



## Mesogenic Schiff Base with Bromo End Group: Synthesis and Thermotropic Properties

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A new homologous series of Schiff base esters comprising a terminal bromo substituent was studied. The bromo substituent contributes to the molecular polarizability, thus, affecting intermolecular interactions, hence, resulting in smectic polymorphism. The mesomorphic properties were studied using differential scanning calorimeter and polarizing optical microscope attached to a Linkam hotstage. Whilst the lower members, *n*-ethanoyloxy and *n*-butanoyloxy derivatives were non-mesogens, *n*-hexanoyloxy member exhibited monotropic (less stable) smectic A and smectic B phases. Further lengthening of the alkanoyloxy chain from C8 to C12 (medium members), led to formation of enantiotropic (more stable) smectic A and smectic B mesophases based on the observation of both phases during heating and cooling cycles. The high members of the series, C14, C16 and C18 exhibited enantiotropic smectic A phase and monotropic smectic B phase. The homologous members were compared with structurally related series to establish their chemical structure-mesomorphic behaviour relationships.

**Key Words:** 4-Alkanoyloxybenzylidene -4'-bromoanilines, Thermotropic properties, Smectic A, Smectic B, Polarizability.

### INTRODUCTION

Mesogenic materials have many useful applications in scientific and technological areas, in particular as display devices, organic light emitting diodes, anisotropic networks, photoconductors and semiconductor materials<sup>1-3</sup>. High demand of new liquid crystals (LCs) for applications has led to the preparation and study of numerous mesogens in particular, thermotropic liquid crystals<sup>4,5</sup>. Most thermotropic liquid crystals are calamitic molecules having a rigid core composed two or more phenyl rings and one or more flexible terminal alkyl chains. Schiff base, also known as imine (CH=N), is one of the most well-known linking groups 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<sup>6,7</sup>. Wide-ranging research on Schiff base core systems has been conducted since the discovery of MBBA, which exhibited room temperature nematic phase<sup>8</sup>. Several studies have been conducted on ester type of Schiff bases owing to their interesting properties and substantial temperature range<sup>9-18</sup>.

Perceptive of structure-property relationship is elemental on molecular modifications for synthesis of new mesogens with desirable properties and future practical applications<sup>6</sup>.

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<sup>19-21</sup>. The increased dipole moment enhances the stability of the lattice and melting temperatures<sup>7</sup>. As the ionic radius of the terminal substituent increases, the molecules tend to orientate in a parallel arrangement<sup>22</sup>. Thus, smectic polymorphism is not unusual for mesogens with a terminal bromo substituent and this has been frequently observed as the length of the alkyl or alkoxy chains increases<sup>20,23</sup>.

As a continuation of our previous work, Schiff base ester and bromo terminal moiety are incorporated to form a new series of homologous compounds, 4-alkanoyloxybenzylidene-4'-bromoanilines, nBABr. FT-IR, <sup>1</sup>H and <sup>13</sup>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 differential scanning calorimeter and polarizing optical microscopy analysis. The mesomorphic behaviours 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.

## EXPERIMENTAL

Acetic acid, butyric acid, hexanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, 4-hydroxybenzaldehyde, 4-bromoaniline and 4-dimethylaminopyridine were obtained from Merck (Germany) without further purification. 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 CHNS/O analyser. FT-IR data were acquired with a Perkin Elmer 2000-FTIR spectrophotometer in the frequency range of 4000–400 cm<sup>-1</sup> with samples embedded in KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> using a Bruker Avance 300 MHz NMR Spectrometer with TMS as the internal standard. Thin layer chromatography analyses were carried out using aluminum backed silica gel plates (Merck 60 F<sub>254</sub>) and were examined under shortwave UV light.

**Liquid crystal study:** The phase transition temperatures were measured using a Mettler Toledo DSC823 differential scanning calorimeter (DSC) at a scanning rate of 10 °C min<sup>-1</sup>. Liquid crystalline properties were investigated by polarizing optical microscopy (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.

The synthetic route of 4-alkanoyloxybenzylidene-4'-bromoanilines, nBABr is illustrated in Fig. 1. The intermediate and title compounds were prepared according to reported methods<sup>10,11</sup>.

