

Full Length Research Paper

Schiff base liquid crystals with terminal iodo group: Synthesis and thermotropic properties

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Accepted 8 September, 2011

A new homologous series of Schiff base esters comprising a terminal iodo substituent was studied. The iodo substituent contributes to the molecular polarizability, thus, affecting intermolecular interactions, hence, resulting in smectic polymorphism. The mesomorphic properties were studied using differential scanning calorimeter (DSC) and polarizing optical microscope (POM). Whilst the lower members, *n*-ethanoyloxy, *n*-propanoyloxy, *n*-butanoyloxy and *n*-pentanoyloxy derivatives were non-mesogens, enantiotropic smectogenic A phase was observed in the medium members (*n*-hexyloxy and *n*-heptanoyloxy derivatives). Further lengthening of the alkyl chain from C8 to C18 members saw the induction of new phase which was identified as smectic B phase under microscope. The homologous members were compared with structurally related series to establish their chemical structure-mesomorphic behavior relationships.

Key words: 4-[(4-iodophenyl) imino] methyl} phenyl alkanoate, thermotropic properties, smectic A, smectic B, polarizability.

INTRODUCTION

Liquid crystalline materials have many practical applications in scientific and technological areas, in particular as display devices, organic light emitting diodes, anisotropic networks, photoconductors and semiconductor materials (Petti et al., 2010; Shurpo et al., 2010; Hoang et al., 2010). High demand of new liquid crystals for applications 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 rod-like molecules having a rigid core possessed of two or more phenyl rings and one or more flexible terminal alkyl chains. Schiff base, also known as imine (CH=N), is a linking group used in connecting the rigid core groups. Though it provides a stepped core structure, yet it retains molecular linearity, hence providing higher stability and enabling formation of mesophase (Collings and Hird, 1998; Singh and Dunmur, 2002). Comprehensive studies on Schiff base core systems have been conducted since the discovery of N-(4-Methoxybenzylidene)-4-butylaniline (MBBA) which exhibited a nematic phase at room temperature (Kelker and Scheurle, 1969). Several studies have been conducted on Schiff base esters owing to their interesting properties and substantial 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). Understanding of

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Abbreviations: DSC, Differential scanning calorimeter; POM, polarizing optical microscope; MBBA, N-(4-Methoxybenzylidene)-4-butylaniline; EI-MS, electron ionization mass spectrum; NMR, nuclear magnetic resonance; TMS, trimethylsilane; DMF, dimethylformamide; DMAP, dimethylaminopyridine UV, ultraviolet; IR, Infrared; FTIR, fourier transform infrared.

structure-property relationship is elemental on molecular modifications for synthesis of new mesogens with desirable properties and future applications (Collings and Hird, 1998). Typical terminal moieties exhibiting liquid crystal properties are those with electronegative atoms, such as halogens. Halogens (F, Cl, Br and I) are polar substituents possessing strong dipole moments, thus having the ability to promote mesomorphic properties (Galewski, 1994; Galewski and Coles, 1999; Sakagami and Nakamizo, 1980).

The increased dipole moment enhances the stability of the lattice and melting temperatures (Singh and Dunmur, 2002). As the ionic radius of the terminal substituent increases, the molecules tend to orientate in a parallel arrangement (Dave and Menon, 2000). Thus, smectic polymorphism is not unusual for mesogens with a terminal iodo substituent, and this has been frequently observed as the length of the alkyl or alkoxy chains increases (Galewski and Coles, 1999; Petrov et al., 2001). As a continuation of our previous work, Schiff base ester and iodo terminal moiety are incorporated to form a new series of homologous compounds, 4-[[4-(4-iodophenyl)imino]methyl]phenyl alkananoate, nBAI. FT-IR, ^1H and ^{13}C NMR, EI-MS and elemental analysis were employed to elucidate the molecular structure of the title compounds whereas the liquid crystal properties were determined by DSC and POM analysis. The mesomorphic behaviors of the homologous compounds are rationalized based on the varying lengths of the alkyl chain. In addition, the relationship between the molecular structure and liquid crystal properties is also discussed in this paper.

MATERIALS AND METHODS

Materials

Acetic acid, butyric acid, hexanoic acid, heptanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, 4-hydroxybenzaldehyde, 4-iodoaniline and 4-dimethylaminopyridine were obtained from Merck (Germany) without further purification. Propionic acid, pentanoic acid, octanoic acid and N, N-dicyclohexylcarbodiimide were purchased from Acros Organics (USA). Electron ionization mass spectrum (EI-MS) was recorded using a Finnigan MAT95XL-T mass spectrometer operating at 70 eV ionizing energy. Samples were introduced using a direct inlet system with a source temperature of 200°C. Microanalyses were carried out on a Perkin Elmer 2400 LS Series Elemental analyser. FT-IR data were acquired with a Perkin Elmer 2000-Fourier Transform Infrared spectrophotometer in the frequency range of 4000 to 400 cm^{-1} with samples embedded in KBr pellets. ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded in CDCl_3 using a Bruker Avance 300 MHz NMR Spectrometer with Trimethylsilane (TMS) as the internal standard. Thin layer chromatography analyses were carried out using aluminum backed silica gel plates (Merck 60 F_{254}) and were examined under shortwave ultraviolet (UV) light. The phase transition temperatures were measured using a Mettler Toledo DSC823 at a scanning rate of 10°C min^{-1} . Liquid crystalline properties were investigated by POM using a Carl Zeiss Polarizing Optical Microscope attached to a Linkam Hotstage. The texture of

the compounds were observed using polarized light with crossed polarizers, the sample being prepared as a thin film sandwiched between a glass slide and a cover. A video camera (Video Master coomo20P) was installed on the polarizing microscope and coupled to a video capture card (Video master coomo600), allowing real-time video capture and image saving.

Synthesis

The intermediate and title compounds were prepared according to previously reported methods (Ha et al., 2009a, 2009b).

Synthesis of 4-[[4-(4-iodophenyl)imino]methyl]phenol, OHBAI

Equal amounts of 4-hydroxybenzaldehyde and 4-iodoaniline, along with 30 ml of ethanol were refluxed for three hours. The mixture was cooled to room temperature and filtered. The yellow product was washed with cold ethanol.

