

Synthesis of New Schiff Bases with Dialkylamino End Groups and Effect of Terminal Branching on Mesomorphic Properties

¹Sie-Tiong Ha, ²Lay-Khoon Ong, ³Yasodha Sivasothy and ¹Yip-Foo Win

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

³Department of Chemistry, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

Abstract: Mesomorphic properties of two homologous series of Schiff base esters possessing dimethyl and diethyl terminal groups have been investigated. These molecules contained different length of alkanoyloxy chain ($C_{n-1}H_{2n-1}COO-$) at the other end of the molecules. They are 4-(dimethylamino)benzylidene-4'-alkanoyloxyanilines (nDMABA) and 4-(diethylamino)benzylidene-4'-alkanoyloxyanilines (nDEABA). Their transition temperatures and mesophase characteristics were studied by differential scanning calorimetry and optical polarizing microscopy techniques. Whilst nDMABA members are monotropic liquid crystals, nDEABA did not display liquid crystal phase. Lengthening of dialkylamino terminal branch has caused depression of mesomorphic property in nDEABA.

Key words: Schiff base · Dialkylamino group · Terminal branching · Liquid crystal

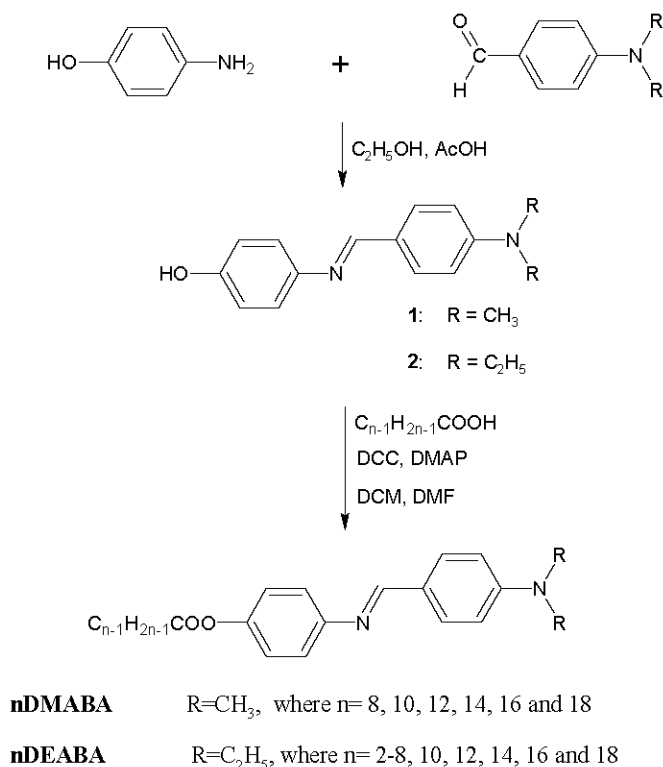
INTRODUCTION

Mesomorphic properties of organic compounds mainly depend on the mesogenic core structure, molecular geometry, polarisability ratio, lateral to terminal attractive force ratio and the length to breadth ratio [1]. Currently, one of the most extensively studied types of mesogens is thermotropic liquid crystal [2,3]. 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 a linking group used to connect between core groups. It provides a stepped core structure but still maintains the molecular linearity in order to exhibit higher stability and form mesophases [4,5]. Extensive studies on Schiff base core systems have been conducted ever since the discovery of MBBA showing nematic phase at room temperature [6]. Nowadays, a lot of studies have been conducted on the Schiff base possessing ester chain or called Schiff base esters owing to their interesting properties and considerable temperature range [7-12].

Terminal substituents tend to be used for fine-tuning mesomorphic properties by creating dipoles along the molecular axis [4]. It is known that terminally substituted compounds exhibit more stable mesophases compared to unsubstituted mesogenic compounds. Terminal substituents are many and varied, including either a small polar substituent (cyano, halogen, etc.) or a fairly long, straight hydrocarbon chain (alkyl or alkoxy) [13]. One of the interesting studies of terminal substituents is by lengthening the branch of terminal group. Therefore, in the present studies, mesomorphic properties of two homologous series of Schiff bases with branching terminal groups, dimethylamino and diethylamino, in the respective first and second series were investigated. The liquid crystal properties were determined by using differential scanning calorimetry (DSC) and polarizing optical microscope (POM).

MATERIALS AND METHODS

Techniques: Electron Impact Mass Spectrum (EI-MS) was recorded by a Finnigan MAT95XL-T mass spectrometer operating at 70 eV ionizing energy.



