

Synthesis and mesomorphic properties of Schiff base esters possessing terminal chloro substituent

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Abstract

A homologous series of Schiff base esters, 4-chlorobenzylidene-4'-*n*-alkanoyloxyanilines, containing even number of carbons at the end groups of the molecules ($C_{n-1}H_{2n-1}COO-$, $n = 4, 6, 8, 10, 12, 14, 16$) were synthesized. The mesomorphic properties were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). It was found that the end groups of the molecules had an effect on the mesomorphic properties. *n*-Butanoyloxy was found non-mesogenic, whilst *n*-hexanoyloxy exhibited monotropic smectic phase. The higher members in this homologous series were enantiotropic smectogens.

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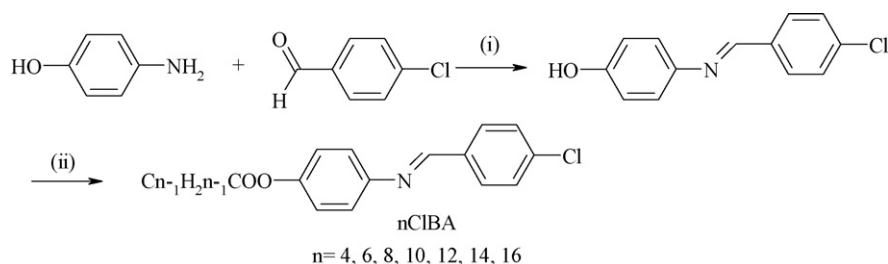
Keywords: Schiff base esters; Smectic A; Smectic B; Liquid crystal

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

In the previous studies, it was revealed that ester and Schiff base 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 possessing terminal halogen substituent, 4-chlorobenzylidene-4'-*n*-alkanoyloxyanilines. The synthesis of the target molecules is shown in Scheme 1, where 4-chlorobenzaldehyde was coupled with 4-aminophenol by heating under reflux for about 3 h in ethanol solution. Then, the Schiff base intermediate was subjected to esterification with

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Scheme 1. Synthetic route of 4-chlorobenzylidene-4'-alkanoyloxyanilines, *n*CIBA. (i) $\text{C}_2\text{H}_5\text{OH}$ and (ii) $\text{C}_{n-1}\text{H}_{2n-1}\text{COOH}$, DCC, DMAP, DMF, CH_2Cl_2 .

Table 1
Phase transitions and transition enthalpy for *n*CIBA upon heating and cooling cycle.

Compound	Transition temperatures, °C (ΔH , kJ mol ⁻¹)	
	Heating	Cooling
4CIBA	Cr 108.3 (30.1) I	I 83.5 (32.3) Cr
6CIBA	Cr 100.2 (33.9) I	I 88.7 (5.4) SmA 81.5 (3.3) SmB 66.0 (21.8) Cr
8CIBA	Cr 93.0 (38.2) SmA 98.1 (6.4) I	I 96.6 (6.7) SmA 83.4 (3.8) SmB 70.8 (32.2) Cr
10CIBA	Cr ₁ 93.4 (33.5) SmA 101.5 (5.6) I	I 99.8 (5.6) SmA 82.2 (2.8) SmB 55.5 (29.6) Cr
12CIBA	Cr 94.6 (39.8) SmA 101.3 (6.3) I	I 100.3 (6.5) SmA 79.9 (2.8) SmB 66.9 (36.7) Cr
14CIBA	Cr 97.0 (43.5) SmA 100.1 (5.5) I	I 98.7 (6.7) SmA 76.7 (2.8) SmB 70.3 (42.1) Cr
16CIBA	Cr 92.9 (50.6) SmA 101.0 (8.3) I	I 99.3 (9.0) SmA 82.0 (4.5) SmB 51.0 (44.1) Cr

Cr, crystal; SmA, smectic A; SmB, smectic B; I, isotropic.

appropriate fatty acids in the presence of DCC and DMAP [8]. 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 [9].

Mesophase 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 the literature [10,11]. Transition temperatures and associated enthalpy changes were measured using differential scanning calorimeter (DSC). The results obtained were listed in Table 1.

n-Butanoyloxy having the shortest alkyl chain length was found to be non-mesogenic. This is evident from the DSC thermogram whereby an endotherm and an exotherm were observed during heating and cooling cycles, respectively. However, three exotherms were observed for *n*-hexanoyloxy during cooling cycle and this suggested that the presence of two mesophases in this compound. Higher members of the series, *n*-octanoyloxy to *n*-hexadecanoyloxy showed two endotherms in the DSC thermograms (Fig. 1) which can be attributed to the isotropic liquid to mesophase and mesophase-crystal transitions.

