New Mesogenic Schiff Base Esters Containing Chloro End Group: Synthesis and Thermotropic Properties

1Sie-Tiong Ha and 2Lay-Khoon Ong

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 and Science, Universiti Tunku Abdul Rahman, Jln Genting Klang, Setapak, 53300 Kuala Lumpur, Malaysia

Abstract: A new series of Schiff base esters containing even number of carbons at the end group of the molecules (CnH2n+1COO, n = 6, 8, 10, 12, 14, 16, 18) and chloro substituent at the other terminal of the molecules were synthesized. It was also found that the end groups of the molecules had effect on the mesomorphic properties. Whilst lowest member (n = 6) exhibited monotropic smectic A and B phases, highest member (n = 18) displayed enantiotropic smectic A phase. Enantiotropic mesogenic A and monotropic smectogenic B were observed in the medium members, n-octanoyloxy to n-hexadecanoyloxy derivatives.

Key words: Schiff base esters • Smectic A • Smectic B • Mesomorphic

INTRODUCTION

Thermotropic liquid crystal is one type of mesogens which is being extensively currently studied. Most thermotropic liquid crystals are rod-like molecules having a rigid core composed of two or more aromatic rings and one or more flexible terminal chains. Schiff base, also known as imine (CH=N), is used as a linking group to connect between core groups. Extensive studies on Schiff base core system had been carried out since the discovery of MBBA showing nematic phase at room temperature in displays sparked a renewed interest liquid crystals and in research to establish structure-liquid crystal property relationships [1]. The understanding of structure-property relationships is essential to improvising molecular modifications for the synthesis of new mesogens with desirable properties and potential applications [2].

Previous studies revealed that ester and Schiff base linking units are the useful functional groups for generating mesomorphism in two and three aromatic rings thermotropic liquid crystals [3-7]. Therefore, an ongoing effort has been carried out which focused on the synthesis of a new series of Schiff base esters possessing halogen end group, 4-alkanoyloxybenzylidene-4’-chloroanilines.

MATERIALS AND METHODS

The synthesis of the target molecules is shown in Scheme 1, where 4-hydroxybenzaldehyde was reacted with 4-chloroaniline under reflux for about three hours in ethanol solution. Then, the obtained Schiff base was subjected to esterification with appropriate fatty acids in the presence of DCC and DMAP [8,9]. The final products were recrystallised with ethanol until constant transition temperature was obtained. The structure of the products was elucidated using elemental analysis, IR, NMR and EI-MS spectroscopic techniques. Analytical and spectroscopic data for compound 12SBCL is given below as the representative data.

Analytical and spectroscopic data for 12SBCL: Yield 74%, EI-MS m/z (rel. int. %): 413.6 (M), 231 (100), IR (KBr, cm⁻¹): 2922, 2830 (C-H aliphatic); 1754(C=O ester); 1621 (C=N); 1599, 1481 (C=O aromatic), 1H NMR (300 MHz, CDCl₃): δ 0.88 (t, 3H, J = 6.3 Hz, CH₃), 1.27 - 1.41 (m, 16H, CH₂(CH₃)₂), 1.76 (q, 2H, J = 7.4 Hz, -CH₂CH₂COO⁻), 2.56 (t, 2H, J = 7.7 Hz, -CH₂CH₂COO⁻), 7.14 (d, 2H, J = 8.5 Hz, Ar-H), 7.21 (d, 2H, J = 8.6 Hz, Ar-H), 7.36 (d, 1H, J = 8.6 Hz, Ar-H), 7.92 (d, 1H, J = 8.2, Ar-H), 8.40 (s, 1H, CH=N), 13C NMR (75 MHz, CDCl₃): δ 14.08 (CH₃), 22.64, 24.78, 29.03, 29.19, 29.21, 29.30, 30.06, 30.11, 31.87 for methylene carbons.
Scheme 1: Synthetic route of Schiff bases nSBCL. (i) C₆H₅OH (ii) C₆H₅Cl, COOH, DCC, DMAP, DMF, CH₂Cl₂.

(CH₃CH₂)₄N, 34.38 (CH₃COO⁻), 116.17, 122.07, 122.33, 129.20, 130.00, 148.82, 150.30, 155.56 for aromatic carbons, 159.40 (CH=N), 171.89 (COO), Anal. Calc'd. For C₆H₅ClN₂O₂: C, 72.53%; H, 7.79%; N, 3.38%; Found: C, 72.42%; H, 7.87%; N, 3.43%.

The liquid crystalline textures of the title compounds were observed under a polarizing optical microscope equipped with a hot stage and temperature regulator. Phase identification was made by comparing the observed textures with those reported in the literature [10,11]. Transition temperatures and corresponding enthalpy changes were determined using a differential scanning calorimeter.