**Synthesis of 4-hydroxybenzylidene- 4'-bromoaniline (OHBABr):** Equal amounts (5 mmol) of 4-hydroxybenzaldehyde and 4-bromoaniline, along with 30 mL of methanol were refluxed for 3 h. The mixture was cooled to room temperature and filtered. The yellow product was washed with methanol.

**Synthesis of 4-alkanoyloxybenzylidene-4'-bromoanilines (nBABr):** 4-Hydroxybenzylidene- 4'-bromoaniline (OHBABr) (0.2433 g, 4 mmol), 3 mmol of fatty acids (C<sub>n</sub>H<sub>2n-1</sub>COOH, n = 2, 4, 6, 8, 10, 12, 14, 16, 18), DMAP (0.0244 g, 0.6 mmol) and DCC (0.2063 g, 3 mmol) were mixed and stirred at room temperature for six hours in appropriate amount of THF. Solvent of reaction mixture was removed by evaporation till dryness. Precipitate obtained was recrystallized several times with hexane and methanol whereupon pure compound was isolated. The percentage yield and analytical data of the title compounds are tabulated in Table-1.

EI-MS, IR, <sup>1</sup>H and <sup>13</sup>C NMR data of the representative compound 12BABr are given as follows:

**12BABr:** EI-MS m/z (rel. int. %): 459.2 (7.4) [M<sup>+</sup>+2], 457.2 (7.3) [M<sup>+</sup>], 277.0 (98.0), 275.0 (100.00). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 2948 (C-H aromatic), 2919, 2850 (C-H aliphatic), 1749

(C=O ester), 1622 (C=N), 1206, 1098 (C-O ester). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 0.89 (t, 3H, CH<sub>3</sub>), 1.26-1.45 (m, 16H, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>8</sub>-), 1.77 (quint, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-COO-), 2.58 (t, 2H, -CH<sub>2</sub>-COO-), 7.09 (d, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 7.51 (d, 2H, Ar-H), 7.92 (d, 2H, Ar-H), 8.40 (s, 1H, -CH=N-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 14.24 (CH<sub>3</sub>-), 22.83 (CH<sub>3</sub>CH<sub>2</sub>-), 25.05 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-), 29.26, 29.46, 29.48, 29.60, 29.75, for methylene carbons (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-(CH<sub>2</sub>)<sub>6</sub>-), 32.06 (-CH<sub>2</sub>CH<sub>2</sub>COO-), 34.60 (-CH<sub>2</sub>COO-), 122.10, 122.35, 122.56, 130.05, 131.16, 132.21, 150.90, 153.38 for aromatic carbons, 159.44 (-CH=N-), 171.86 (-COO-).

