

Full Length Research Paper

Effect of terminal branching on mesomorphism of a homologous series of Schiff base ethers

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A lot of studies have been focused on the Schiff base's alkyl and alkyloxy possessing polar terminal group. Yet, the thermotropic properties of Schiff base's ether (alkyloxy) with dialkylamino terminal group remained less studied. A series of 4-(dialkylamino)benzylidene-4'-alkyloxylanilines were prepared and all the members are differed by the alkyloxy chain length, $C_nH_{2n+1}O$, where $n = 6, 8, 10, 12, 14, 16$ and 18 . Their transition temperatures and mesophase characteristics were studied by differential scanning calorimetry and optical polarizing microscopy techniques. DSC thermograms exhibited direct isotropization and recrystallization during heating and cooling cycles, respectively. The crystal phase texture changed to dark region isotropic without displaying any mesophase. Lengthening of dialkylamino terminal branch has caused depression of mesomorphic property in the compounds studied.

Key words: Schiff base, dialkylamino group, terminal branching, mesophase.

INTRODUCTION

Development of liquid crystal science and technology has led to the preparation and study of numerous mesogens in particular, thermotropic liquid crystals (Yuksel et al., 2007; Zhang et al., 2005). Most thermotropic liquid crystals are calamitic molecules having 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 well-known linking group used in connecting two core groups. Though it provides a stepped core structure, yet it maintains molecular linearity, hence providing higher stability and enabling the formation

mesophase (Collings and Hird, 1998; Singh and Dunmur, 2002). Extensive investigation on Schiff base core system had been conducted since the discovery of 4-methoxybenzylidene-4'-butylaniline (MBBA) which exhibited nematic phase at room temperature (Kelker and Scheurle, 1969). Several studies have been conducted on Schiff base esters owing to their interesting properties and considerable temperature range (Eran et al., 2008; Ha et al., 2009a, 2009b; Parra et al., 2004; Prajapati and Varia, 2008; Vora et al., 2001; Yeap et al., 2004, 2006a, 2006b, 2006c).

Terminal substituents tend to be used for fine-tune mesomorphic properties by creating dipoles along the molecular axis (Collings and Hird, 1998). It is known that terminally substituted compound exhibited more stable

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Table 1. Percentage yields, analytical data and IR frequencies of 4-(diethylamino)benzylidene-4'-alkyloxylanilines.

Compound	Yield* (%)	Formula	% Found (% Cald.)			IR (cm ⁻¹)		
			C	H	N	ν (C-H aliphatic)	ν (C=N)	ν (C-O)
6DEBA	36	C ₂₃ H ₃₂ N ₂ O	78.47 (78.36)	9.08 (9.15)	8.01 (7.95)	2976, 2936, 2868	1598	1244
8DEBA	40	C ₂₅ H ₃₆ N ₂ O	79.12 (78.90)	9.58 (9.53)	7.31 (7.36)	2972, 2929, 2855	1592	1241
10DEBA	40	C ₂₇ H ₄₀ N ₂ O	79.29 (79.36)	9.91 (9.87)	6.96 (6.86)	2967, 2923, 2850	1599	1246
12DEBA	43	C ₂₉ H ₄₄ N ₂ O	79.80 (79.76)	10.21 (10.16)	6.33 (6.42)	2975, 2919, 2847	1603	1241
14DEBA	50	C ₃₁ H ₄₈ N ₂ O	80.00 (80.12)	10.50 (10.41)	6.11 (6.03)	2955, 2920, 2851	1600	1241
16DEBA	42	C ₃₃ H ₅₂ N ₂ O	80.51 (80.43)	10.59 (10.64)	5.75 (5.68)	2956, 2920, 2851	1606	1243
18DEBA	44	C ₃₅ H ₅₆ N ₂ O	80.79 (80.71)	10.81 (10.84)	5.45 (5.38)	2972, 2920, 2851	1607	1242

* Percentage yield was calculated based on the final step in the synthesis.

mesophase as compared to unsubstituted mesogenic compounds. Various types of terminal substituents have been studied, including either a small polar substituent or a fairly long hydrocarbon chain (Kumar, 2001). One of the interesting topics of terminal substituents is by lengthening the branch of terminal group. Therefore, in the present study, mesomorphic properties of a homologous series of Schiff bases with diethylamino end group was investigated and compared with their analogous compounds bearing dimethylamino end group (Ha et al., 2009c).

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. 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 - 400 cm⁻¹ with samples embedded in KBr discs. NMR spectra were recorded in CDCl₃ by utilizing JEOL 400 MHz 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°C/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, 1-bromoalkanes, 4-(diethylamino)benzaldehyde, potassium hydroxide and potassium iodide were obtained commercially. The synthetic route for the title compounds are illustrated in Scheme 1.