Synthesis of 4-[[4-(4-iodophenyl)imino]methyl]phenyl alkananoate, nBAI

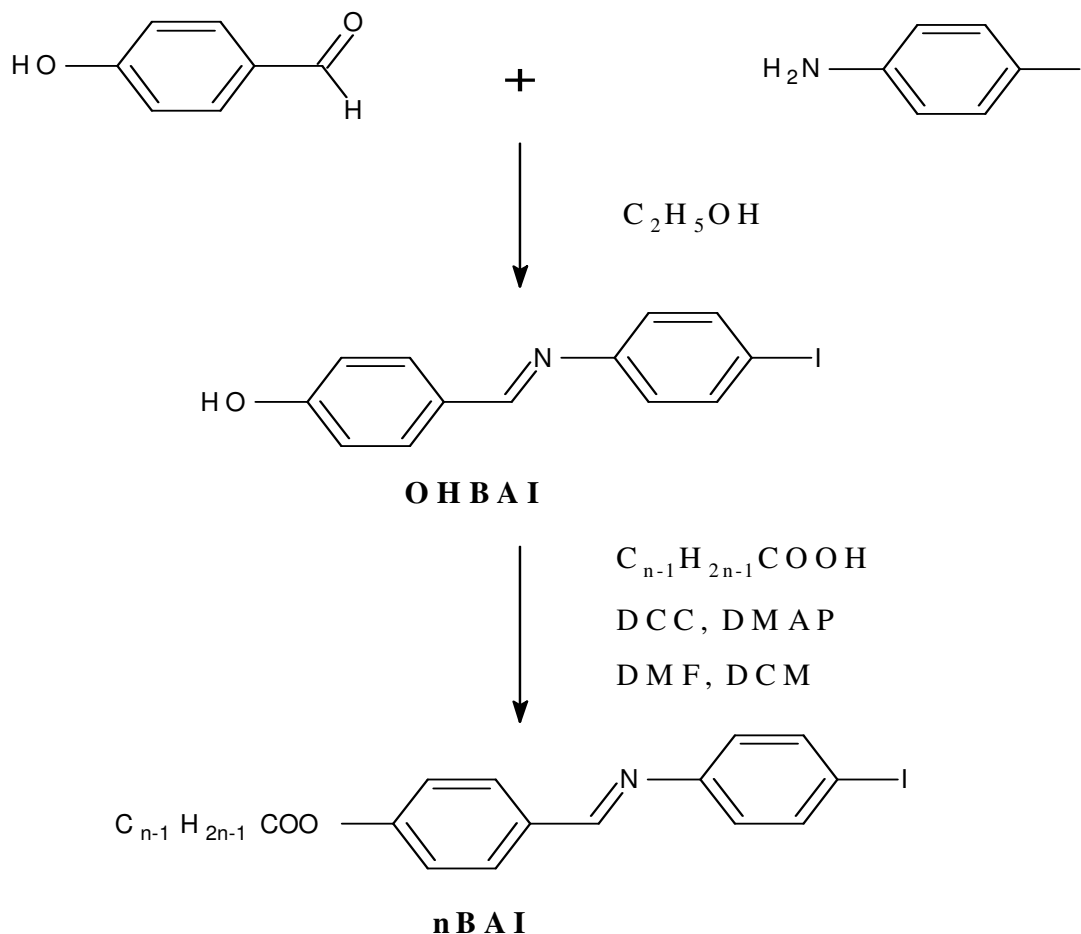
OHBAI (2 mmol) was initially dissolved in a minimum amount of dimethylformamide (DMF) and added into a mixture of fatty acid (2 mmol) and dimethylaminopyridine (DMAP) (0.2 mmol) which has been already dissolved in dichloromethane (20 ml). DCC (2 mmol) in dichloromethane (5 mL) was added dropwise into the mixture upon stirring at 0°C for an hour, which was then further stirred at room temperature for another three hours. Finally, the mixture was filtered and the excess solvent was removed from the filtrate by evaporation. The pale yellow product was recrystallized with ethanol until its transition temperature remained constant (Scheme 1). The percentage yield and analytical data of the title compounds are tabulated in Table 1. EI-MS, IR, ^1H and ^{13}C NMR data of the representative compound 12BAI are given as follows:

12BAI: EI-MS (m/z , relative intensity): 505 (11) [M^+], 323 (100); IR (KBr) (cm^{-1}): 2947, 2920, 2850 (C-H stretching); 1751 (C=O ester); 1617 (C=N), 1205 (C-O); ^1H NMR (300 MHz, CDCl_3): δ 0.88 (t, 3H, $J = 6.6\text{Hz}$, CH_3 -), 1.30 (m, 16H, CH_3 - $(\text{CH}_2)_8$ -), 1.76 (quint, 2H, $J = 7.4\text{Hz}$, $-\text{CH}_2-\text{CH}_2-\text{COO}-$), 2.57 (t, 2H, $J = 7.5\text{Hz}$, $-\text{CH}_2-\text{COO}-$), 6.95 (d, 2H, $J = 8.7\text{Hz}$, Ar-H), 7.20 (d, $J = 8.4\text{Hz}$, 2H, Ar-H), 7.69 (d, $J = 8.7\text{Hz}$, 2H, Ar-H), 7.90 (d, $J = 8.4\text{Hz}$, 2H, Ar-H), 8.39 (s, 1H, $-\text{CH}=\text{N}-$); ^{13}C NMR (100 MHz, CDCl_3): δ 14.1 (CH_3 -), 22.7 (CH_3CH_2 -), 24.9 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.1, 29.2, 29.3, 29.5, 29.6 for methylene carbons ($\text{CH}_3\text{CH}_2\text{CH}_2$ - $(\text{CH}_2)_8$ -), 31.9 ($-\text{CH}_2\text{CH}_2\text{COO}-$), 34.4 ($-\text{CH}_2\text{COO}-$), 90.3, 122.1, 122.9, 130.1, 133.5, 138.2, 151.6, 153.4 for aromatic carbons, 159.5 ($-\text{CH}=\text{N}-$), 171.9 ($-\text{COO}-$).

RESULTS AND DISCUSSION

Synthesis and spectral studies

Structure elucidation of compounds nBAI was ascertained by using elemental analysis, mass spectrometry and IR and spectroscopic methods (Figures 1 to 4). The experimental and theoretical values obtained from the elemental analysis of nBAI (where $n = 2-8, 10, 12, 14, 16$ and 18) (Table 1) were in good agreement. The molecular ion peak at $m/z = 505.2$ in the mass spectrum of the representative compound 12BAI (Figure 1)



Scheme 1. Synthetic route of **nBAI**; Where $n = 2, 8, 10, 12, 14, 16$ and 18 .

Table 1. Percentage yields and analytical data of **nBAI**.