RESULTS AND DISCUSSION

The transition temperatures obtained from the DSC analysis are tabulated in Table 1. n-Hexanoyloxy having the shortest alkyl chain length was found to be monotropic liquid crystal. This is evident from the DSC thermogram (Fig. 1) whereby an endotherm attributed to direct isotropization process was observed during heating cycle. However, three exotherms were observed for n-hexanoyloxy during cooling cycle and this confirmed that the presence of two mesophases in this compound. Higher members of the series, n-octanoyloxy to n-octadecanoyloxy showed two endotherms in the DSC thermograms which can be attributed to the crystal-mesophase and mesophase-isotropic liquid transitions, respectively.

With aids of polarized light, n-hexanoyloxy derivatives exhibited monotropic smectic phases. In the monotropic mesogens, the melting points were always equal to or higher than the clearing points, hence exhibiting supercooling properties [12]. Homologous members C₈ to C₁₆ are enantiotropic mesogens. During cooling cycle, these compounds exhibited fan-shaped textures (Fig. 2a) which can be assigned as smectic A phase. On further cooling, the fan-shaped textures changes to a series of temporary dark-lines (Fig. 2b), running parallel to the layers, which identified as smectic B phase. Smectic B phase exhibited metastable state below the melting point, indicated monotropic properties [13]. As for the highest member of the series, C₁₈ member, SmA phase was observed during both cycles. Thus, C₁₈ is an enantiotropic mesogen.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition temperatures, °C (ΔH, kJmol⁻¹)</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>6SBCL</td>
<td>Cr 95.94 (46.32) I, SmA 77.50 (3.20), SmB 32.07 I</td>
<td>95.25 (6.44) SmA 77.50</td>
<td>95.25 (6.44) SmA 77.50</td>
</tr>
<tr>
<td>8SBCL</td>
<td>Cr 84.0 (34.6) SmA 104.8 (6.7) I</td>
<td>102.7 (6.9) SmA 104.8</td>
<td>102.7 (6.9) SmA 104.8</td>
</tr>
<tr>
<td>10SBCL</td>
<td>Cr 83.4 (35.4) SmA 106.7 (8.9) I</td>
<td>105.1 (8.2) SmA 106.7</td>
<td>105.1 (8.2) SmA 106.7</td>
</tr>
<tr>
<td>12SBCL</td>
<td>Cr 86.3 (40.6) SmA 106.5 (8.9) I</td>
<td>104.5 (8.1) SmA 106.5</td>
<td>104.5 (8.1) SmA 106.5</td>
</tr>
<tr>
<td>14SBCL</td>
<td>Cr 89.8 (55.3) SmA 105.1 (9.2) I</td>
<td>103.5 (9.1) SmA 105.1</td>
<td>103.5 (9.1) SmA 105.1</td>
</tr>
<tr>
<td>16SBCL</td>
<td>Cr 92.8 (58.3) SmA 102.4 (8.6) I</td>
<td>100.7 (9.4) SmA 102.4</td>
<td>100.7 (9.4) SmA 102.4</td>
</tr>
<tr>
<td>18SBCL</td>
<td>Cr 94.5 (72.0) SmA 98.8 (8.9) I</td>
<td>97.1 (10.1) SmA 76.7</td>
<td>97.1 (10.1) SmA 76.7</td>
</tr>
</tbody>
</table>

Cr, crystal; SmA, smectic A; SmB, smectic B; I, isotropic
Fig. 1: DSC thermogram of 8SBCL

Fig. 2: Optical photomicographs of 8SBCL taken during cooling run.
(a) Fan-conic shaped textures (a) which assigned to smectic A phase and temporary transition bars
(b) when changing from smectic A to smectic B

Fig. 3: Plot of transition temperatures versus number of carbon in alkanoyloxy chain of nSBCL during heating cycle
A plot of transition temperatures versus number of carbon in alkanoyloxy chain of nSBC1 during heating cycle is shown in Fig. 3. Based on the plot, it can be deduced that the mesophase were greatly influenced by the length of terminal chain. With the increasing length of terminal chain, the homologous series had shown the changes from monotropic to enantiotropic properties. This is due to the flexibility of alkyl chain has balanced with rigidity of the core system, which promote enantiotropic mesogear [10]. In addition, the melting points is gradually decreased from C6 to C10 due to the dilution of core system. As increasing length from C12 to C18, the melting point increased because of the increase in van der Waals attraction. Transition temperatures of SmA-to-I are descending from C10 to C18 members. This depression is due to the strength of terminal intermolecular attractions. As the alkanoyloxy chains grow longer, the terminal attractions become weaker, allow partial penetration of the layers and destruct the smectic molecular order, therefore depress the SmA-to-I transition temperatures [14,15].

ACKNOWLEDGEMENT

The author (S.T. Ha) would like to thank Universiti Tunku Abdul Rahman (UTAR) for the research facilities and financial support through UTAR Postgraduate Bench Fee (Vote No. 6202/005). L.K. Ong would like to acknowledge UTAR for the award of the research and teaching assistantships.

REFERENCES