

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

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Received 3 December 2008

Abstract

A new series of Schiff base esters, 4-(dimethylamino)benzylidene-4'-alkanoyloxyanilines containing even number of carbons at the end group of the molecules ($C_{n-1}H_{2n-1}COO$, $n = 6, 8, 10, 12, 14, 16, 18$) 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.

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Keywords: Liquid crystals; Schiff base esters; Monotropic compounds; Mesomorphic properties

The discovery of thermotropic liquid crystal 4-methoxybenzylidene-4'-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'-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

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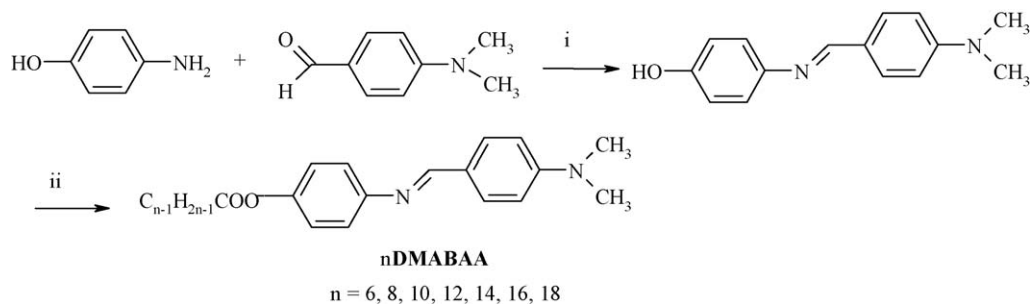
Scheme 1. Synthetic route toward the target compounds: (i) C₂H₅OH and (ii) C_{n-1}H_{2n-1}COOH, DCC, DMAP, CH₂Cl₂, DMF.

Table 1

Phase transitions and transition enthalpy changes for **nDMABAA** upon heating and cooling.

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

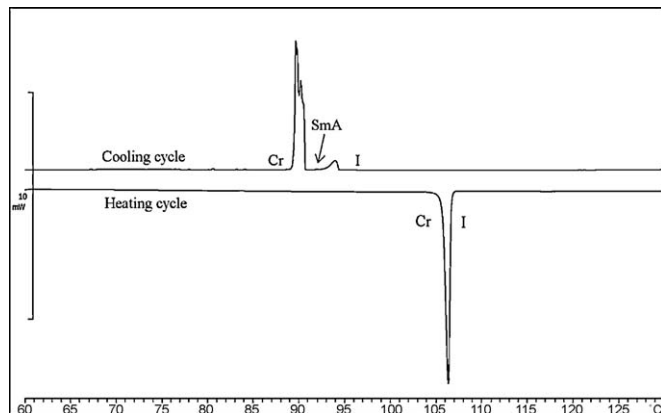
Cr, crystal; N, nematic; SmA, smectic A; I, isotropic.

^a Polarizing optical microscopy data.

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

Fig. 1. DSC thermograms of **14DMABAA**.

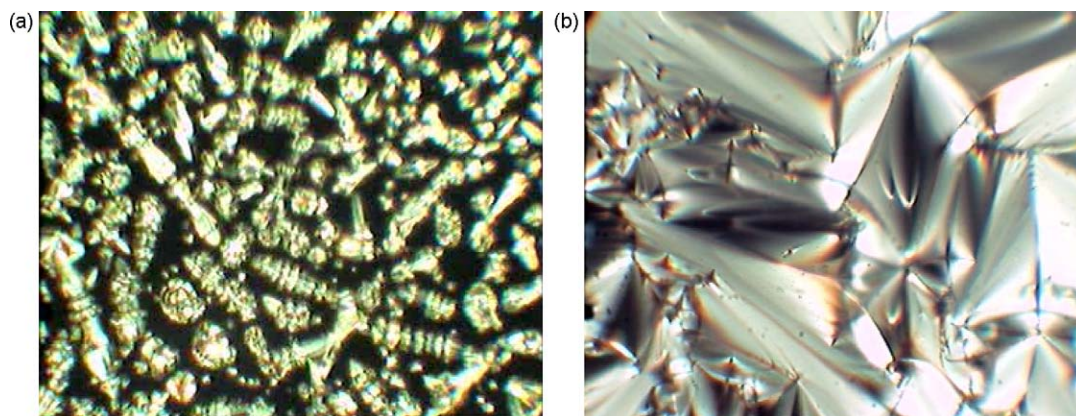


Fig. 2. Liquid crystal textures (100 \times) of 14DMABAA on cooling. The battonets (a) coalesced to form the fan-shaped texture of SmA phase in (b).

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 $C_6H_5CH=NC_6H_5$ compounds, the number of carbons in the alkyl chain must be at least 12 ($n \geq 12$).

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

The author (S.T. Ha) would like to thank Universiti Tunku Abdul Rahman (UTAR) for the research facilities and financial support through UTAR Vote No. 6202/O05, and Universiti Sains Malaysia for the use of its research facilities. L.K. Ong would like to acknowledge UTAR for the award of the research assistantship.

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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, CDCl_3 , δ ppm): 0.90 (t, 3H, $J = 6.5$ Hz, CH_3), 1.28–1.42 {m, 20H, $\text{CH}_3(\text{CH}_2)_{10}$ }, 1.77 (qt, 2H, $J = 7.3$ Hz, $-\text{CH}_2\text{CH}_2\text{COO}-$), 2.58 (t, 2H, $J = 7.4$ Hz, $-\text{CH}_2\text{COO}-$), 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), ^{13}C NMR (75 MHz, CDCl_3 , δ ppm): 14.63 (CH_3), 23.17, 29.57, 29.74, 29.83, 29.93, 30.06, 30.11, 30.14, 32.38 for methylene carbons ($\text{CH}_3(\text{CH}_2)_{10}$), 25.41 ($-\text{CH}_2\text{CH}_2\text{COO}-$), 34.85 ($-\text{CH}_2\text{COO}-$), 40.63 { $\text{N}(\text{CH}_3)_2$ }, 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 $\text{C}_{29}\text{H}_{42}\text{N}_2\text{O}_2$: C, 77.29%, H, 9.39%, N, 6.22%; found: C, 77.37%, H, 9.47%, N, 6.16%.
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