Compound	Yield (%)	Formula	% Found (% Calcd.)		
			C	H	N
2BAI	13.96	$C_{15}H_{12}INO_2$	49.47 (49.34)	3.25 (3.31)	3.80 (3.84)
3BAI	15.08	$C_{16}H_{14}INO_2$	50.78 (50.68)	3.65 (3.72)	3.73 (3.69)
4BAI	28.38	$C_{17}H_{16}INO_2$	51.86 (51.93)	4.13 (4.10)	3.61 (3.56)
5BAI	27.35	$C_{18}H_{18}INO_2$	53.15 (53.09)	4.51 (4.46)	3.49 (3.44)
6BAI	34.01	$C_{19}H_{20}INO_2$	54.29 (54.17)	4.82 (4.79)	3.37 (3.32)
7BAI	31.13	$C_{20}H_{22}INO_2$	55.30 (55.18)	5.01 (5.09)	3.20 (3.22)
8BAI	41.05	$C_{21}H_{24}INO_2$	56.07 (56.13)	5.44 (5.38)	3.18 (3.12)
10BAI	42.81	$C_{23}H_{28}INO_2$	57.94 (57.87)	5.99 (5.91)	2.99 (2.93)
12BAI	56.60	$C_{25}H_{32}INO_2$	59.55 (59.41)	6.40 (6.38)	2.57 (2.77)
14BAI	60.53	$C_{27}H_{36}INO_2$	60.65 (60.79)	6.77 (6.80)	2.68 (2.63)
16BAI	67.02	$C_{29}H_{40}INO_2$	61.93 (62.03)	7.22 (7.18)	2.41 (2.49)
18BAI	68.67	$C_{31}H_{44}INO_2$	63.21 (63.15)	7.42 (7.52)	2.31 (2.38)

suggested that 12BAI with a molecular formula of ($C_{25}H_{32}INO_2$) was successfully synthesized. Fourier

transform infrared (FTIR) spectrum (Figure 2) show that the diagnostic bands assignable to the stretching of

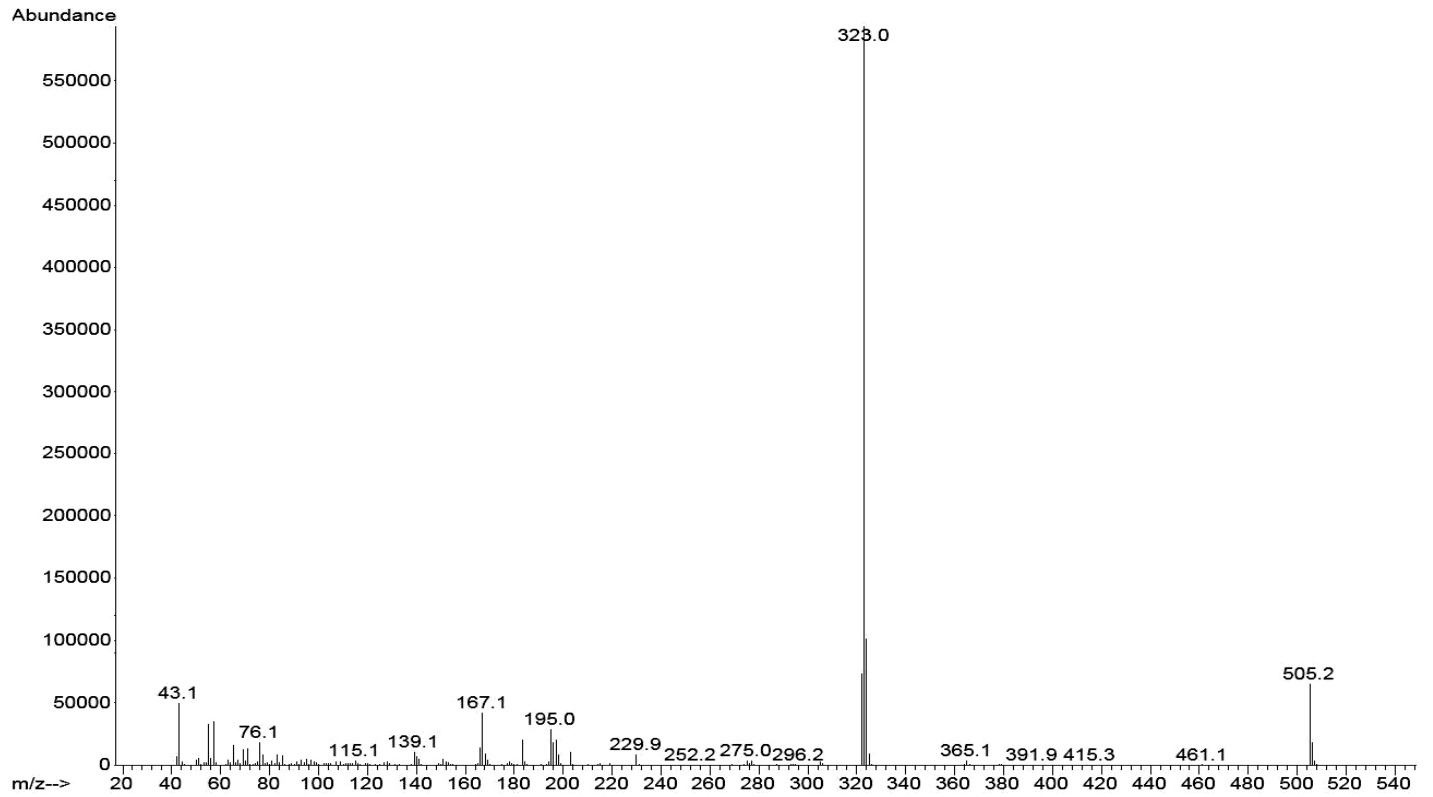


Figure 1. EI-MS Spectrum of 12BAI.