Synthesis of 4-(diethylamino)benzylidene-4'-alkyloxylanilines (nDEBA)

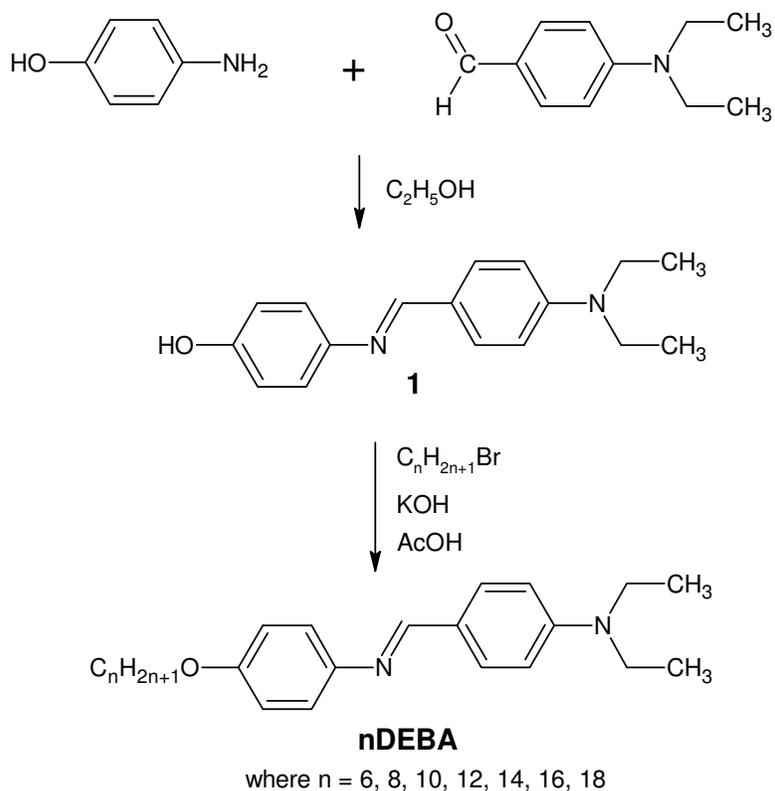
A solution of 4-diethylaminobenzaldehyde (8 mmol) and 4-aminophenol (8 mmol) in absolute ethanol (40 mL) was heated under reflux for three hours. Schiff base 1 thus obtained was

recrystallized from absolute ethanol. Then, Schiff base 1 (2.0 mmol) in acetone (40 ml), was added to a solution of potassium hydroxide (2.0 mmol) in distilled water (10 ml). This was followed by addition of a small amount of potassium iodide into the mixture. The reaction mixture was heated under reflux for an hour upon stirring. 1-Bromoalkane (3.0 mmol) was then added to the flask and reflux was continued for 24 h. The yellow product obtained was repeatedly recrystallized with absolute ethanol whereupon the pure compound was isolated as a yellow solid.

The IR, NMR (¹H and ¹³C) and mass spectral data of the representative compound, 12DEBA are summarized as 12DEBA: EI-MS *m/z* (rel. int. %): 436(100) [M]⁺, 421.3(27), 267.1(64), 253.1(17), 223.0(32); IR (KBr) ν_{\max} cm⁻¹: 2975, 2919, 2847 (C-H aliphatic), 1603 (C=N), 1241 (C-O); ¹H NMR (400 MHz, CDCl₃, δ ppm): 0.88 (t, 3H, CH₃), 1.20 (t, 6H, -N(CH₂CH₃)₂), 1.26-1.41 {m, 18H, CH₃(CH₂)₉}, 1.77 (quint, 2H, -CH₂CH₂O-), 3.43 (qt, 4H, -N(CH₂CH₃)₂), 3.95 (t, 2H, -CH₂O-), 6.67 (d, 2H, Ar-H), 6.88 (d, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 7.70 (d, 2H, Ar-H), 8.30 (s, 1H, CH=N); ¹³C NMR (100 MHz, CDCl₃ δ ppm): 12.45 [-N(CH₂CH₃)₂], 14.10 (CH₃), 22.67, 26.05, 29.33, 29.37, 29.41, 29.57, 29.59, 29.62, 29.65, 31.91 for methylene carbons [CH₃(CH₂)₁₀], 44.45 [-N(CH₂CH₃)₂], 68.29 (-CH₂O-), 111.04, 114.91, 121.90, 123.86, 130.44, 145.89, 149.87, 157.48 for aromatic carbons, 158.51 (CH=N).

RESULTS

Spectral characteristics of nDEBA were studied by using mass spectrometric and spectroscopic methods. The percentage yields and the analytical data are tabulated in Table 1. The phase transition temperatures and their associated enthalpy obtained from DSC analysis over heating and cooling cycles are tabulated in Table 2. Representative EI mass spectrum is depicted in Figure 1. Whilst representative IR spectrum of 12DEBA is shown in Figure 2, ¹H and ¹³C NMR spectra are given in Figures 3 and 4, respectively. DSC thermograms of 12DEBA, 14DEBA and 16DEBA upon heating and cooling cycles are shown in Figures 5 and 6, respectively. The effect of alkyl chain length on melting and recrystallization points is illustrated in Figure 7. Influence of dialkylamino terminal branching on the mesomorphism is best presented in Figure 8.



