

Full Length Research Paper

Mesogenic azomethine esters with different end groups: Synthesis and thermotropic properties

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Series of elongated azomethine esters containing two aromatic rings with stearyl moiety as one of the terminal carbon chain and various substituents X (where X = H, F, Cl, Br, OCH₃, CH₃ and C₂H₅) at the other end of molecule have been isolated and their structures were proposed via physical measurement. The mesomorphic properties of these compounds were investigated via differential scanning calorimetry and polarizing optical microscopy. The thermal data indicate that compounds with fluoro, chloro, bromo and methoxy substituents exhibit mesomorphic properties and the rest of the compounds are non mesogenic materials. While compound with X = OCH₃, show nematic phase, the compounds containing halogen F, Cl and Br are smectogenic in nature. The presence of a lateral hydroxyl group has been claimed to contribute to the enhanced molecular ordering, leading to a higher clearing temperature.

Key words: Schiff bases, smectic A, nematic, substituent effects.

INTRODUCTION

The growth 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 a rigid core composed of two or more aromatic rings and one or more flexible terminal chains. Azomethine, also known as Schiff base (CH=N), is a 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 mesophase formation (Collings and Hird, 1998; Singh and Dunmur, 2002).

Extensive investigation on azomethine system has been conducted since the discovery of 4-methoxybenzylidene-4'-butylaniline (MBBA) which exhibited a nematic phase at room temperature (Kelker and Scheurle, 1969; Ma et al., 2009).

Sakagami and Takase (1995) studied the mesomorphic behavior of a homologous series of 2-hydroxy-4-*n*-alkoxybenzylidene-4'-hydroxyanilines with different number of carbons at the terminal chain ranging from one

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to eighteen. They reported that the compounds with an alkoxy chain of C10 to C18 exhibited smectic phase wherein the intermolecular as well as the intramolecular hydrogen bondings contributed greatly to the formation of the mesophase. It is well reported that the smectic mesophase can be easily introduced by increasing the terminal chain length as reported for 2-hydroxy-4-methoxybenzylidene-4'-alkanoyloxyanilines (Yeap et al., 2006). No liquid crystalline phases were observed in the case of the homologous series with a short terminal chain in which the alkoxy chain ranges from C1 to C9.

Instead of studying the mesomorphism of imines with different lengths of alkyl chain, imines with different substituents residing at the end along the axis are also of current interest. Recently, Yeap et al. (2002) studied mesomorphic properties of a series of Schiff base esters with various para-substituents (R) at the aniline fragment. The compounds reported are 4-*n*-octadecanoyloxybenzylidene-4'-X-substituted-anilines, where X = CN, NO₂, OH or COOH. In the current project, an additional ortho-hydroxyl group was introduced into the aldehyde fragment of the existing core system. This was carried out through the preparation of a series of 3-hydroxy-4-[(4-X-substitutedphenyl)imino]methyl]phenyl octadecanoate, **SB-X**, in which X is H, F, Cl, Br, OCH₃, CH₃, C₂H₅ (Figure 1). The influences of the hydroxyl (OH) group and the different X substituents on the mesomorphic properties of compounds **SB-X** were studied.

The analogous 2-hydroxy-4-*n*-alkyloxybenzylidene-4'-alkylanilines (Sakagami et al., 2001) and 2-hydroxy-4-*n*-alkyloxybenzylidene-4'-isopropoxy-anilines (Sakagami et al., 2002) which were reported have the similar core structure as compounds **SB-X** but possessed a different linkage at the terminal alkyl chain of the aldehyde fragment. While the present compounds **SB-X** possesses an ester linkage to the alkyl chain (C_nH_{2n+1}COO-), their analogous compounds possessed an ether linkage to the alkyl chain (C_nH_{2n+1}O). However, the compounds in the **SB-X** series have hitherto not been reported in the literature.