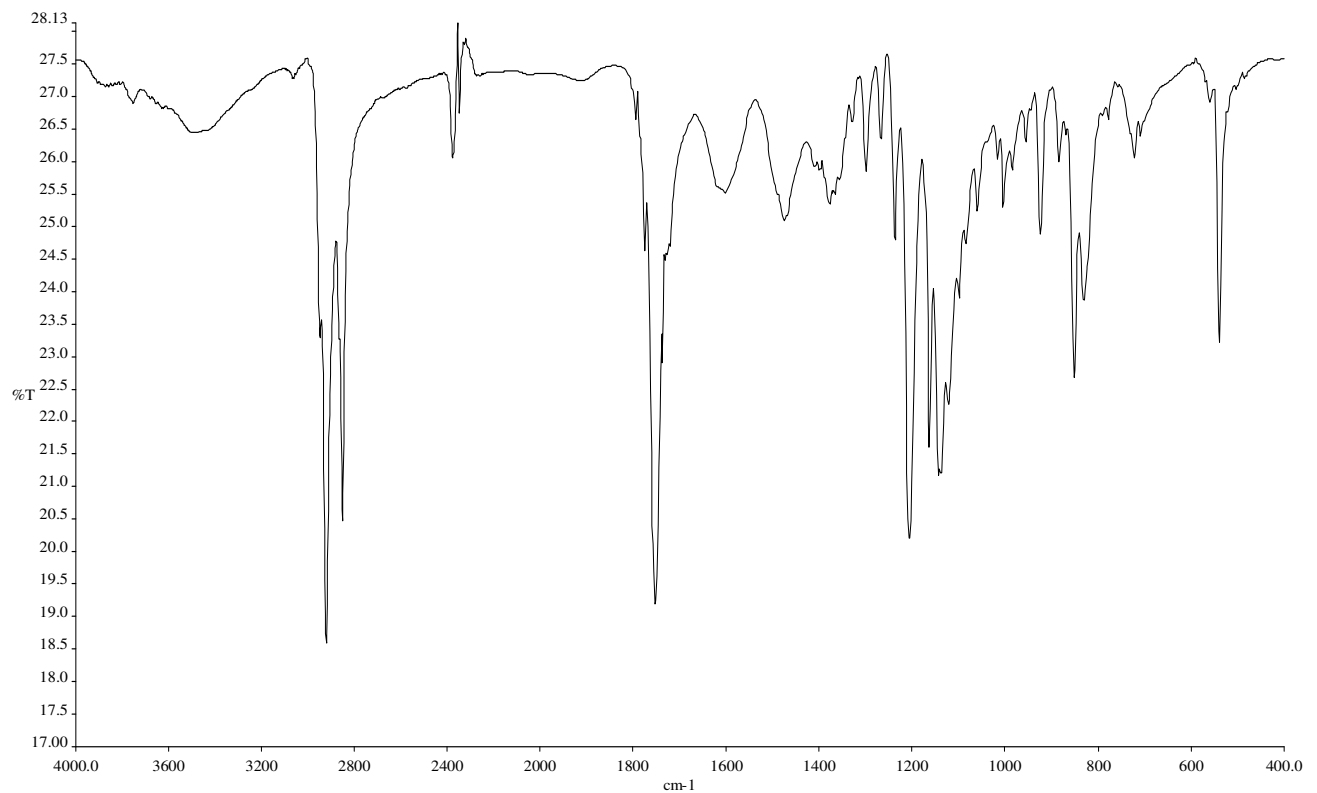


Figure 2. FTIR Spectrum of 12BAI.

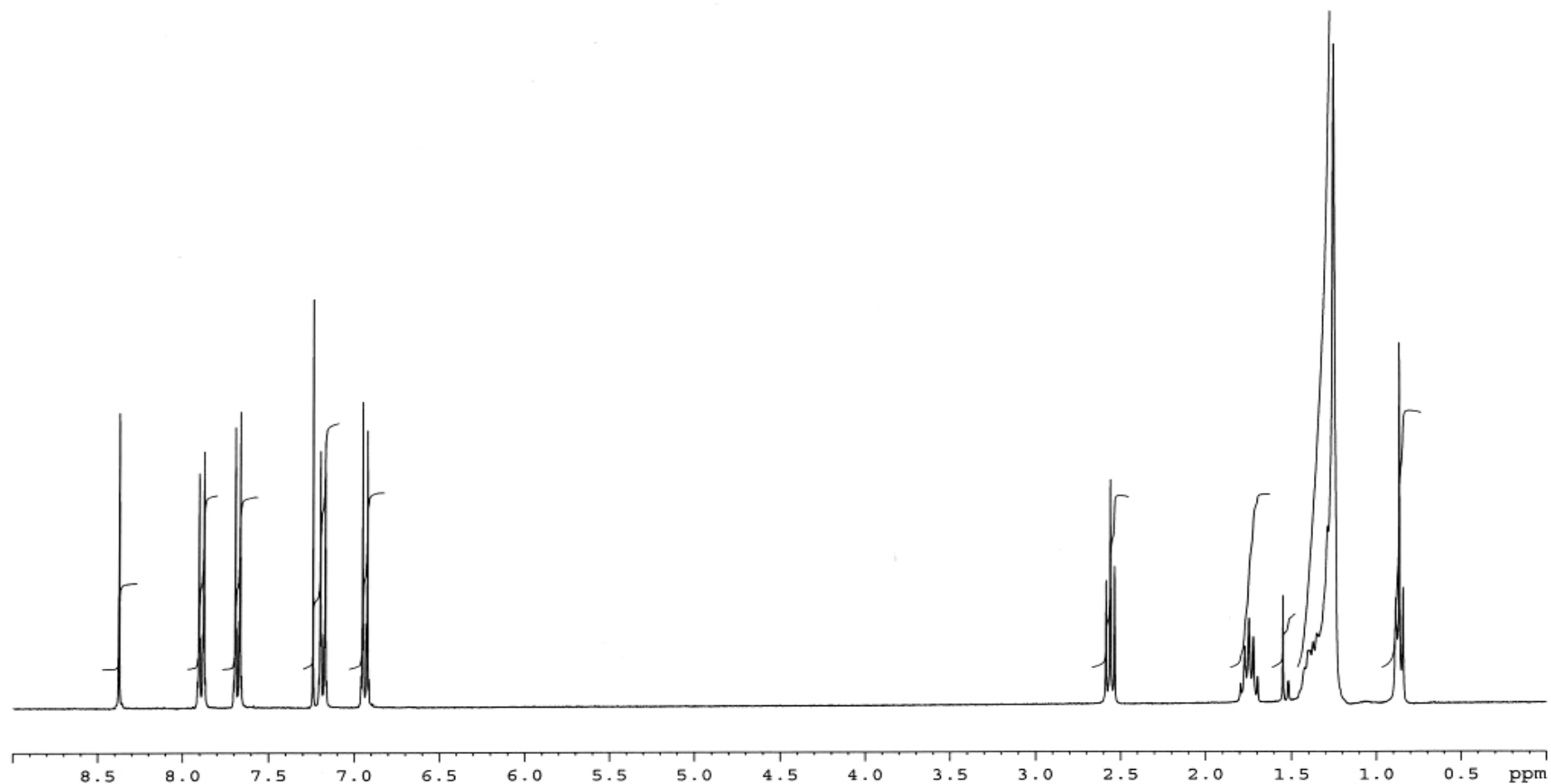


Figure 3. ^1H NMR Spectrum of 12BAI.

aliphatic C-H and carbonyl (C=O of ester) of representative compound 12-BAI were observed at the respective frequencies 2947, 2920, 2850 and 1751 cm^{-1} . The absorption band assignable to the stretching of C=N bond was observed at frequency of 1617 cm^{-1} , and these values conform

with those reported in the Infrared (IR) spectra for various substituted aromatic Schiff bases that possesses the formulation $\text{HOC}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5$ (Yeap et al., 2004). The ^1H NMR spectrum of 12BAI (Figure 3) further supported its structure. The two triplets at $\delta = 0.88\text{ ppm}$ and $\delta = 2.57\text{ ppm}$,

were, respectively ascribed to the methyl and methylene protons ($-\text{CH}_2\text{COO-Ar}$), while the multiplet at $\delta = 1.30\text{ ppm}$ was assigned to the methylene protons of the long alkyl chain $\{\text{CH}_3(\text{CH}_2)_8-\}$. The four distinct doublets between $\delta = 6.95\text{-}7.90\text{ ppm}$ were indicative of the aromatic