Scheme 1. Synthetic route of 4-(diethylamino)benzylidene-4'-alkoxyanilines.

Table 2. Transition temperature and associated enthalpy changes of 4-(diethylamino)benzylidene-4'-alkoxyanilines upon heating and cooling cycles.

Compound	Transition temperature, °C (ΔH , kJ mol ⁻¹)	Heating cooling
6DEBA	Cr 54.5 ^a I I 19.8 ^a Cr	
8DEBA	Cr 73.3 (31.6) I I 36.0 (23.0) Cr	
10DEBA	Cr 63.2 (28.8) I I 53.1 (28.6) Cr	
12DEBA	Cr 70.0 (48.9) I I 59.1 (47.3) Cr	
14DEBA	Cr ₁ 48.2 (4.1) Cr ₂ 72.6 (39.2) I I 63.9 (38.3) Cr ₂ 43.7 (5.3) Cr ₁	
16DEBA	Cr ₁ 53.5 (2.1) Cr ₂ 65.9 (1.9) Cr ₃ 75.0 (49.9) I I 70.0 (50.3) Cr ₂ 61.8 (2.5) Cr ₁	
18DEBA	Cr ₁ 58.5 (1.0) Cr ₂ 80.6 (55.4) I I 72.7 (60.1) Cr ₂ 55.3 (0.5) Cr ₁	

Cr₁, Cr₂, Cr, crystal; N, nematic; SmA, smectic A; I, isotropic ^aPolarizing optical microscopy data.

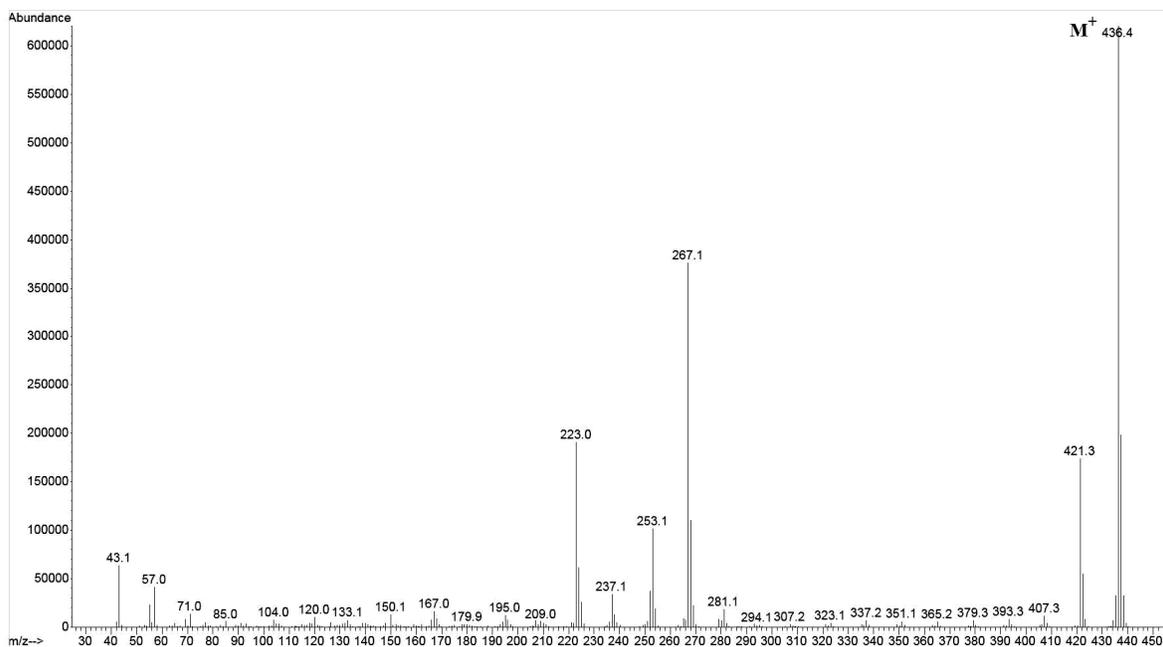


Figure 1. EI Mass spectrum of 4-(diethylamino)benzylidene-4'-dodecyloxyaniline showing molecular ion peak (M⁺).

