Synthesis and mesomorphic properties of new Schiff base esters with different alkyl chains

Sie Tiong Ha \textsuperscript{a,\*}, Lay Khoon Ong \textsuperscript{a}, Siew Teng Ong \textsuperscript{a}, Guan Yeow Yeap \textsuperscript{b}, Joanna Pik Wan Wong \textsuperscript{a,1}, Teck Ming Koh \textsuperscript{a}, Hong Cheu Lin \textsuperscript{c}

\textsuperscript{a} Faculty of Engineering & Science, Universiti Tunku Abdul Rahman, Jln Genting Klang, Setapak, 53300 Kuala Lumpur, Malaysia
\textsuperscript{b} Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
\textsuperscript{c} Department of Materials Science & Engineering, National Chiao Tung University, 1001 Ta-Hsueh Road, Hsinchu 300, Taiwan

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Abstract

A new series of Schiff base esters, 4-(dimethylamino)benzylidene-4\textsuperscript{0}-alkanoyloxyanilines containing even number of carbons at the end group of the molecules (C\textsubscript{\textit{n}}-\textsubscript{1}H\textsubscript{\textit{n}}\textsubscript{1}COO, \textit{n} = 6, 8, 10, 12, 14, 16, 18) were synthesized. The present compounds were monotropic liquid crystals. It was also found that the end groups of the molecules had effect on the mesomorphic properties.

The discovery of thermotropic liquid crystal 4-methoxybenzylidene-4\textsuperscript{0}-butylaniline (MBBA) and the application of its room temperature nematic phase in displays sparked a renewed interest liquid crystals and in research to establish structure–property relationships [1,2]. The understanding of structure–property correlations is elemental to selecting molecular modifications for the synthesis of new mesogens with desirable properties and future applications [3].

In our earlier studies, the results revealed that ester and azomethine linking units are the useful structural components for generating mesomorphism in two and three aromatic rings thermotropic liquid crystals [4–7]. Therefore, a continuing effort has been carried out which focused on the synthesis and characterization of a new series of Schiff base esters, 4-(dimethylamino)benzylidene-4\textsuperscript{0}-alkanoyloxyanilines. The synthesis of the target molecules is outlined in Scheme 1, where 4-dimethylaminobenzaldehyde was coupled with 4-aminophenol by heating under reflux for about 3 h in ethanol solution. Then, the Schiff base intermediate was subjected to Steglich esterification with suitable fatty acids in the presence of DCC and DMAP [8]. The crude products were purified by repeated crystallization from ethanol. The structure of the products was confirmed using elemental analysis, IR, NMR and EI-MS spectroscopic techniques [9].

The liquid crystalline texture studies and phase transition temperatures were determined by means of polarizing microscope equipped with hotstage and temperature regulator. Phase identification was made by comparing the
observed textures with those reported in literatures [10,11]. Transition temperatures and associated enthalpy changes were measured using differential scanning calorimeter (DSC). The results obtained were listed in Table 1. All of the compounds exhibited an endotherm corresponding to the direct melting of the crystal phase to the isotropic liquid phase during heating cycle (Fig. 1). The subsequent cooling of these compounds demonstrated exotherms characteristic of the isotropic–mesophase and mesophase–crystal transitions which is indicative of the monotropic properties.

Under the polarizing microscope, *n*-hexanoyloxy, *n*-octanoyloxy, *n*-decanoyloxy and *n*-dodecanoyloxy derivatives exhibited monotropic nematic phase. In the monotropic mesogens, the melting points were always equal to or higher than the clearing points, hence exhibiting supercooling properties [12]. The mesophase was identified by the nematic droplets texture. Brownian flashes, a characteristic of the nematic phase were also observed before recrystallization [13]. An interesting phenomenon was observed for *n*-dodecanoyloxy derivative where an additional phase with