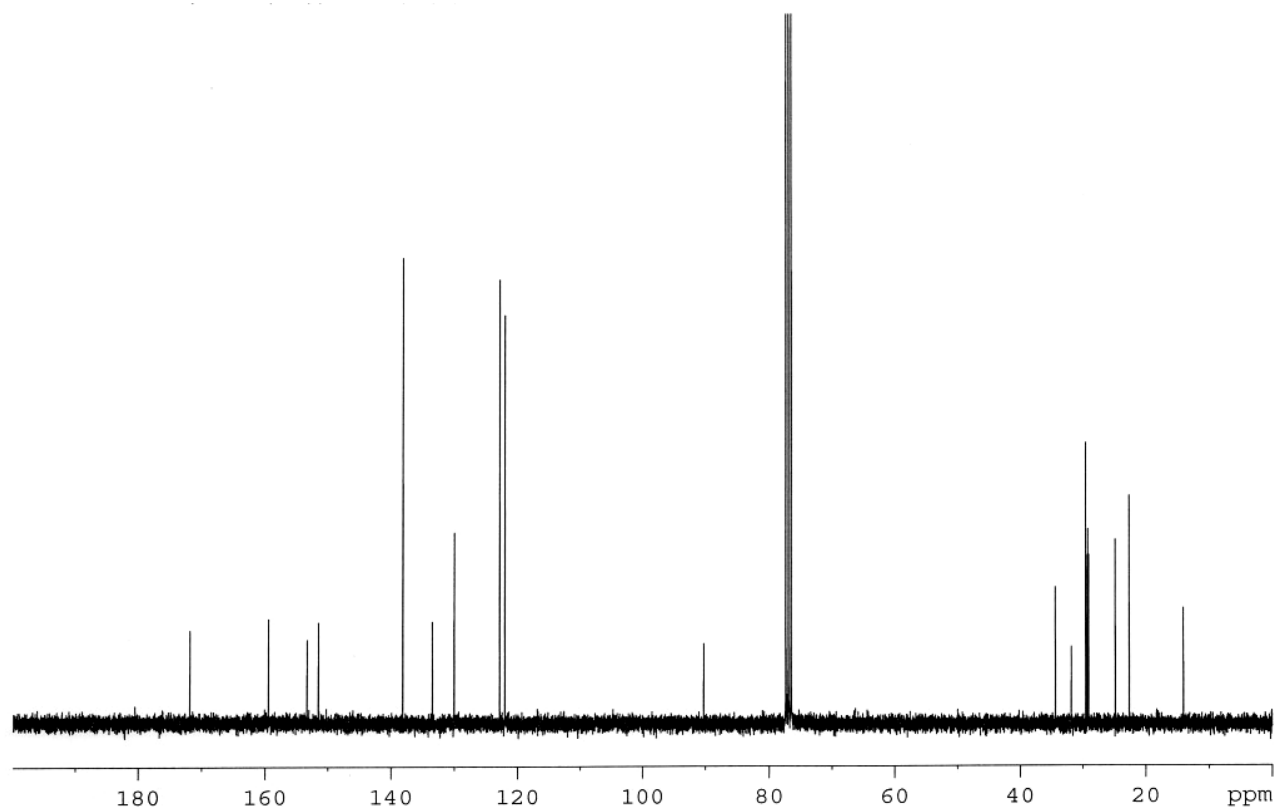


Figure 4. ^{13}C NMR Spectrum of 12BAI.

protons. The singlet observed at the most downfield region, $\delta = 8.39$ ppm, supported the presence of the imine linking group (Yeap et al., 2006c). The molecular structure of 12BAI was further verified by using ^{13}C NMR spectroscopy (Figure 4). The peak at $\delta = 14.1$ ppm was attributed to the methyl carbon while the peaks between $\delta = 22.6$ - 34.4 ppm represented the methylene carbons of the long alkyl chain. The 12 carbons of the aromatic ring in 12BAI resonated between $\delta = 122.1$ to 153.4 ppm. The peak at $\delta = 159.5$ ppm and $\delta = 171.9$ ppm confirmed the presence of the azomethine carbon and the carbonyl group in the molecule.

Mesomorphic properties

8BAI exhibited interesting thermotropic properties and its melting behavior was carefully monitored by POM during both heating and cooling scans. Optical photomicrographs of 8BAI are shown in Figure 5 as the representative illustration. The results from the POM observation were verified by the DSC measurements. The transition temperatures, enthalpy changes, and phase sequences are summarized in Table 2. 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 (1966) and Gray and Goodby (1984). Under POM, focal conic fan-shaped textures of a smectic A phase was observed during the cooling cycle (Figure 5a). Upon further cooling, the back of the fan-shaped domains developed a series of dark-lines, which is transitory in nature (Figure 5b) (Singh and Dunmur, 2002; Goodby and Gray, 1979). When further cooled, the bands expanded, met and eventually coalesce to produce a polygonal-like texture (Figure 5c) (Galewski and Coles, 1999). This phase is identified as a smectic B phase. This similar behavior was also reported for a closely-related compound, 4-butyloxybenzylidene-4-chloroaniline (Cozan et al., 2009).

Influence of alkyl chain length on mesomorphic properties

Representative DSC thermograms for nBAI (where $n = 2, 6, 14$) upon heating and cooling are depicted in Figure 6. A plot of the transition temperatures against the number of carbons in the alkanoyloxy chain during the heating cycle are shown in Figure 7. Out of the twelve compounds, the first four members (2, 3, 4 and C5) did