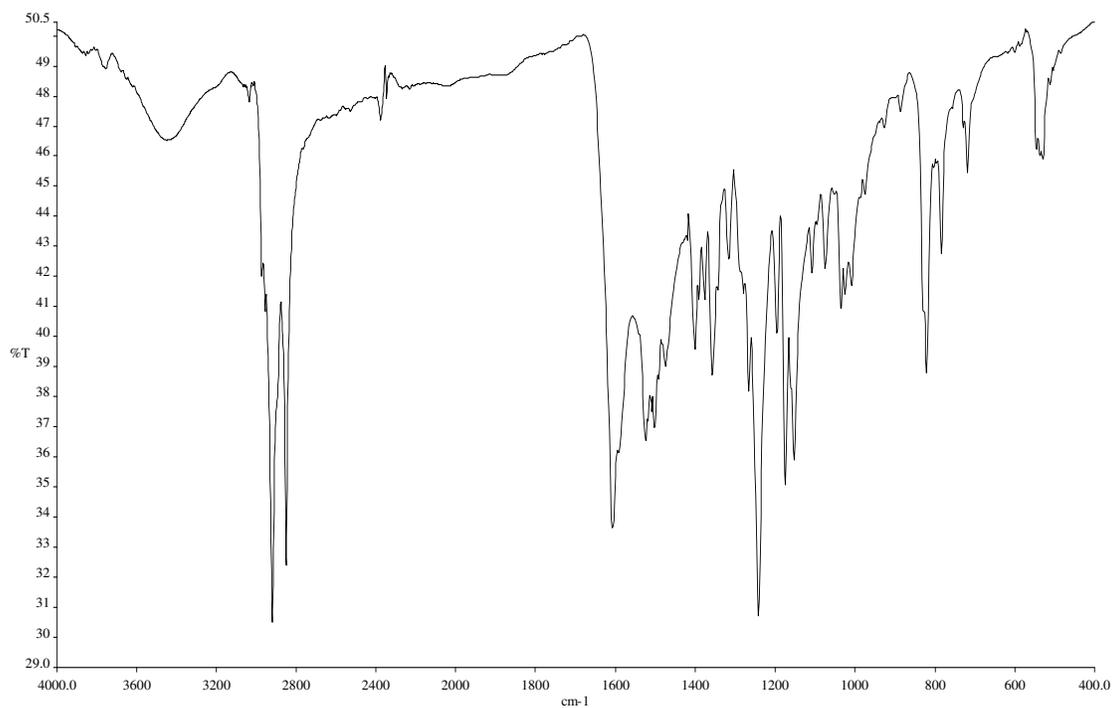


Figure 2. FT-IR spectrum of 4-(diethylamino)benzylidene-4'-dodecyloxyaniline.

DISCUSSION

Physical characterization

A very good agreement was found between the

calculated and experimental values obtained from elemental analysis of nDEBA (Table 1). From the mass spectrum (Figure 1), the molecular ion peak at $m/z = 436$ which was corresponding to molecular mass of $C_{29}H_{44}N_2O$ suggested that 12DEBA was successfully