Scheme 1: Synthetic route of nDMABA and nDEABA

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 $4000\text{--}400\text{ cm}^{-1}$ with samples embedded in KBr discs. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 by utilizing JEOL 400MHz NMR Spectrometer with TMS as internal standard. The phase transition temperatures were measured by Mettler Toledo DSC823 Differential Scanning Calorimeter (DSC) at a scanning rate of $10^\circ\text{C}/\text{min}$. Liquid crystalline properties were investigated by Polarizing Optical Microscopy (POM) using a Carl Zeiss Polarizing Optical Microscope (POM) attached to a Linkam Hotstage.

Materials: 4-Aminophenol, 4-dimethylaminobenzaldehyde, 4-diethylaminobenzaldehyde, 4-dimethylaminopyridine (DMAP), N,N' -dicyclohexylcarbodiimide (DCC) and fatty acids were obtained commercially. The synthetic route for all the title compounds are illustrated in Scheme 1.

Synthesis of 4-(dimethylamino)benzylidene-4'-alkanoyloxylanilines (nDMABA): The synthesis of these compounds have been previously reported by our group [14].

Synthesis of 4-(diethylamino)benzylidene-4'-alkanoyloxylanilines (nDEABA): A solution of 4-diethylaminobenzaldehyde (50 mmole) and 4-aminophenol (50 mmole) in absolute ethanol (50 mL) was heated under reflux for three hours. Schiff base 2 thus obtained was recrystallized from absolute ethanol. Then, Schiff base 2 (2 mmole) in dimethylformamide (DMF) (1 mL), was added to a solution of fatty acid (2 mmole) and 4-dimethylaminopyridine (DMAP) (1 mmole) in dichloromethane (20 mL). The resulting mixture was stirred in an ice bath. N,N' -dicyclohexylcarbodiimide (DCC) (2 mmole) dissolved in dichloromethane (10 mL) was added dropwise into this mixture 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. Recrystallization from absolute ethanol yielded a yellow product.

The percentage yields and the analytical data are tabulated in Table 1. The IR, NMR (^1H and ^{13}C) and mass spectral data of the representative compound, 16DEABA are summarized as below.

Table 1: Percentage yields and analytical data of nDEABA

Compound	Yield (%)	Formula	% Found (%Cald.)		
			C	H	N
8DEABA	18	C ₂₅ H ₃₄ N ₂ O ₂	76.23(76.10)	8.60(8.69)	7.05(7.10)
10DEABA	44	C ₂₇ H ₃₈ N ₂ O ₂	76.80(76.74)	9.00(9.06)	6.67(6.63)
12DEABA	75	C ₂₉ H ₄₂ N ₂ O ₂	77.45(77.29)	9.33(9.39)	6.24(6.22)
14DEABA	62	C ₃₁ H ₄₆ N ₂ O ₂	77.67(77.78)	9.78(9.69)	5.91(5.85)
16DEABA	54	C ₃₃ H ₅₀ N ₂ O ₂	78.33(78.21)	9.87(9.94)	5.48(5.53)
18DEABA	60	C ₃₅ H ₅₄ N ₂ O ₂	78.71(78.60)	10.15(10.18)	5.20(5.24)

16DEABA: IR (KBr) ν_{max} cm⁻¹: 2920, 2850 (C-H aliphatic), 1753 (C=O ester), 1602 (C=N), 1583, 1488 (C=C aromatic); ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.88 (t, 3H, CH₃), 1.20 (t, 6H, -N(CH₂CH₃)₂), 1.26-1.42 {m, 24H, CH₃(CH₂)₁₂-}, 1.75 (qt, 2H, -CH₂CH₂COO-), 2.58 (t, 2H, -CH₂COO-), 3.43 (qt, 4H, -N(CH₂CH₃)₂), 6.77 (d, 2H, Ar-H), 7.04 (d, 2H, Ar-H), 7.17 (d, 1H, Ar-H), 7.71 (d, 1H, Ar-H), 8.28 (s, 1H, CH=N), ¹³C NMR (100 MHz, CDCl₃, δ ppm): 12.55 [-N(CH₂CH₃)₂], 14.01 (CH₃), 22.67, 29.10, 29.25, 29.34, 29.48, 29.58, 29.63, 29.67, 31.90 for methylene carbons [CH₃(CH₂)₁₂-], 24.96 (-CH₂CH₂COO-), 34.41 (-CH₂COO-), 44.50 [N(CH₂CH₃)₂], 110.98, 121.65, 121.95, 122.11, 123.48, 130.72, 148.00, 150.11, 150.63 for aromatic carbons, 160.25 (CH=N), 172.49 (COO), EI-MS m/z (rel. int. %): 506.4(20) [M]⁺, 268.1 (100).