![Scheme 1. Synthetic route toward the target compounds: (i) C<sub>2</sub>H<sub>5</sub>OH and (ii) C<sub>n</sub>-1H<sub>2n</sub>-1COOH, DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, DMF.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase transitions, °C (heating/cooling) (corresponding enthalpy changes, kJ mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6DMABAA</td>
<td>Cr 108.6 (36.5) II 97.2 (1.5) N 91.3 (28.0) Cr</td>
</tr>
<tr>
<td>8DMABAA</td>
<td>Cr 109.8 (37.0) II 94.4 (1.2) N 87.6 (32.4) Cr</td>
</tr>
<tr>
<td>10DMABAA</td>
<td>Cr 110.0 (51.0) II 94.5 (1.6) N 87.4 (44.4) Cr</td>
</tr>
<tr>
<td>12DMABAA</td>
<td>Cr 104.8 (46.8) II 93.2 (1.7) N 91.5 (0.26) SmA 88.3 (42.5) Cr</td>
</tr>
<tr>
<td>14DMABAA</td>
<td>Cr 105.7 (38.9) II 94.0 (2.7) SmA 89.6 (34.6) Cr</td>
</tr>
<tr>
<td>16DMABAA</td>
<td>Cr 108.1 (42.6) II 96.6&lt;sup&gt;a&lt;/sup&gt; SmA 94.3 (43.1) Cr</td>
</tr>
<tr>
<td>18DMABAA</td>
<td>Cr 109.3 (59.8) II 99.4&lt;sup&gt;a&lt;/sup&gt; SmA 94.6 (60.3) Cr</td>
</tr>
</tbody>
</table>

Cr, crystal; N, nematic; SmA, smectic A; I, isotropic.

*Polarizing optical microscopy data.

![Fig. 1. DSC thermograms of 14DMABAA.](image)
fan-shaped texture assigned as smectic A (SmA) phase was observed after the formation of the nematic phase on the cooling run.

Further increase in the molecular length of these compounds from C14 to C18 did not show co-existence of nematic and smectic phases. These compounds exhibited only fan-shaped textures. This feature is a characteristic of the SmA phase owing to the formation of battonets (Fig. 2a) that coalesce to form the fan-shaped texture (Fig. 2b). This indicates that with increasing in the length of the terminal chain, the nematic properties decreased and led to the emergence of the smectic phase. This is due to attraction between the long alkyl chains leading to their intertwining, which facilitates the lamellar packing and is essential for the smectic phase [14]. It can therefore be proposed that in order to generate the smectic phase in the analogous substituted C6H5CH=NC6H5 compounds, the number of carbons in the alkyl chain must be at least 12 (n ≥ 12).

In conclusion, all the target compounds exhibited monotropic liquid crystal properties. The early members of the series (n = 6, 8, 10) had only nematic phases, medium member (n = 12) displayed co-existence of both nematic and smectic phases and higher members (n = 14, 16, 18) exhibited only SmA phase. The tendency of liquid crystal formation has been strongly enhanced by dimethylamino terminal group as compared to the unsubstituted compound, benzylidene-4-octyloxyaniline which did not exhibit liquid crystal phase [15]. Owing to the presence of dimethylamino as donor group, these compounds may also serve as mesogenic charge-transfer donors in our future studies by interacting with acceptor molecules to form binary liquid crystals [16].

Acknowledgments

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References

Analytical and spectroscopic data for the representative compound 14DMABAA: Yield 21%, EI-MS m/z (rel. int. %): 451 (6) [M+1]+, 450 (20) [M]+, 240 (100), IR (KBr, cm⁻¹): 2953, 2918, 2850 (C–H aliphatic); 1752 (C=O ester); 1608 (C=C aromatic), ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.90 (t, 3H, J = 6.5 Hz, CH₃), 1.28–1.42 (m, 20H, CH₃(CH₂)₁₀–), 1.77 (qt, 2H, J = 7.3 Hz, –CH₂CH₂COO–), 2.58 (t, 2H, J = 7.4 Hz, –CH₂COO–), 6.74 (d, 2H, J = 8.9 Hz, Ar-H), 7.07 (d, 2H, J = 8.8 Hz, Ar-H), 7.20 (d, 1H, J = 8.8 Hz, Ar-H), 7.76 (d, 1H, J = 8.9, Ar-H), 8.33 (s, 1H, CH=N), ¹³C NMR (75 MHz, CDCl₃ δ ppm): 14.63 (CH₃), 23.17, 29.57, 29.74, 29.83, 29.93, 30.06, 30.11, 30.14, 32.38 for methylene carbons (CH₃(CH₂)₁₀–), 25.41 (–CH₂CH₂COO–), 34.85 (–CH₂COO–), 40.63 [N(CH₃)₂], 111.92, 122.18, 122.48, 124.53, 130.91, 148.48, 150.90, 152.89 for aromatic carbons, 160.93 (CH=N), 173.09 (COO), Anal. Calcd. For C₂₉H₄₂N₂O₂: C, 77.29%, H, 9.39%, N, 6.22%; found: C, 77.37%, H, 9.47%, N, 6.16%.