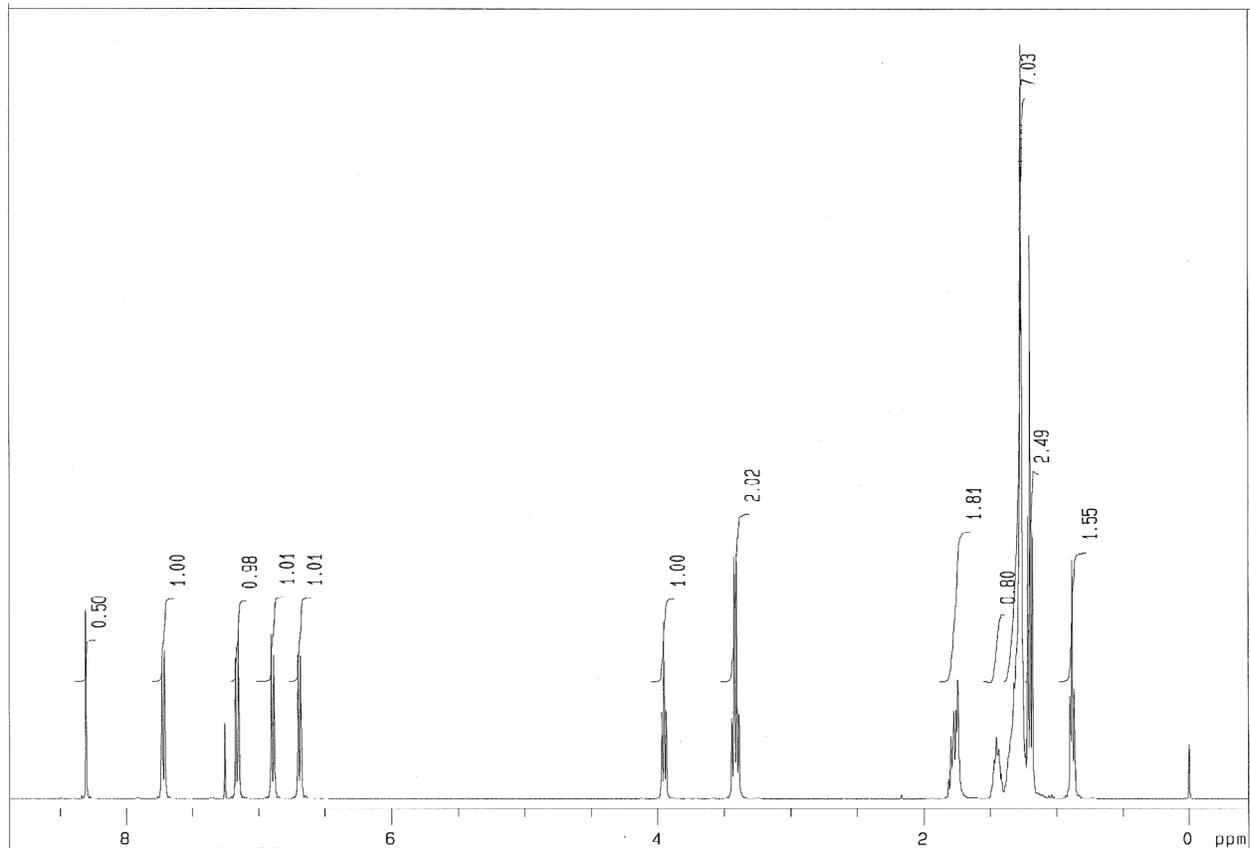


Figure 3. ¹H NMR spectrum of 4-(diethylamino)benzylidene-4'-dodecyloxyaniline.

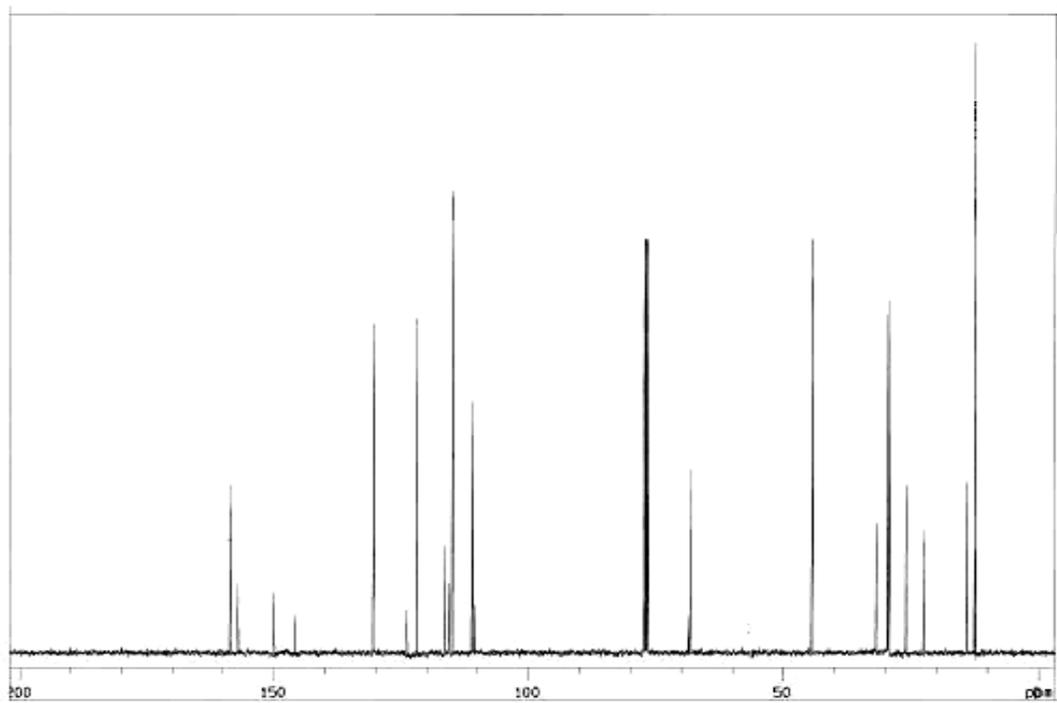


Figure 4. ¹³C NMR spectrum of 4-(diethylamino)benzylidene-4'-dodecyloxyaniline.