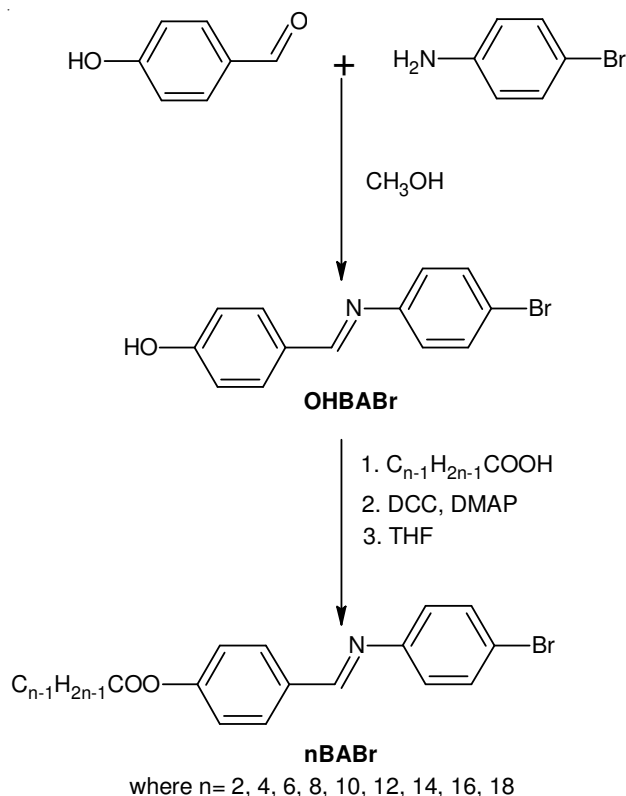


Fig. 1. Synthetic route of nBABr

TABLE-1  
PERCENTAGE YIELD AND ANALYTICAL DATA OF nBABr

Compound	Yield (%)	% Found (calcd. %)			
		m.f.	C	H	N
2BABr	26	C <sub>15</sub> H <sub>12</sub> NO <sub>2</sub> Br (56.62)	56.52 (56.62)	3.73 (3.80)	4.35 (4.40)
4BABr	32	C <sub>17</sub> H <sub>16</sub> NO <sub>2</sub> Br (58.97)	58.90 (58.97)	4.56 (4.66)	4.13 (4.05)
6BABr	37	C <sub>19</sub> H <sub>20</sub> NO <sub>2</sub> Br (60.91)	60.91 (60.97)	5.43 (5.39)	3.79 (3.74)
8BABr	41	C <sub>21</sub> H <sub>24</sub> NO <sub>2</sub> Br (62.80)	62.80 (62.69)	6.11 (6.01)	3.55 (3.48)
10BABr	44	C <sub>23</sub> H <sub>28</sub> NO <sub>2</sub> Br (64.19)	64.28 (64.19)	6.65 (6.56)	3.19 (3.25)
12BABr	46	C <sub>25</sub> H <sub>32</sub> NO <sub>2</sub> Br (65.45)	65.45 (65.50)	7.00 (7.04)	3.11 (3.06)
14BABr	48	C <sub>27</sub> H <sub>36</sub> NO <sub>2</sub> Br (66.66)	66.59 (66.66)	7.43 (7.46)	2.85 (2.88)
16BABr	53	C <sub>29</sub> H <sub>40</sub> NO <sub>2</sub> Br (67.64)	67.64 (67.69)	7.84 (7.84)	2.68 (2.72)
18BABr	61	C <sub>31</sub> H <sub>44</sub> NO <sub>2</sub> Br (68.93)	68.93 (68.62)	8.41 (8.17)	2.48 (2.58)

## RESULTS AND DISCUSSION

Structural identification of nBABr was carried out by employing a combination of elemental analysis and spectroscopic techniques (FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and EI-MS). Percentages of C, H and N from the elemental analysis conform with composition of nBABr as presented in Table-1. Molecular ion peak at  $m/z$  457 suggested molecular formula of  $\text{C}_{25}\text{H}_{32}\text{NO}_2\text{Br}$ , which supported the proposed structure of 12BABr.

**FTIR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral studies:** Based on FT-IR spectrum of 12BABr, absorption peak at 2948, 2919, 2850  $\text{cm}^{-1}$  can be assigned to aliphatic ( $\text{CH}_3$  and  $\text{CH}_2$ ) groups. Three absorption peaks due to the ester group were observed at 1749, 1206, 1098  $\text{cm}^{-1}$ . Relative intensity of absorption bands of aliphatic group increased upon ascending the series due to the increasing number of carbons in the alkanoyloxy chain. Absorption peak of imine ( $\text{C}=\text{N}$ ) group was observed at 1622  $\text{cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum, two triplets at  $\delta = 0.89$  ppm and  $\delta = 2.58$  ppm, were respectively ascribed to the methyl and methylene protons ( $-\text{CH}_2\text{COO}-\text{Ar}$ ), while the multiplet between  $\delta = 1.26$ -1.45 ppm was assigned to the methylene protons of the long alkyl chain  $\{-(\text{CH}_2)_8-\}$ . The four distinct doublets between  $\delta = 7.09$ -7.92 ppm were indicative of the aromatic protons. The singlet observed at the most downfield region,  $\delta = 8.40$  ppm, supported the presence of the imine linking group<sup>18</sup>. The molecular structure of 12BABr was further verified by using  $^{13}\text{C}$  NMR spectroscopy. The peak at  $\delta = 14.24$  ppm was attributed to the methyl carbon while the peaks between  $\delta = 22.83$ -34.60 ppm represented the methylene carbons of the long alkyl chain. Twelve aromatic carbons is resonated between  $\delta = 122.10$ -153.38 ppm. The peaks at  $\delta = 159.44$  ppm and  $\delta = 171.86$  ppm confirmed the presence of the azomethine carbon and the carbonyl group in the molecule.