MATERIALS AND METHODS

Materials

4-Bromoaniline, 4-chloroaniline, 4-ethylaniline, octadecanoic acid, 4-dimethylaminopyridine (DMAP) were obtained from Merck (Germany). 2, 4-Dihydroxybenzaldehyde, 4-fluoroaniline and N, N-dicyclohexylcarbodiimide (DCC) were purchased from Acros Organics (USA). While 4-methoxyaniline was purchased from Fluka Chemie (Switzerland), 4-methylaniline was obtained from Riedel-de Haen (Germany). Aniline was obtained from BDH (England).

Microanalyses were carried out on a Perkin Elmer 2400 LS Series CHNS/O analyzer. Electron impact 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. FT-IR data were acquired with a Perkin Elmer 2000-FTIR spectrophotometer

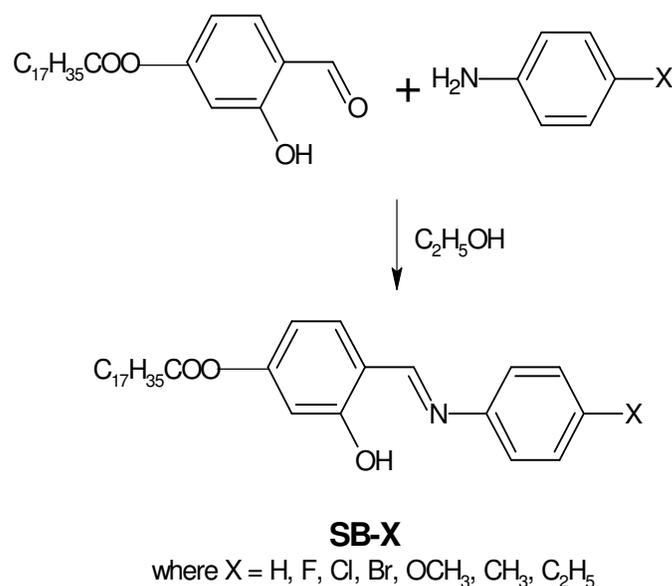


Figure 1. Synthetic route of Schiff base liquid crystals **SB-X**.

in the frequency range of 4000 – 400 cm⁻¹ with samples embedded in KBr discs. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using a Bruker 400 MHz NMR spectrometer with TMS as the internal standard. Thin layer chromatography analyses were carried out using aluminum backed silica gel plates (Merck 60 F₂₅₄) and were examined under shortwave UV light.

Liquid crystalline properties were investigated by polarizing optical microscopy (POM) using a Carl Zeiss Polarizing Optical Microscope (POM) 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 phase transition temperatures were measured using a Mettler Toledo DSC823 differential scanning calorimeter at a scanning rate of 10°C min⁻¹.

Synthesis

Synthesis of 3-hydroxy-4-[(4-X-substitutedphenyl)imino]methyl]phenyl octadecanoates (**SB-X**, where X = H, F, CL, BR, OME, ME, ET)

4-Formyl-3-hydroxyphenyl octadecanoate was previously prepared via Steglich esterification (Ha et al., 2009). In a round-bottom flask, a mixture of the aldehyde (5.0 mmol), aniline (5.0 mmol) and absolute ethanol (40 mL) was refluxed with stirring. The reaction mixture was filtered and the solvent was removed from the filtrate by evaporation. Recrystallization from absolute ethanol gave the title compounds as yellow solid. EI-MS, IR, ¹H and ¹³C NMR data of the representative compounds **SB-H** and **SB-ME** are given as follows:

SB-H: Yield 51%. MS(EI): M⁺ (m/z) = 479; IR (KBr, cm⁻¹): 3445 (O-H), 2953, 2917, 2848 (C-H aliphatic); 1757 (C=O ester); 1628 (C=N); 1596, 1472 (C=C aromatic); ¹H NMR (400 MHz, CDCl₃):

Table 1. Transition temperatures and associated enthalpy changes of **SB-X** upon heating and cooling scans.