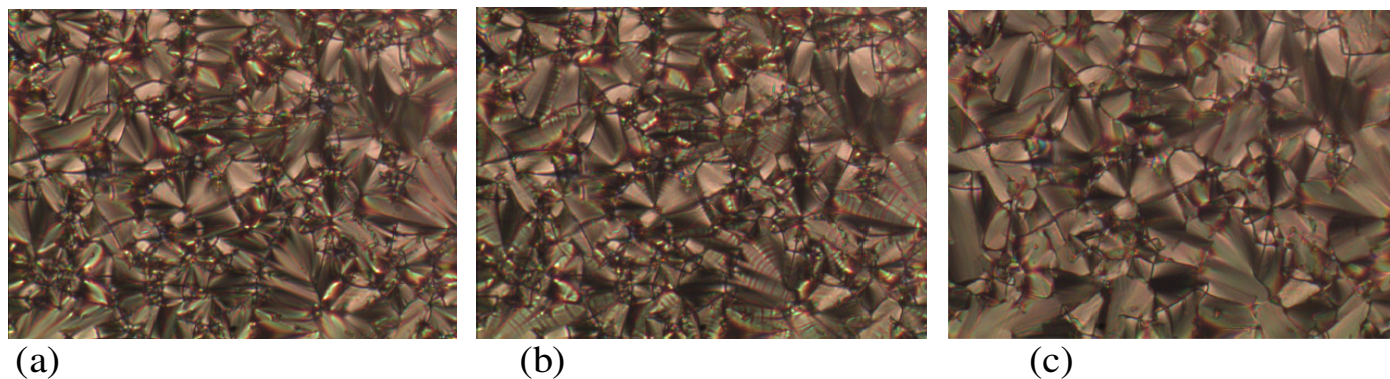


Figure 5. Optical photomicrographs (100 x) of 8BAI taken during the cooling cycle; (a) optical photomicrograph showing fan-shaped textures of a SmA phase; (b) optical photomicrograph exhibiting transition bar at the SmA to SmB transition; (c) optical photomicrograph displaying mosaic textures of a SmB phase.

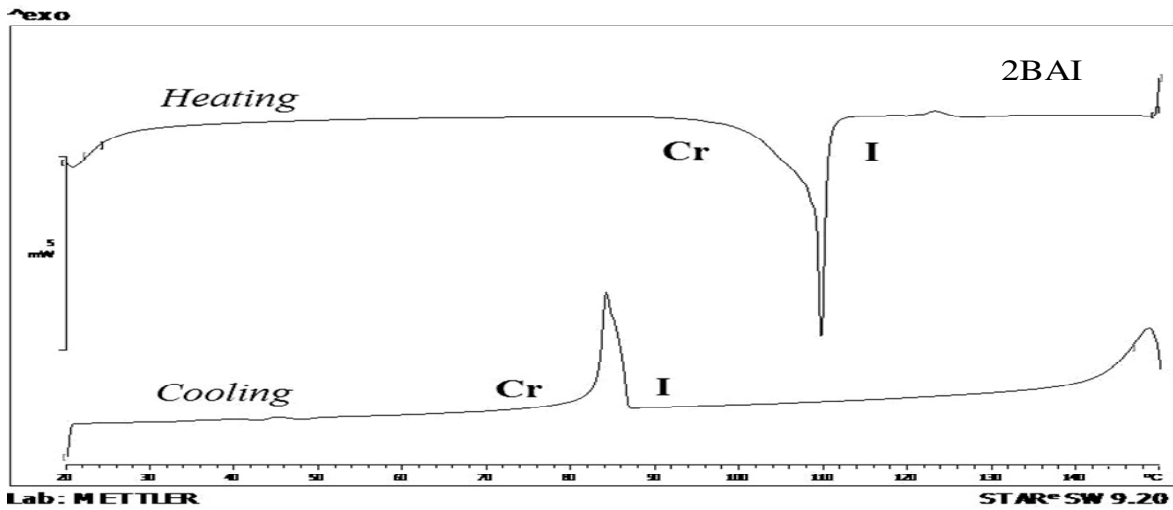
Table 2. Transition temperatures and associated enthalpy changes of nBAI upon heating and cooling scans.

Compound	Transition temperatures, °C (ΔH , kJmol ⁻¹)	Heat cooling
2BAI	Cr 109.6 (26.6) I, I 84.6 (13.8) Cr	
3BAI	Cr 105.9 (19.7) I, I 82.5 (13.6) Cr	
4BAI	Cr 116.1 (11.8) I, I 112.1 (11.6) Cr	
5BAI	Cr 110.6 (15.3) I, I 103.6 (11.9) Cr	
6BAI	Cr 101.3 (30.0) SmA 111.1 (6.1) I, I 104.3 (9.7) SmA 31.4 (15.4) Cr	
7BAI	Cr 97.1 (19.2) SmA 114.1 (12.4) I, I 108.5 (12.7) SmA 51.1 (18.8) Cr	
8BAI	Cr 86.6 (26.0) SmB 110.7 (2.2) SmA 115.2 (4.7) I, I 107.8 (3.2) SmA 104.3 (1.6) SmB 36.4 (19.6) Cr	
10BAI	Cr 86.6 (29.4) SmB 110.4 (1.1) SmA 115.7 (3.0) I, I 108.3 (2.8) SmA 104.3 (1.6) SmB 27.5 (18.5) Cr	
12BAI	Cr 101.6 (39.5) SmB 106.4 (2.9) SmA 109.6 (5.9) I, I 102.0 (8.1) SmA 98.8 (4.0) SmB 84.3 (35.5) Cr	
14BAI	Cr 94.3 (37.6) SmB 111.5 (4.1) SmA 116.5 (8.7) I, I 110.1 (8.7) SmA 105.4 (3.5) SmB 61.6 (39.7) Cr	
16BAI	Cr 99.4 (54.7) SmB 110.4 (5.3) SmA 114.4 (10.9) I, I 108.3 (11.4) SmA 104.4 (5.2) SmB 72.7 (54.9) Cr	
18BAI	Cr 101.5 (46.8) SmB 106.8 (3.9) SmA 109.8 (8.4) I, I 107.4 (8.6) SmA 104.6 (4.1) SmB 79.5 (48.6) Cr	

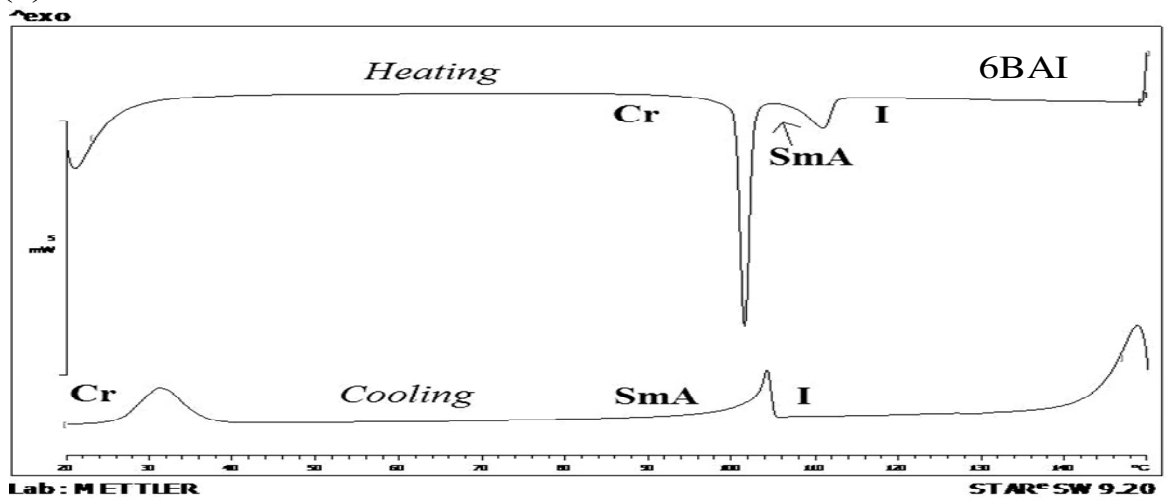
Cr = Crystal; SmA = Smectic A; SmB = Smectic B; I = Isotropic liquid.