**Mesomorphic properties:** 10BABr exhibited interesting thermotropic properties and its melting behaviour was carefully monitored by polarizing optical microscopy during both heating and cooling scans. Optical photomicrographs of 10BABr are shown in Fig. 2 as the representative illustration. The results from the polarizing optical microscopy observation were verified by the differential scanning calorimeter 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<sup>24</sup> and Gray and Goodby<sup>25</sup>.

Under polarizing optical microscopy, focal conic fan-shaped textures of a smectic A phase was observed during the cooling cycle (Fig. 2a). Upon further cooling, the back of the fan-shaped domains developed a series of dark-lines, which is transitory in nature<sup>7,26</sup> (Fig. 2b). On further cooling, the bands expanded, met and eventually coalesce to produce a polygonal-like texture<sup>20</sup> (Fig. 2c). This phase is identified as a smectic B phase. This similar behaviour was also reported for a closely-related compound, 4-butyloxybenzylidene-4-chloroaniline<sup>27</sup>.

**X-Ray diffraction studies:** In order to study the molecular arrangement of the mesophase, temperature-dependent XRD analysis was done for 18BABr. The XRD pattern of the

representative compound 18BABr is shown in Fig. 3 while the powder X-ray diffraction data is tabulated in Table-3. Two pseudo-Bragg low angle diffraction peaks,  $2.03^\circ$  and  $4.01^\circ$  are observable from the XRD diffractogram (Fig. 3). Ratio of angle of diffraction ( $2\theta^\circ$ ) of these peaks was found to be 1 and 2, which indicate a smectic phase (1-D stack of layers)<sup>28</sup>. On the other hand, diffuse maxima, broad diffraction peak in wide angle region indicates the characteristic of liquid-like order of alkyl chains within smectic planes. Distance for wide angle found is 4.5 Å, which is the typical values (4.4 to 4.6 Å) for calamitic mesophase. It also means that there is no regular intermolecular distance inside the layers, which confirmed is smectic A phase<sup>29</sup>.

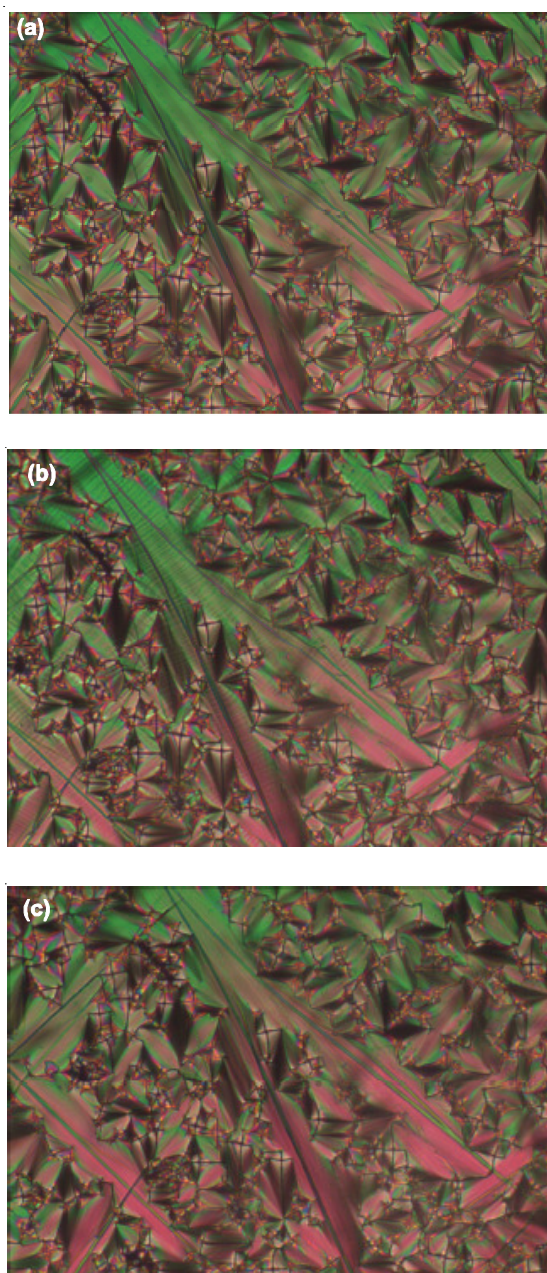


Fig. 2. Optical photomicrographs of 10BABr taken during the cooling cycle. (a) optical photomicrograph showing fan-shaped textures of a smectic A phase. (b) optical photomicrograph exhibiting transition bar at the smectic A to smectic B transition. (c) optical photomicrograph displaying mosaic textures of a SmB phase