Compound	Transition temperatures, °C (ΔH , kJmol ⁻¹)	Heating and cooling
SB-H	Cr 84.50 (83.16) I Cr 70.04 (84.33) I	
SB-F	Cr 95.43 (74.92) I Cr ₁ 68.86 (3.32) Cr ₂ 74.24 (80.17) SmA 80.17 (0.88) I	
SB-CL	Cr ₁ 94.81 (12.29) Cr ₂ 116.14 (65.93) SmA 123.75 (10.24) I Cr ₁ 78.61 (11.18) Cr ₂ 104.82 (68.90) SmA 119.75 (10.58) I	
SB-BR	Cr ₁ 88.47 (38.86) Cr ₂ 110.05 (47.51) SmA 119.00 (1.78) I Cr ₁ 85.39 (6.49) Cr ₂ 96.30 (55.51) SmA 116.65 (7.73) I	
SB-OME	Cr ₁ 61.22 (5.57) Cr ₂ 100.08 (78.07) I Cr ₁ 49.12 (5.35) Cr ₂ 77.79 (72.17) N 99.35 (4.72) I	
SB-ME	Cr ₁ 59.68 (4.82) Cr ₂ 95.42 (85.57) I Cr ₁ 50.88 (4.80) Cr ₂ 77.52 (85.78) I	
SB-ET	Cr ₁ 56.76 (4.93) Cr ₂ 86.22 (67.65) I Cr ₁ 45.18 (4.24) Cr ₂ 72.69 (67.87) I	

Cr = Crystal; SmA = Smectic A; N = Nematic; I = Isotropic liquid.

δ /ppm 0.91 (t, 3H, $J = 6.7$ Hz, CH₃), 1.28-1.46 {m, 28H, CH₃(CH₂)₁₄-}, 1.78 (quint, 2H, $J = 7.4$ Hz, -CH₂CH₂COO-), 2.59 (t, 2H, $J = 7.4$ Hz, -CH₂COO-), 6.71 (dd, 1H, $J = 2.2, 8.4$ Hz, Ar-H), 6.79 (d, 1H, $J = 2.2$ Hz, Ar-H), 7.30 (m, 3H, Ar-H), 7.40 (d, 1H, $J = 8.4$ Hz, Ar-H), 7.45 (m, 2H, Ar-H), 8.62 (s, 1H, CH=N), 13.60 (s, 1H, OH); ¹³C NMR (100 MHz, CDCl₃): δ /ppm 172.1 (COO), 162.2 (CH=N), 163.0, 154.9, 148.6, 133.5, 129.8, 127.4, 121.6, 117.5, 113.3, 110.9 (aromatic carbons), 34.86 (-CH₂COO-), 25.30 (-CH₂CH₂COO-), 32.34, 30.11, 30.07, 30.02, 29.88, 29.78, 29.67, 29.50, 23.11 (CH₃(CH₂)₁₄-), 14.54 (CH₃); Elemental analysis: Calculated for C₃₁H₄₅NO₃ C, 77.62%, H, 9.46%, N, 2.92%; Found: C, 77.75%, H, 9.50%, N, 2.88%.

SB-ME: Yield 39%. MS(EI): M⁺ (m/z) = 493; IR (KBr, cm⁻¹): 3433 (O-H), 2953, 2918, 2849 (C-H aliphatic); 1759 (C=O ester); 1623 (C=N); 1607, 1471 (C=C aromatic); ¹H NMR (400 MHz, CDCl₃): δ /ppm 0.92 (t, 3H, $J = 7.1$ Hz, CH₃), 1.28-1.46 {m, 28H, CH₃(CH₂)₁₄-}, 1.79 (quint, 2H, $J = 7.3$ Hz, -CH₂CH₂COO-), 2.41 (s, 1H, Ar-CH₃), 2.58 (t, 2H, $J = 7.4$ Hz, -CH₂COO-), 6.70 (dd, 1H, $J = 2.2, 8.4$ Hz, Ar-H), 6.77 (d, 1H, $J = 2.2$ Hz, Ar-H), 7.25-7.29 (m, 4H, Ar-H), 7.37 (d, 1H, $J = 8.4$ Hz, Ar-H), 8.62 (s, 1H, CH=N), 13.71 (s, 1H, OH); ¹³C NMR (100 MHz, CDCl₃): δ /ppm 172.1 (COO), 161.2 (CH=N), 163.0, 154.8, 146.0, 137.4, 133.3, 130.4, 121.4, 117.6, 113.1, 110.8 (aromatic carbons), 34.9 (-CH₂COO-), 25.3 (-CH₂CH₂COO-), 32.3, 30.1, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 23.1 (CH₃(CH₂)₁₄-), 21.4 (Ar-CH₃), 14.5 (CH₃(CH₂)₁₄); Elemental analysis: Calculated for C₃₂H₄₇NO₃ C, 77.85%, H, 9.60%, N, 2.84%; Found: C, 77.77%, H, 9.68%, N, 2.90%.