not possess mesomorphic properties. These molecules with short alkanoyloxy chains are too rigid, therefore have high melting points, thus impeding their liquid crystal properties (Kumar et al., 2001). Once the length of the terminal chain is increased, the molecule becomes more flexible, hence promoting a single mesophase in a particular compound. Therefore, the C6 and C7 members exhibited smectic A (SmA) phase only. The rest of the members, C8 and C18 members showed polymorphism properties whereby these compounds displayed SmA and SmB phases. All compounds, from C6 and C18 are enantiotropic liquid crystals because the stable mesophases were observed during both heating and cooling processes. From the graph, the lower member of the homologous series, C4, possessed the highest melting temperature ($T_m = 116.1^\circ\text{C}$). The melting point decreased as the length of the chain increased to the C10 member ($T_m = 86.6^\circ\text{C}$). This resulted from the increase in the flexibility of the molecule owing to the longer alkyl chain.

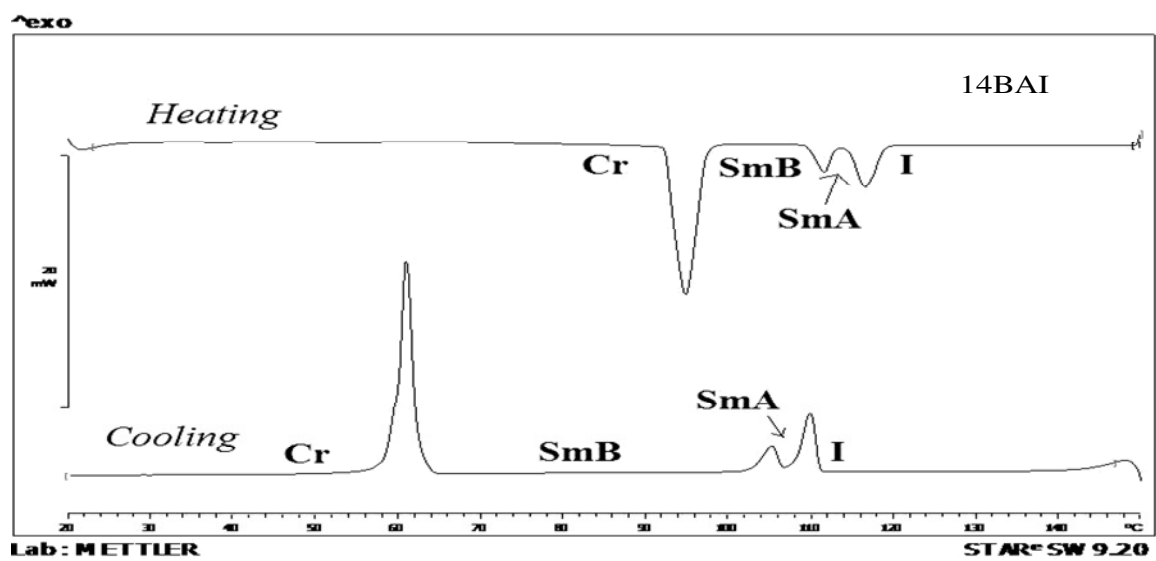
It is also common that the melting temperature increases from the medium chain member onwards following a decrease from the short to the medium chain members (Kelker and Hatz, 1980). An increase in the melting temperature was also observed from the *n*-decanoyloxy ($T_m = 86.6^\circ\text{C}$) to the *n*-octadecanoyloxy ($T_m = 101.5^\circ\text{C}$) derivative with the exception of the C12 member. This ascending trend could have been attributed to the increase in the *Van der Waals* attractive forces between the molecules (Gray, 1962). The zig-zag pattern or the odd-even effect is observed in the melting temperatures of the lower members of the homologous series (C2, C3, C4 and C5). As the series ascends from the C2 to the C5 member, the Cr-to- I transition temperatures attenuates consistently. The even members possessed high clearing temperatures compared to their odd member counterparts. Such attenuation of the melting temperatures has been observed in various homologous systems of liquid crystals (Kumar, 2001). While the C6 to



(a)



(b)



(c)

Figure 6. DSC thermograms of (a) 2BAI, (b) 6BAI and (c) 14BAI during heating and cooling cycles.