RESULTS AND DISCUSSION

Synthesis and Spectral Studies: Structural elucidation of compounds nDEABA was ascertained by using elemental analysis, mass spectrometric and spectroscopic methods (FT-IR and NMR). A very good agreement was found between the calculated and experimental values obtained from elemental analysis of nDEABA (Table 1). From the mass spectrum, the molecular ion peak at $m/z = 506$ which was corresponding to molecular mass of C₃₃H₅₀N₂O₂ suggested that 16DEABA was successfully synthesized.

Strong absorption bands appeared at 2920 and 2850 cm⁻¹ in FTIR spectrum of 16DEABA indicates the presence of aliphatic C-H in alkyl chain. A medium band at 1753 cm⁻¹ can be ascribed to C=O bonds of ester

Table 2: Transition temperature and associated enthalpy changes of nDMABA upon heating and cooling

Compound	Transition Temperature, °C (ΔH , kJ mol ⁻¹)	Heating Cooling
2DMABA	Cr 160.2 (29.4) I I 130.9 (27.5) Cr	
3DMABA	Cr 119.5 (22.0) I I 98.7 (22.4) Cr	
4DMABA	Cr 129.32 (28.7) I I 102.01 (29.4) Cr	
5DMABA	Cr 105.89 (28.8) I I 86.47 (27.3) Cr	
6DMABA	Cr 108.6 (36.5) I I 97.2 (1.5) N 91.3 (28.0) Cr	
7DMABA	Cr 105.2 (35.5) I I 88.1 (1.1) N 83.88 (30.9) Cr	
8DMABA	Cr 109.8 (37.0) I I 94.4 (1.2) N 87.6 (32.4) Cr	
10DMABA	Cr 110.0 (51.0) I I 94.5 (1.6) N 87.4 (44.4) Cr	
12DMABA	Cr 104.8 (46.8) I I 93.2 (1.7) N 91.5 (0.26) SmA 88.3 (42.5) Cr	
14DMABA	Cr 105.7 (38.9) I I 94.0 (2.7) SmA 89.6 (34.6) Cr	
16DMABA	Cr 108.1 (42.6) I I 96.6a SmA 94.3 (43.1) Cr	
18DMABA	Cr 109.3 (59.8) I I 99.4a SmA 94.6 (60.3) Cr	

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

*Polarizing optical microscopy data

Table 3: Transition temperature and associated enthalpy changes of nDEABA upon heating and cooling

Compound	Transition Temperature, °C (ΔH , kJ mol ⁻¹)	Heating Cooling
8DEABA	Cr 82.74 (24.4) I I 63.37 (23.6) Cr	
10DEABA	Cr 73.3 (40.4) I I 45.6 (42.3) Cr	
12DEABA	Cr 82.5 (46.8) I I 71.9 (42.5) Cr	
14DEABA	Cr 83.2 (45.0) I I 76.4 (46.6) Cr	
16DEABA	Cr 89.6 (47.7) I I 78.5 (50.2) Cr	
18DEABA	Cr 92.3 (61.9) I I 83.8 (63.2) Cr	