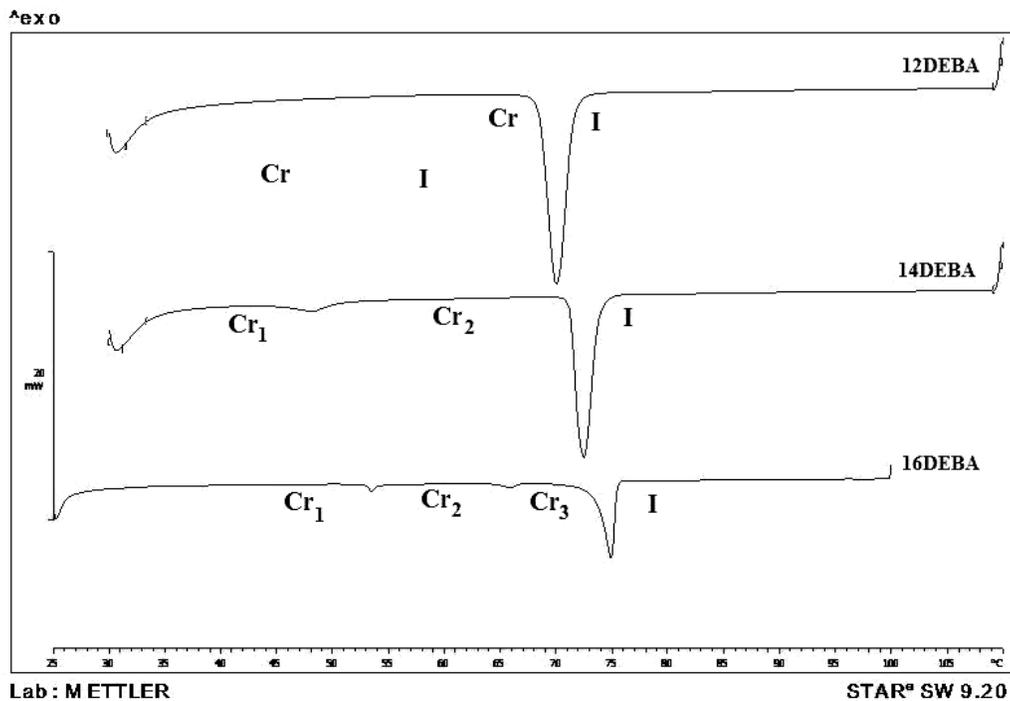


Figure 5. DSC thermograms of 12DEBA, 14DEBA and 16DEBA during heating cycle.

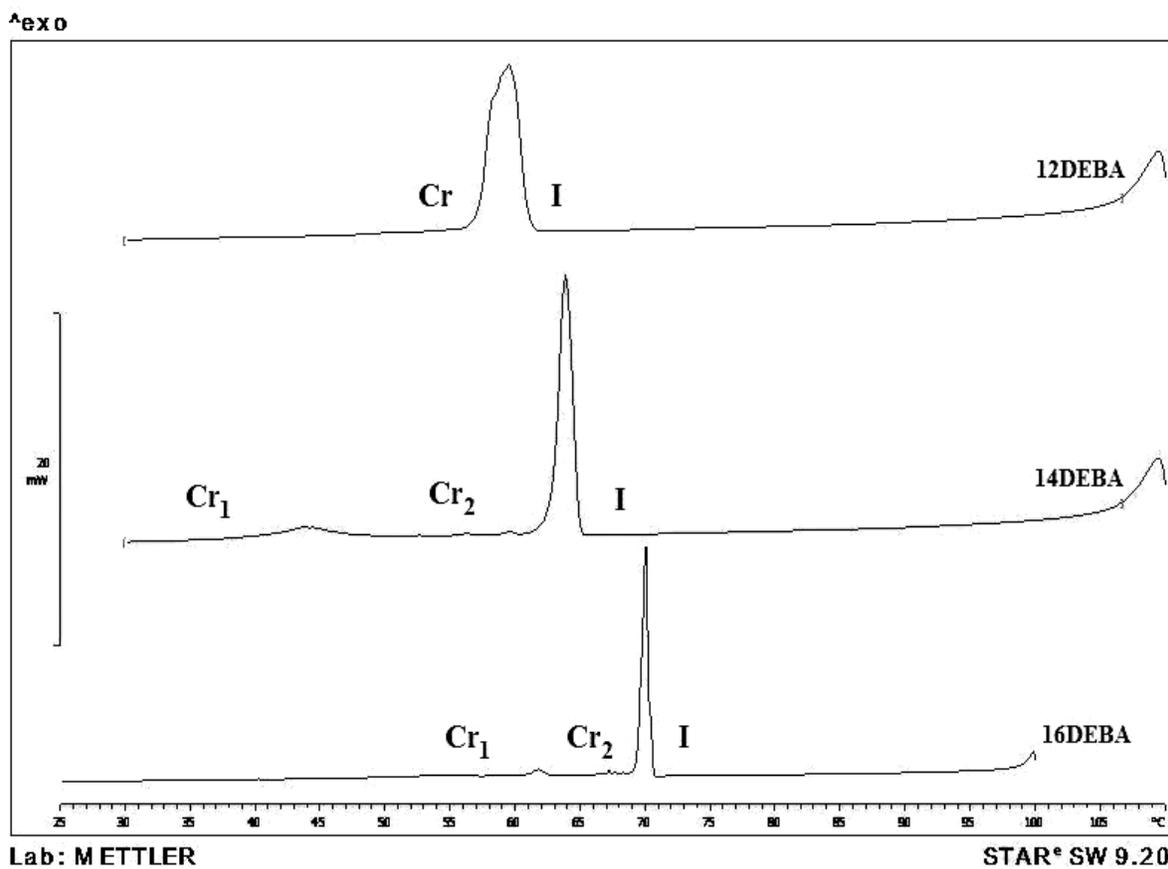


Figure 6. DSC thermograms of 12DEBA, 14DEBA and 16DEBA during cooling cycle.

synthesized. Strong absorption bands appeared at 2919 and 2847 cm^{-1} in FTIR spectrum of 12DEBA (Figure 2) indicates the presence of aliphatic C-H in alkyl chain. A sharp band at 1241 cm^{-1} can be ascribed to C-O bonds of aromatic ether linking group. Absorption band emerged at 1603 cm^{-1} designates for C=N linking group. This value falls within the frequency range reported for Schiff base linkage (Yeap et al., 2006a, 2006b, 2006c).