TABLE-2  
TRANSITION TEMPERATURES AND ASSOCIATED ENTHALPY CHANGES OF nBABr UPON HEATING AND COOLING SCANS

Compound	Transition temperatures (°C) ( $\Delta H$ , kJ mol <sup>-1</sup> )
2BABr	Cr 97.17 (24.77) I
	I 60.77 (16.50) Cr
4BABr	Cr 95.82 (9.70) I
	I 89.33 (9.70) Cr
6BABr	Cr 102.86 (39.80) I
	I 99.63 (6.30) SmA 88.28 (3.38) SmB 39.35 (24.80) Cr
8BABr	Cr 89.62 (25.09) SmB 94.40 (2.27) SmA 110.55 (6.39) I
	I 106.78 (6.53) SmA 91.03 (3.02) SmB 46.16 (10.64) Cr
10BABr	Cr 86.70 (26.28) SmB 96.17 (2.78) SmA 113.55 (8.16) I
	I 108.44 (8.65) SmA 92.33 (3.27) SmB 40.48 (28.73) Cr
12BABr	Cr 90.95 (31.54) SmB 96.50 (3.09) SmA 115.08 (8.16) I
	I 108.82 (7.46) SmA 90.83 (3.20) SmB 53.47 (31.75) Cr
14BABr	Cr 91.26 (41.08) SmA 110.55 (8.08) I
	I 105.72 (8.00) SmA 84.83 (3.25) SmB 54.15 (36.98) Cr
16BABr	Cr 94.35 (53.70) SmA 107.13 (9.27) I
	I 102.16 (10.45) SmA 84.13 (3.79) SmB 70.74 (50.79) Cr
18BABr	Cr 97.11 (73.88) SmA 105.50 (11.44) I
	I 102.39 (11.93) SmA 83.92 (4.52) SmB 74.26 (69.16) Cr

Note: Cr= crystal; SmA= smectic A; SmB= smectic B; I= isotropic

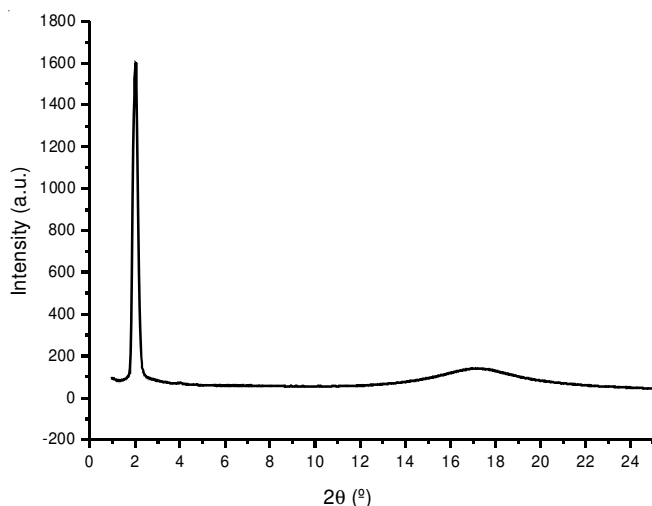


Fig. 3. X-ray diffractogram of 18BABr at 90°C upon cooling from isotropic phase

TABLE-3  
POWDER X-RAY DIFFRACTION DATA OF 18BABr

Phase observed	smectic A
Temperature (°C)	90
2θ (°)	2.03; 4.01
d-Spacing (Å)	37.6
Length, l (Å)	34.7
Aspect ratio (d/l)	1.08
Distance for wide angle (Å)	4.5

From the XRD analysis data, *d*-layer spacing (37.6 Å) was found larger than molecular length (34.7 Å) obtained by MM2 molecular calculation and *d/l* ratio was calculated to be 1.08 (approximately to 1), which confirmed monolayer of SmA phase was being observed for 18BABr<sup>30</sup>. Therefore, it can be deduced that on an average, the long molecular axis of 18BABr pointed in one favourable direction with a small interaction coefficient.