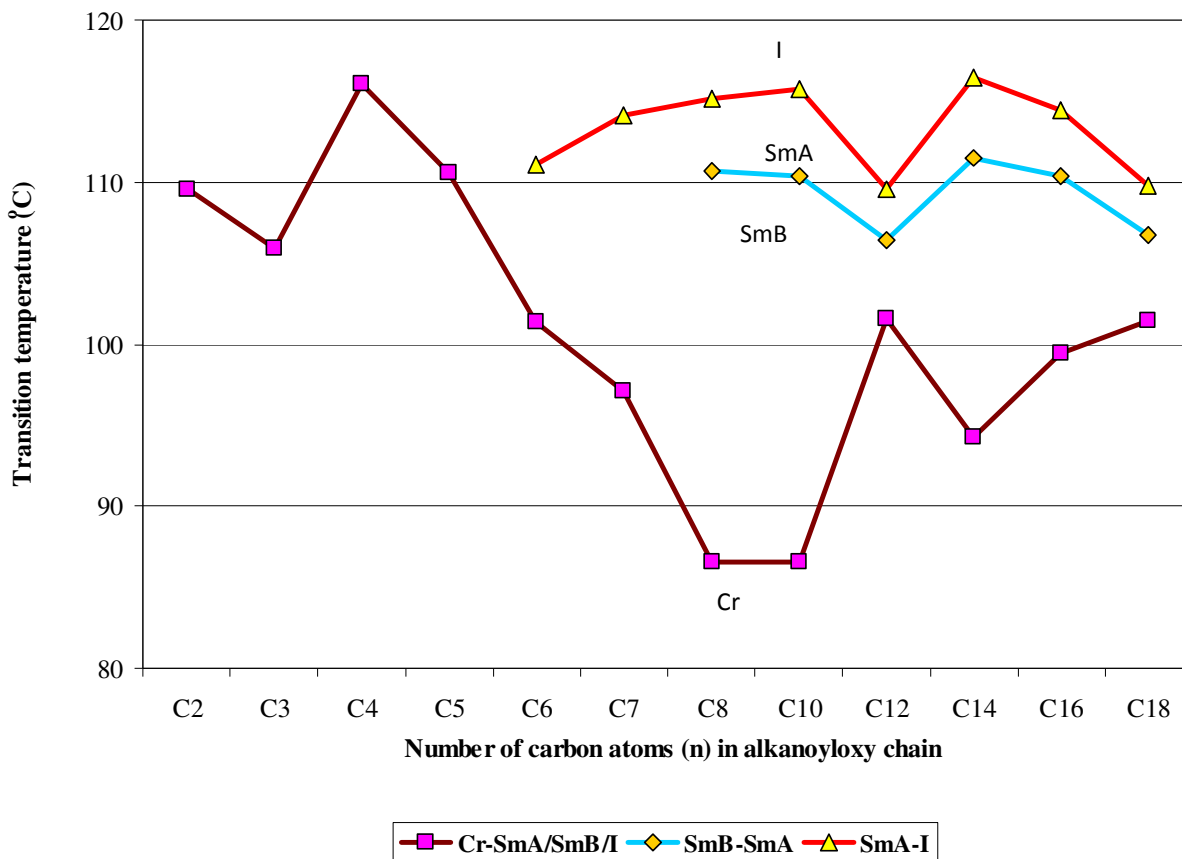


Figure 7. Plot of transition temperature versus the length of alkanoyloxy chain of nBAI during heating cycle.

C10 members exhibited an increase in their transition temperatures during the SmA-to-I transition, the opposite was observed for the C14 to C18 members. The terminal intermolecular attractions play a role in determining the SmA-I transition temperatures, that is, the destruction of the smectic molecular order is determined by the fact that the terminal attractions become weaker, allowing partial interpenetration of the layers to occur more easily as the alkanoyloxy chains grow longer, in turn depressing the SmA-to-I transition temperatures (Prajapati and Bonde, 2009; Gray, 1962).

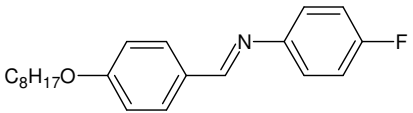
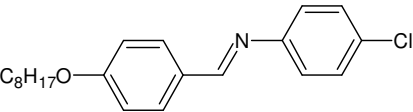
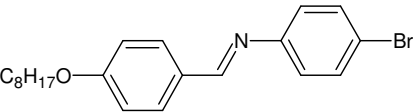
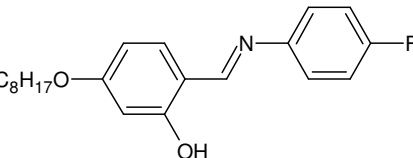
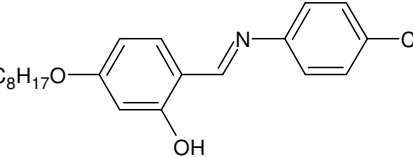
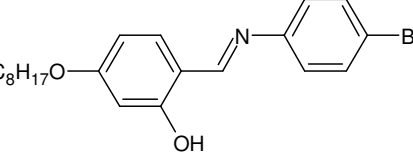
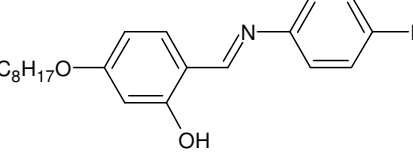
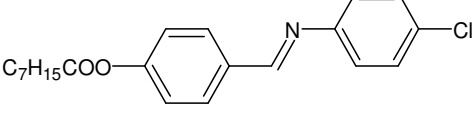
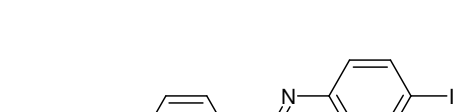
Structure- mesomorphic property relationships

Molecular structure of organic compounds and their liquid crystalline properties are closely related. Table 3 summarizes the transition temperatures, mesomorphic behavior and molecular structures of 8BAI and structurally related compounds (Gandolfo, 1988; Galewski, 1994; Sakagami et al., 2002; Ha et al., 2010) reported in literature. Halogen groups at the terminal position showed strong influence on the mesomorphic properties of a molecule as indicated by the current work

(Table 3). It can be seen that the melting and transition temperatures of 8BAI are higher than those of 8BACl. The iodine atom is larger than the chlorine atom and therefore more easily polarized due to the electrons on this atom which are loosely held and far from the nucleus (Solomons, 1994). Higher molecular polarizability contributed by the larger iodine atom led to higher phase stability in 8BAI (Yeap et al., 2004). This phenomenon is supported by the similar characteristic observed for X-AB and X-ABOH series (where X = F, Cl, Br and I) wherein the melting and transition temperatures ascended as the size of halogen group increasing. Secondly, polarisability of halogen terminal groups can also control the phase stability of liquid crystal molecules. Compound having lower polarisability halogen group (8BACl) possessed less stable monotropic SmB phase than 8BAI which exhibited enantiotropic SmB phase. Similar pattern was also appeared in the X-AB series whereby F-AB (monotropic phase) possessed lower phase stability than Cl-AB (enantiotropic phase).

Influence of lateral hydroxyl group was rather obvious on the mesomorphic properties of Schiff base. Intramolecular hydrogen bonding between *ortho* hydroxyl group and nitrogen atom of azomethine has increased

Table 3. Comparison of mesomorphic behaviour of 8BAI with structurally related compounds.

Compound	Structure	Phase Transition (°C)
F-AB		Cr (55.1)* SmB 62.2 SmA 65.2 I
Gandolfo, 1988		
Cl-AB		Cr 61.0 SmB 87.7 SmA 98.5 I
Galewski, 1994		
Br-AB		Cr 89.0 SmB 104.0 SmA 113.0 I
Galewski, 1994		
F-ABOH		Cr 64 SmA 76 I
Sakagami, 2002		
Cl-ABOH		Cr 67 SmA 123 I
Sakagami, 2002		
Br-ABOH		Cr 73 SmA 132 I
Sakagami, 2002		
I-ABOH		Cr 109 SmA 133 I
Sakagami, 2002		
8BACl		Cr (80.2)* SmB 84.0 SmA 104.8 I
Ha, 2010		
8BAI		Cr 86.6 SmB 110.7 SmA 115.2 I
[Present study]		

(*) indicates monotropic phase.

the molecular polarisability and therefore compounds with hydroxyl group (X-ABOH series) possessed high melting and clearing temperatures than their analogous

compounds without hydroxyl group (X-AB, 8BACl and 8BAI). However, the increased polarisability at the lateral of a molecule caused depression of SmB arrangement

and thus impeding SmB formation in the X-ABOH series.

ACKNOWLEDGEMENT

The authors would like to thank Universiti Tunku Abdul Rahman and Ministry of Higher Education (MOHE) for the financial supports and research facilities.

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