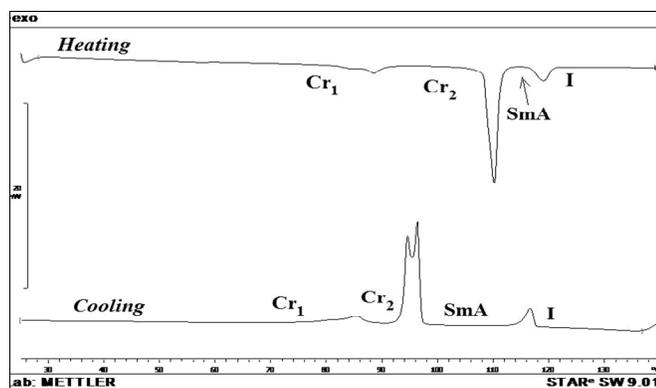
RESULTS AND DISCUSSION

Mesomorphic properties

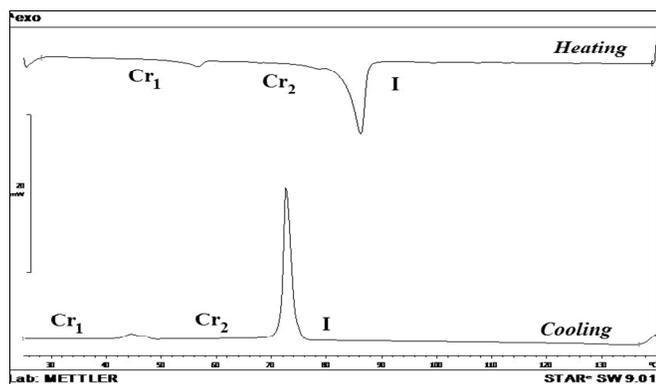
The phase transition temperatures and their associated enthalpy obtained from DSC analysis over heating and cooling cycles are tabulated in Table 1. Representative DSC thermograms of compounds **SB-CL** and **SB-ET** during both heating and cooling scans are shown in Figure 2. It is clearly shown that upon heating, **SB-CL** (Figure 2a) and **SB-BR** show enantiotropic properties

and exhibit endotherms characteristic of the crystal–mesophase and mesophase–isotropic transitions at temperatures greater than melting temperature (T_m). It is very clear that an endotherm that appeared over heating cycle for compounds **SB-H** and **SB-F** suggests a direct melting from crystal-to-isotropic phase. However, the thermograms of compounds **SB-OME**, **SB-ME** and **SB-ET** (Figure 2b) each shown an endotherm before the isotropization. The texture observed under the polarizing microscope is indicative of the presence of subphases within the crystal phase (Cr₁-Cr₂) as those phenomena observed for isoflavone derivatives (Belmar et al., 1999). While the clearing points for compounds **SB-CL** and **SB-BR** represent the transition temperature of SmA-I, the clearing temperatures observed for compound **SB-F** is merely for the crystal-isotropic phase transition. These phenomena could be ascribed to the increase of the melting point, which lies above the mesophase–isotropic liquid transition temperatures (Gray, 1962).