**Influence of alkyl chain length on mesomorphic properties:** Representative differential scanning calorimeter

thermogram for 8BABr upon heating and cooling are depicted in Fig. 4. A plot of the transition temperatures against the number of carbons in the alkanoyloxy chain during the heating cycle are shown in Fig. 5.

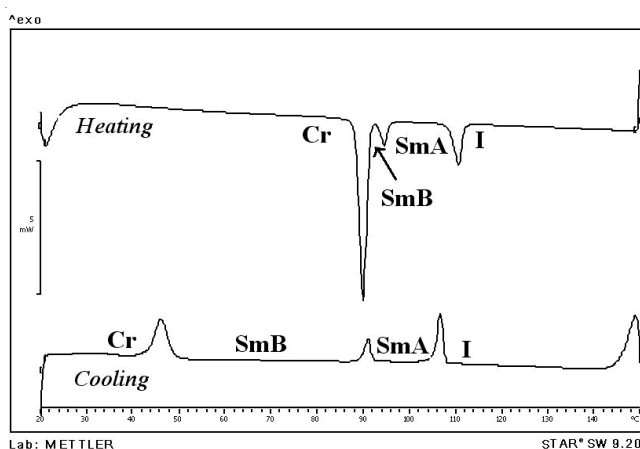


Fig. 4. DSC thermogram of 8BABr

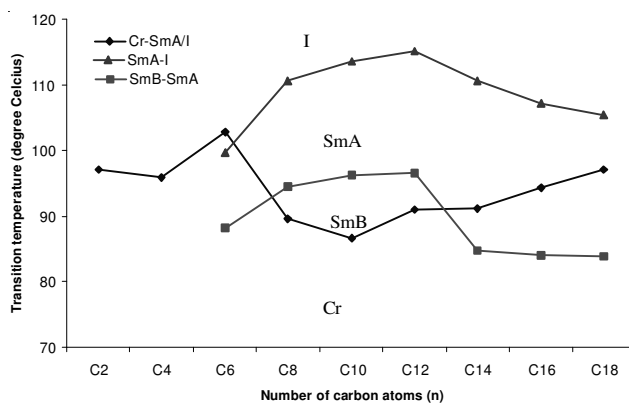


Fig. 5. Plot of transition temperature against number of carbon atoms (n) in alkanoyloxy chain of nBABr

Based on the plot, it can be deduced that mesomorphic behaviour of nBABr was greatly influenced by length of terminal alkanoyloxy chain. Out of the twelve compounds, the first two members (C2 and C4) did not possess mesomorphic properties. These molecules with short alkanoyloxy chains are too rigid, therefore have high melting points, thus impeding their liquid crystal properties<sup>31</sup>. Once the length of the terminal chain is increased, the molecule becomes more flexible, hence promoting a monotropic (less stable) mesophase in a particular compound. Therefore, C6 member is monotropic smectogen whereby mesophases (smectic A and smectic B) were only observed during the cooling scan. In monotropic mesogens, the melting points were always equal to or higher than the clearing points, hence exhibiting supercooling properties. Further lengthening of the alkanoyloxy chain from C8 to C12 (medium members) has led to formation of enantiotropic (more stable) smectic A and smectic B mesophases during both heating and cooling processes. This is due to enhancement of flexibility resulted by longer terminal alkanoyloxy which contributed to the suitable balancing of rigidity and flexibility of these compounds and subsequently promotes the exhibition of enantiotropic smectic A and smectic

B phases<sup>32</sup>. The higher members, C14-C18 members exhibited enantiotropic smectic A and monotropic smectic B phases.