Cr, crystal; I, isotropic

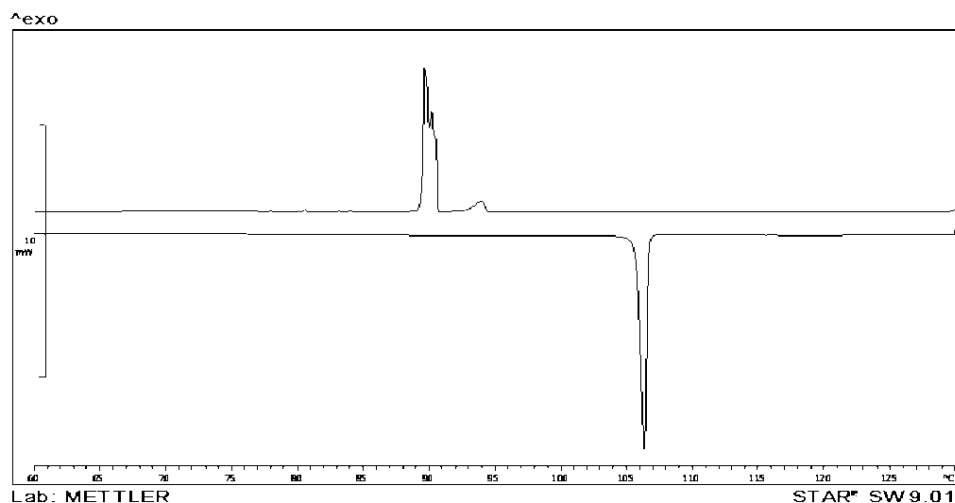


Fig. 1: DSC thermogram of 14DMABA upon heating and cooling cycles

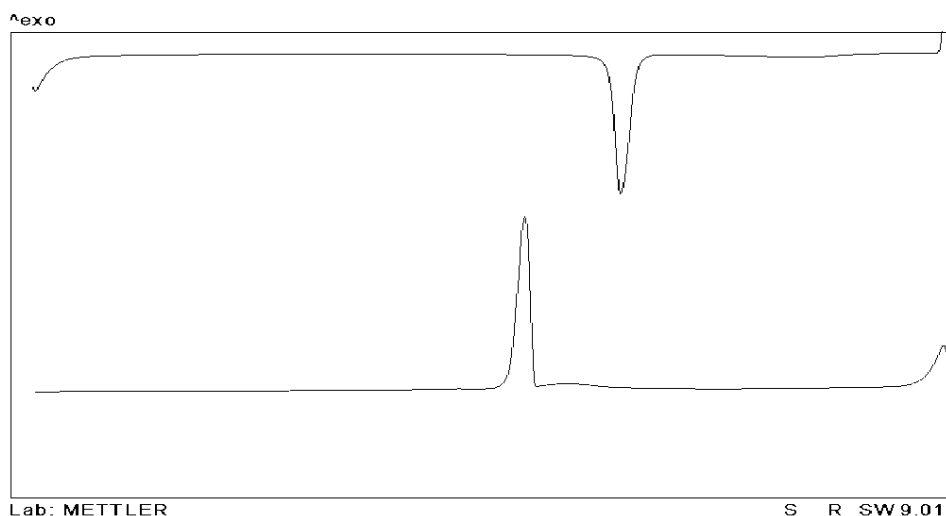


Fig. 2: DSC thermogram of 16DEABA upon heating and cooling cycles

linking group. Absorption band emerged at 1602 cm^{-1} designates for C=N linking group. This value falls within the frequency range reported for Schiff base linkage [9-12].

In ^1H NMR spectrum of 16DEABA, two triplets were observed at $\delta = 0.88\text{ ppm}$ and $\delta = 2.58\text{ ppm}$, which can be ascribed to the methyl and methylene protons ($-\text{CH}_2\text{COO-Ar}$). The chemical shifts at $\delta = 1.26\text{-}1.42\text{ ppm}$ can be assigned to methylene protons of long alkyl chain $\{-(\text{CH}_2)_{12}-\}$. The four distinct double doublets were detected at $\delta = 6.77\text{-}7.71\text{ ppm}$ can be assigned to aromatic protons. A singlet was observed at the most downfield region, $\delta = 8.28\text{ ppm}$ is due to proton of imine linking group [10-12]. The molecular structure of 16DEABA was further verified by using ^{13}C NMR spectroscopy. A peak at $\delta = 14.01\text{ ppm}$ is attributed to the methyl carbon

and peaks at $\delta = 22.67\text{-}31.90\text{ ppm}$ is contributed by the methylene carbons of long alkyl chain. Peaks at $\delta = 110.98\text{-}150.63\text{ ppm}$ is assigned to twelve aromatic carbons in 16DEABA. The peak at $\delta = 160.25\text{ ppm}$ due to existence of azomethine carbon. The most downfield peak in the spectrum, $\delta = 172.49\text{ ppm}$, is ascribed to carbon of ester group.

Mesomorphic Properties: The phase temperature and enthalpy values of both series are summarized in Tables 2 and 3, respectively whilst Figures 1 and 2 showed the representative of DSC thermogram for each series.

All the compounds in nDMABA series exhibited direct melting of the crystal phase to isotropic phase during the heating cycle. However, for nDMABA

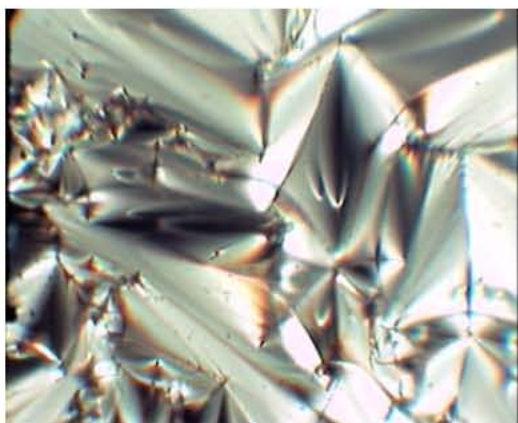


Fig. 3: Optical photomicrograph of 14DMABAA exhibiting the fan-shaped textures of SmA phase

(where $n = 6, 7, 8, 10, 12, 14, 16, 18$), these compounds exhibited exotherms characteristics of the isotropic-mesophase and mesophase-crystal transitions, indicating the monotropic properties. The melting point of the monotropic mesogens is always equal to or higher than the clearing points, hence causing them to exhibit supercooling properties [15].