In ^1H NMR spectrum of 12DEBA (Figure 3), two triplets were observed at $\delta = 0.88$ ppm and $\delta = 3.95$ ppm, which can be ascribed to the methyl and methylene protons ($-\text{CH}_2\text{O}-$), respectively. The chemical shifts at $\delta = 1.26 - 1.41$ ppm can be assigned to methylene protons of long alkyl chain $\{\text{CH}_3-(\text{CH}_2)_9\}$. The four distinct double doublets were detected at $\delta = 6.67 - 7.70$ ppm can be assigned to eight aromatic protons. A singlet was observed at the most downfield region, $\delta = 8.30$ ppm is due to proton of imine linking group (Yeap et al., 2006a, 2006b, 2006c). The molecular structure of 12DEBA was further verified by using ^{13}C NMR spectroscopy (Figure 4). A peak at $\delta = 14.10$ ppm is attributed to the methyl carbon and peaks at $\delta = 22.67-31.91$ ppm is contributed by the methylene carbons of long alkyl chain. Peaks at $\delta = 111.04 - 157.48$ ppm is assigned to twelve aromatic carbons in 12DEBA. The most downfield peak at $\delta = 158.51$ ppm is due to existence of azomethine carbon.

Phase transition behaviors and optical texture studies

All the members in the nDEBA series were non-mesogenic compounds. In the representative DSC thermogram of 12DEBA (Figures 5 and 6), 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. Other low members, nDEBA (where $n = 6, 8, 10$) showed the similar characteristics as those found for 12DEBA.

As for 14DEBA, the thermogram showed an endotherm at 48.2°C before isotropization. The texture observed under the polarizing microscope is indicative of the presence of subphases within the crystal phase (Cr_1 - Cr_2) as those observed in its analogue *o-n*-hydroxy-*p-n*-hexadecanoyloxybenzylidene-fluoroaniline (Yeap et al., 2004). Similar subphases were also observed for 18DEBA. Three endotherms appeared in the thermogram of 16DEBA but all these phases are merely crystal phases (Cr_1 , Cr_2 , Cr_3) and not liquid crystal phase.

Effect of alkyl chain length on transition temperatures

A further examination of DSC data also illustrates the

evolution of the Cr-I transition with the lengthening of terminal chains. A plot of the melting and recrystallization temperatures against the number of carbons in the alkyloxy chain during the heating and cooling cycles is shown in Figure 7. The melting temperatures for Schiff bases 6DEBA to 18DEBA increases as the alkyl chain of $\text{C}_n\text{H}_{2n+1}\text{O}-$ elongates in the range of $n = 6-18$ except for 8DEBA. The ascending melting point could be attributed to the increase of van der Waals attraction when the alkyl chains of the title compounds ($\text{C}_n\text{H}_{2n+1}\text{COO}-$) varied from 6 to 8 and 18. Similar phenomenon was also reported for analogous two homologous of Schiff bases, 2-hydroxy-4-methoxy-4'-alkanoyloxyanilines and 3-methoxy-4'-alkanoyloxybenzylidene-4'-alkanoyloxyanilines (Yeap et al., 2006c). The recrystallization points also show ascending trend as the number of carbons increased.

Effect of terminal branching on mesomorphism

The lengthening of branch terminal group from methyl in 4-(dimethylamino)benzylidene-4'-alkyloxyanilines (nDMBA) (Ha et al., 2009c) to ethyl in nDEBA has drastically influenced the mesomorphic properties as depicted in Figure 8. Compounds in the nDMBA series exhibited liquid crystal phases but compounds in the nDEBA series were non-mesomorphic compounds. Longer alkyl chain in dialkylamino group perturbs the packing of molecules, therefore inhibited the formation of mesophase in the nDEBA series. A similar phenomenon was also observed for the ester derivatives possessing dimethylamino and diethylamino terminal groups (Ha et al., 2009d). Furthermore, nDEBA members possessed lower melting point compared to nDMBA members having the similar number of carbons (n) at the alkyloxy chain. This suggests that the terminal branching of diethylamino group can depress the thermal stability of a compound.

Conclusion

Spectral, optical and thermal behaviors of a homologous series of Schiff base ether possessing dialkylamino end group were studied. Melting and recrystallization points were greatly influenced by the changes of alkyl chain length of alkyloxyaniline group. All compounds in nDEBA series were non-mesomorphic derivatives. The lengthening of dialkylamino terminal branch has significantly suppressed the formation of liquid crystal and thermal stability in nDEBA.