It has been reported that melting point within a homologous series vary depending on molecular mass wherein molecule with lower mass possesses lower melting point in comparison to member with higher mass<sup>6</sup>. Melting point increases when polarizability of the compounds within the same series increases. However, the current trend was not in accordance with this common rule. From the graph, the melting point decreased as the length of the chain increased to the C10 member with the exception of the C6 member. 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<sup>33</sup>. The increased melting temperature from the *n*-decanoyloxy ( $T_m = 86.70$  °C) to the *n*-octadecanoyloxy ( $T_m = 97.11$  °C) derivative could have been attributed to the increase in the Van der Waals attractive forces between the molecules<sup>34</sup>. Therefore, compromise in chain length is required for low melting point, which is in agreement with those reported for alkylcyanobiphenyl homologues<sup>6</sup>.

While the C8 to C12 members exhibited an increase in their transition temperatures as well as smectic A phase range during the smectic A-to-I transition, the reverse trend was observed for the C12 to C18 members. The terminal intermolecular attractions play a role in determining the smectic A-I transition temperatures, *i.e.*, 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 (C12 to C18), in turn depressing the smectic A-to-I transition temperatures<sup>34,35</sup>.

**Structure-mesomorphic property relationships:** Molecular structure of organic compounds and their liquid crystalline properties are closely related. Table-4 summarizes the transition temperatures, mesomorphic behaviour and molecular structures of 8BABr and structurally related compounds reported in literature<sup>19,36-39</sup>.

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 transitions temperatures of 8BABr are higher than those of 8BACl. The bromine 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<sup>40</sup>. Higher molecular polarizability contributed by the larger bromine atom led to higher phase stability in 8BABr<sup>15</sup>. This phenomenon is supported by the similar characteristic observed for X-AB and X-ABOH series (where X = F, Cl, Br, I) wherein the melting and transition temperatures ascended as the size of halogen group increasing.

Secondly, polarizability 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 smectic B phase than 8BABr (current study) and 8BAI, which exhibited enantiotropic smectic B 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).

Compound	Structure	Phase transition (°C)
F-AB Gandolfo <i>et al.</i> (Ref. 36)		Cr (55.1)* SmB 62.2 SmA 65.2 I
Cl-AB Galewski <i>et al.</i> (Ref. 19)		Cr 61.0 SmB 87.7 SmA 98.5 I
Br-AB Galewski <i>et al.</i> (Ref. 19)		Cr 89.0 SmB 104.0 SmA 113.0 I
F-ABOH Sakagami <i>et al.</i> (Ref. 37)		Cr 64 SmA 76 I
Cl-ABOH Sakagami <i>et al.</i> (Ref. 37)		Cr 67 SmA 123 I
Br-ABOH Sakagami <i>et al.</i> (Ref. 37)		Cr 73 SmA 132 I
I-ABOH Sakagami <i>et al.</i> (Ref. 37)		Cr 109 SmA 133 I
8BACl Ha <i>et al.</i> (Ref. 38)		Cr (80.2)* SmB 84.0 SmA 104.8 I
8BABr [Present study]		Cr 89.6 SmB 94.4 SmA 110.6 I
8BAI Ha <i>et al.</i> (Ref. 39)		Cr 86.6 SmB 110.7 SmA 115.2 I

(\*) indicates monotropic phase

Difference in the linking groups (ester group in 8BABr and ether group in Br-AB) between the phenyl ring and the alkyl chain can also cause change in the mesomorphic properties. The ether linking group provides greater linearity to molecules rather than the ester group, thus resulting in the wider phase range of smectic B phase being observed in Br-AB ( $\Delta SmB = 15$  °C) when compared to 8BABr ( $\Delta SmB = 4.8$  °C). In addition, 8BABr possessed wider phase range of smectic A ( $\Delta SmA = 16.2$  °C) compared to Br-AB ( $\Delta SmA = 9$  °C) owing to the  $\pi$ -electrons associated with the carbonyl group, which provides greater intermolecular interactions among molecules<sup>31</sup>.

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 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, 8BABr, 8BAI). However, the increased polarisability at the lateral of a molecule caused depression of smectic B arrangement and thus impeding smectic B formation in the X-ABOH series.

### Conclusion

In this paper, we reported a homologues series of 4-alkanoyloxybenzylidene-4'-bromoanilines. Whilst *n*-ethanoyloxy and *n*-butanoyloxy derivatives were non-mesogens, the rest members exhibited smectic A and smectic B phases. Comparison of present series with other structurally related compounds revealed that terminal bromo substituent favourable to exhibit mesophase.

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