The data in Table 1 has also shown that upon cooling compounds **SB-F**, **SB-CL** and **SB-BR** exhibit smectic phase. The cooling scan upon compound **SB-CL** shows the presence of mesophase (Figure 3b) with fan-shaped texture. This feature is characteristic of the SmA phase owing to the formation of batonnets (Figure 3a) that coalesce to form the fan-shaped texture. The appearance of SmA phase is found to conform with analogue 4-chlorobenzylidene-4'-octadecanoyloxyaniline (**18A-CL**) as reported earlier (Ha et al., 2010). 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). One of the remarkable features is that the clearing temperature of compound **SB-CL** (123.75°C) is very much greater than

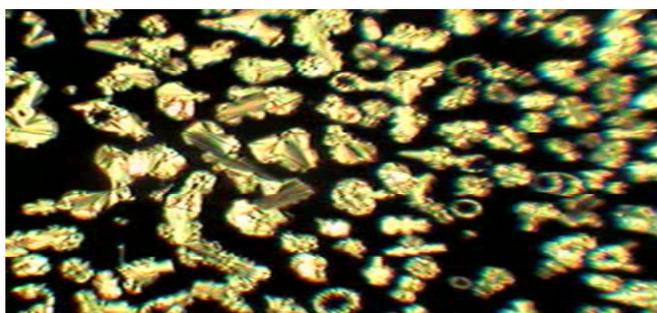


(a)

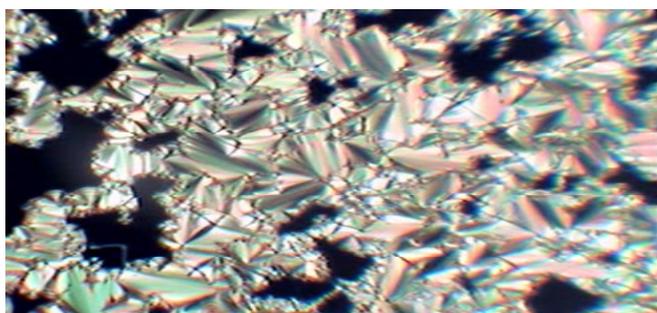


(b)

Figure 2. DSC thermograms of (a) **SB-CL** and (b) **SB-ET** during heating and cooling cycles.



(a)



(b)

Figure 3. Liquid crystal textures of **SB-CL** on cooling. The battonnets (a) coalesced to form the fan-shaped texture of SmA phase in (b).

18A-CL (97.67°C) during heating cycle (Ha et al., 2010).

This information indicates that the introduction of hydroxyl group at *ortho* position in the aldehyde fragment increases the degree of anisotropy of the molecular polarizability of compound **SB-CL** and hence increases the degree of molecular order causing the smectic phase to have increased stability (Collings and Hird, 1998).

Under the polarizing microscope, **SB-OME** 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 (Liu, 1981). The mesophase was identified by the nematic droplets texture. Brownian flashes, a characteristic of the nematic phase were also observed before recrystallization (Singh and Dunmur, 2002). The nematic – isotropic transition temperature of compound **SB-OME** is 4.7°C higher than compound **SB-ME**, although both the compounds differ only slightly in the terminal substituent. This can be due to the oxygen of methoxy (OCH₃) group being in conjugation with the aromatic core, which, in addition to extending the length of the rigid core, enhances the polarizability. Compounds **SB-ME** and **SB-ET**, which possess methyl and ethyl group in the respective aniline fragment, do not exhibit mesomorphic properties. One notable feature is that compound **SB-ME** possesses a higher clearing temperature in comparison with compound **SB-ET**. This phenol-menon is similar with that reported by Artigas et al. (1985), wherein the introduction of the hydroxyl group in the *ortho* position causes the mesophase stability to favor for terminal chains of shorter length. As such, the compound with short terminal length is expected to possess a higher degree of molecular order, which is favored by the increase in the polarizability (Yeap et al., 2004).