With aids of polarized light, *n*-butanoyloxy exhibited direct changing of crystal to isotropic upon heating, and vice versa. *n*-Hexanoyloxy derivatives exhibited monotropic smectic phases. In the monotropic mesogens, the melting

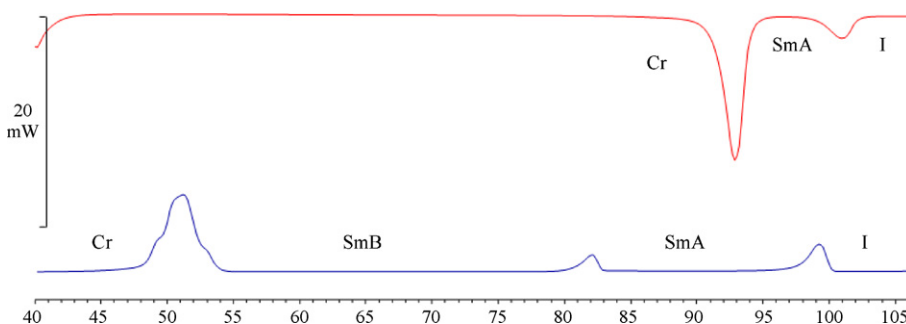


Fig. 1. DSC thermograms of 16CIBA.

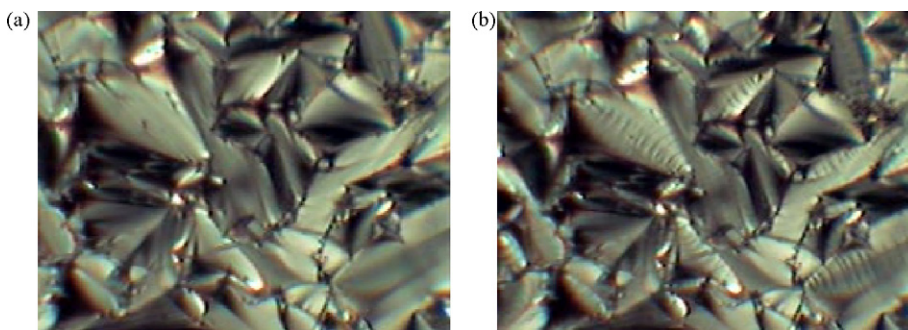


Fig. 2. Liquid crystal texture (100 \times) of 8CIBA upon cooling. Fan-conic shaped textures (a) which indicates smectic A phase and temporary transition bars (b) when changing from smectic A to smectic B.

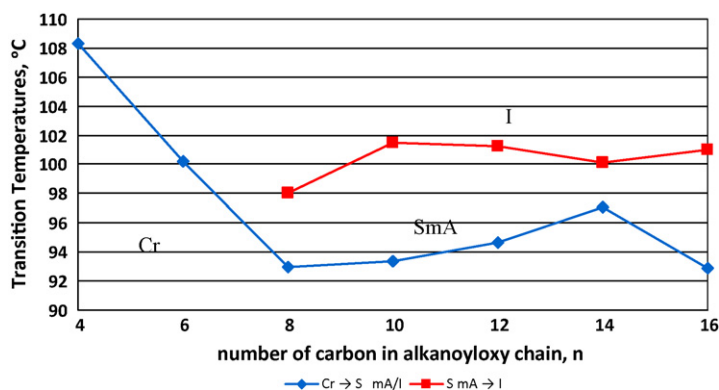


Fig. 3. Plot of transition temperatures versus number of carbon in alkanoyloxy chain of nCIBA during heating cycle.

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 which can be assigned as smectic A phase. Further cooling, the fan-shaped textures changes to a series of temporary dark-lines, 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] (Fig. 2).

A plot of transition temperatures versus number of carbon in alkanoyloxy chain of nCIBA during heating cycle is shown in Fig. 3. Based on the plot, it can be deduced that the mesophase was greatly influenced by the length of terminal chain. As increasing length of terminal chain, the homologous series had shown from non-mesogenic change to monotropic and change to enantiotropic properties. For *n*-butanoyloxy, the core system is too rigid for it to form mesophase [10]. The packing of molecules in hexanoyloxy tends to be less rigid, hence showing monotropic properties. As from *n*-octanoyloxy to *n*-hexadecanoyloxy, the homologous members showed enantiotropic properties. This is because the increase number of carbons enhances the flexibility of the chain and subsequently promotes enantiotropic phase [10]. In addition, the melting points are gradually decreased from C4 to C16 due to the dilution of core system.

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- [9] 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=N); 1590, 1498 (C=C aromatic), ¹H NMR (300 MHz, CDCl₃): δ 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 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%.
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