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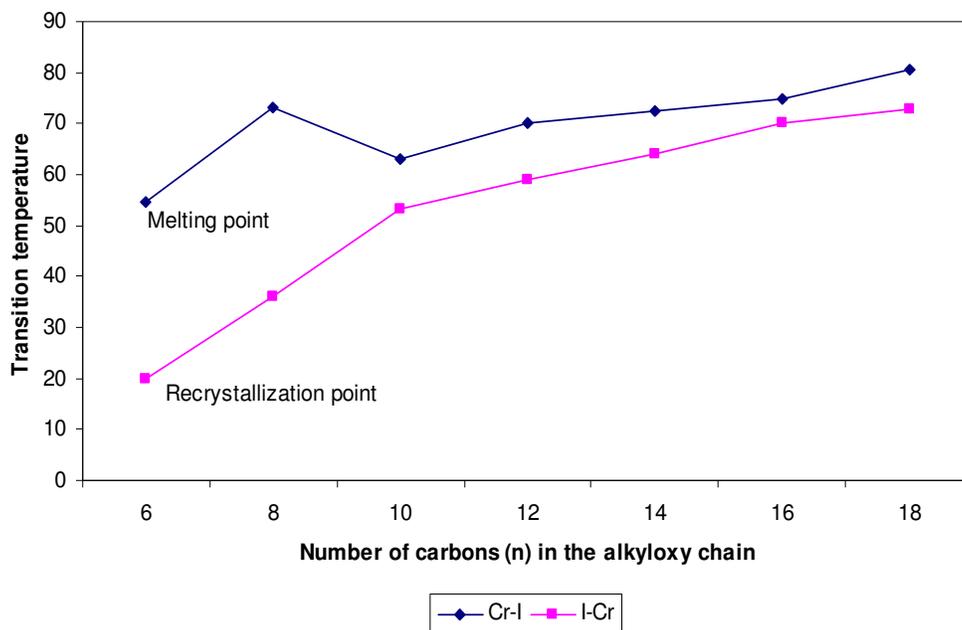


Figure 7. Plot of transition temperatures ($^{\circ}\text{C}$) versus the number of carbons (n) in the alkyloxy chain of 4-(diethylamino)benzylidene-4'-alkoxyanilines.

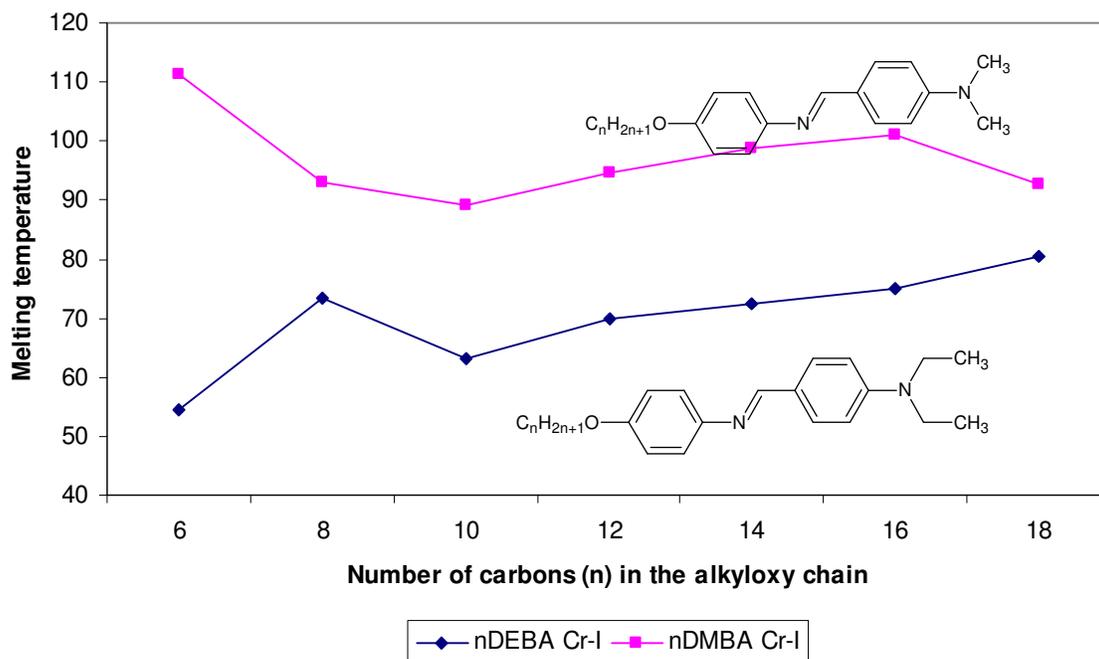


Figure 8. Influence of dialkylamino terminal branching on the mesomorphism of nDEBA and nDMBA. Melting temperature measured in $^{\circ}\text{C}$.

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