All the members in the nDEABA series were non-mesogenic compounds. In the representative DSC thermogram of 14DEABA (Figure 2), it showed an endotherm and exotherm, respectively during both heating and cooling cycles. This observation indicates direct melting of the crystal phase to the isotropic liquid phase and vice versa. Under polarizing optical microscopy (POM) observation, crystal changed to dark region isotropic during heating run. No liquid crystal texture was observed during cooling process.

Under POM, 6DMABA, 7DMABA, 8DMABA, 10DMABA and 12DMABA exhibited monotropic nematic phase. The mesophase was identified by the nematic droplets texture. Brownian flashes, a characteristic of the nematic phase were also observed before recrystallization. A remarkable characteristic was observed for 12DMABA where an additional phase with fan-shaped texture which assigned as smectic A (SmA) phase was observed after the formation of nematic phase upon cooling cycle. Further increase the molecular length of nDMABA series from C14 to C18 did not show co-appearance of nematic and SmA phases. C14-C18 members exhibited only fan-shaped textures of SmA phase (Figure 3). Phase identification was based on the optical textures and the magnitude of isotropization on enthalpies is consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus [16] and Gray and Goodby [1].

Effect of Alkyl Chain Length on Mesomorphic Properties:

The plot of phase transition temperatures against the number of carbons in the alkanoyloxy chain of nDMABA series (Figure 4), enables the effects of the terminal chain on the mesomorphic properties to be established. The adequate geometric anisotropy (ratio between length and width of the molecule) is an important point. Based on Figure 4, the commonly observed zigzag pattern or the odd-even effect on the mesomorphic properties was noticeable when moving from the C2 to the C8 derivatives. The even members possess higher melting temperatures than the odd counterparts. From C10 onwards, the melting temperatures show no regular dependence on the alkyl chain length.

The short chain derivatives ($n = 2, 3, 4$ and 5) are non-mesogenic compounds. The high melting points of the early series may be partially responsible for the lack of mesophase formation. Since the terminal chain of the C6, C7, C8 and C10 derivatives are long enough for promoting mesophase formation, therefore, a nematic phase was observed for each of those derivatives [17]. As the length of the carbon chain increased, co-existence of nematic and SmA phase was observed for the C12 derivative. Similarly, once the carbon chain reached a certain length ($n \geq 14$), only the SmA phase was induced. This suggests that with increasing in the length of alkanoyloxy chain, the nematic properties diminished and led to the formation of 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 [4]. 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 alkanoyloxy chain must be at least 12 ($n \geq 12$).

Effect of Terminal Branching on Mesomorphic Properties:

The lengthening of dialkylamino branch terminal group from methyl in nDMABA [$N(CH_3)_2$] to ethyl in nDEABA [$N(C_2H_5)_2$] has drastically influenced the mesomorphic properties. Compounds in the nDMABA series exhibited liquid crystal phases but compounds in the nDEABA series were non-mesomorphic compounds. Longer alkyl chain in dialkylamino group perturbs the packing of molecules, therefore inhibited the formation of mesophase in the nDEABA series. Furthermore, nDEABA members possessed lower melting point compared to nDMABA members having the similar number of carbons (n) at the alkanoyloxy chain. This suggests that the terminal branching of diethylamino group can depress the thermal stability of a compound.

CONCLUSION

Mesomorphic properties of two series of Schiff base esters, 4-dimethylamino-benzylidene-4'-alkanoyloxyanilines (nDMABA) and 4-diethylaminobenzylidene-4'-alkanoyloxyanilines (nDEABA) have been studied. Short chain members of nDMABA (n = 2-5) did not possess mesomorphic properties. Early members of nDMABA (n = 6, 8, 10) displayed only nematic phases, medium member (n = 12) exhibited co-existence of both nematic and smectic phases and higher derivatives (n = 14, 16, 18) exhibited smectic A phase. All compounds in nDEABA series were non-mesomorphic derivatives. The lengthening of dialkylamino terminal branch has significantly suppressed the formation of liquid crystal in nDEABA.

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