found to be lower than compound 4. The lowering of the melting temperature in compound 5 wherein $n = 18$ could be due to the repulsive (steric) forces leading to larger intermolecular distance. One of the reasons that can explain repulsion among the molecules in compound 5 is the probable deviation from the linearity of the terminal alkanoyloxy chain. Although the molecular structure for compounds 2-4 may be fully stretched, the long molecular axis of compound 5 could be distorted from linearity, which entails molecular packing as reported for the azomethines containing terminal cycloalkyl ring systems (Byron et al., 1995). The melting trend as discussed above (Figure 3) is found to conform with the trend reported for 1-phenyl-3-(4'-alkylcarbonyloxyphenyl)-2-propen-1-one (Yeap et al., 2005).

**Scheme 1:** Synthetic methodology for Schiff bases 2-5

![Scheme 1: Synthetic methodology for Schiff bases 2-5](image)
Fig. 1: Mass spectral fragmentation of Schiff base 5 leading to fragment ion 6 as the base peak.

Fig. 2: DSC thermogram of Schiff base 5

Fig. 3: Plot of transition temperatures versus the number of carbons (n) in the alkanoyloxy chain of Schiff bases 2-5.
Table 1: Transition temperatures and associated enthalpies of Schiff bases 2-5 upon heating and cooling

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition temperatures, °C ( H, kJ mol⁻¹)</th>
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<tbody>
<tr>
<td>2</td>
<td>Cr 86.5 (30.5) I 65.3 (29.5) Cr</td>
</tr>
<tr>
<td>3</td>
<td>Cr 90.5 (47.8) I 69.5 (43.7) Cr</td>
</tr>
<tr>
<td>4</td>
<td>Cr 96.6 (59.7) I 77.8 (57.5) Cr</td>
</tr>
<tr>
<td>5</td>
<td>Cr 92.6 (56.1) I 81.5 (58.1) Cr</td>
</tr>
</tbody>
</table>

The values in italic were taken during cooling cycle.
Cr= Crystal; I= Isotropic liquid

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