The influence of terminal group on mesophase stability can also be considered as one of the factors contributing towards the difference of temperature for transition from mesophase to isotropic phase. Among compounds **SB-X** (where X = F, Cl and Br), wherein each compound possesses the halogen in the aniline fragment, the clearing temperature for compound **SB-F** is very much lower in comparison with **SB-CL** and **SB-BR**. This comparison suggests that the fluorine (F) atom, which is the most electronegative, reduces the degree of molecular order despite the presence of hydroxyl group at *ortho* position. This thermal data also indicates that the influence of steric hindrance caused by the asymmetry of the central core of compound **SB-F** is the least in comparison with compounds **SB-CL** and **SB-BR**, which possess higher clearing temperatures.

Influence of lateral polar hydroxy group on mesomorphic properties

This investigation has also revealed a correlation between the influence of lateral polar hydroxyl group on

Table 2. Percentage yields and analytical data of SB-X.

Compound	Yield (%)	Formula	% Found (% Calc.)		
			C	H	N
SB-H	51	C ₃₁ H ₄₅ NO ₃	77.75 (77.62)	9.50 (9.46)	2.88 (2.92)
SB-F	74	C ₃₁ H ₄₄ FNO ₃	74.92 (75.81)	8.98 (8.91)	2.70 (2.81)
SB-CL	34	C ₃₁ H ₄₄ ClNO ₃	72.30 (72.42)	8.71 (8.63)	2.75 (2.72)
SB-BR	38	C ₃₁ H ₄₄ BrNO ₃	66.78 (66.66)	7.85 (7.94)	2.53 (2.51)
SB-OME	43	C ₃₂ H ₄₇ NO ₄	75.29 (75.40)	9.37 (9.29)	2.81 (2.75)
SB-ME	39	C ₃₂ H ₄₇ NO ₃	77.77 (77.85)	9.68 (9.60)	2.90 (2.84)
SB-ET	41	C ₃₃ H ₄₉ NO ₃	78.18 (78.06)	9.65 (9.73)	2.71 (2.76)

compounds **SB-X** whereby a comparison was made between the data of compounds **SB-X** (Table 2) and their analogues *p-n*-octadecanoyloxybenzylideneaniline (**18B-H**), *p*-chloroaniline (**18B-Cl**) and *p*-methylaniline (**18B-ME**) (Ooi, 2003). The clearing temperature of compounds **SB-H** (84.50 °C), **SB-CL** (123.75 °C) and **SB-ME** (95.42 °C) are found to be higher than those for compounds **18B-H** (78 °C), **18B-Cl** (106 °C) and **18B-ME** (90 °C), respectively. It can therefore be assumed that the presence of an OH group in an *ortho* position in the title compounds confers a higher degree of stability on the mesophase resulting from the increase in van der Waals forces, which in turn is caused by the increased anisotropy of the molecular polarizability.

Physical characterization

The spectroscopic methods (FTIR, ¹H NMR, and ¹³C NMR) have been employed to elucidate the target compounds (**SB-X**) and data of the representative compounds are summarized in the materials and methods section. The formulations and molecular structures of all the compounds are also supported by the microanalytical data wherein the percentages of C, H and N thus found are in good agreement with the theoretical values.

FTIR data show that the diagnostic bands assignable to the stretching of aliphatic C-H and carbonyl (C=O of ester) of representative compound **SB-ME** were observed at the respective frequencies 2849 - 2953 and 1759 cm⁻¹. The absorption bands appeared at higher frequency 3433 cm⁻¹ can be attributed to the stretching of O-H. The absorption bands assignable to the stretching of C=N bond for compound **SB-ME** was observed at frequency of 1623 cm⁻¹, and these values conform with those reported in the IR spectra for various substituted aromatic Schiff bases that possess the formulation HOC₆H₅CH=NC₆H₅ (Yeap et al., 2002). Proton NMR data of **SB-ME** (Figure 4) show the presence of a singlet peak assigned to the azomethine proton (CH=N) at the chemical shift δ = 8.62 ppm. A triplet signal assignable to the methyl group of ester linkage at δ = 0.92 ppm and a multiplet that

occurred at δ = 1.28 – 2.58 ppm can be ascribed to methylene (CH₃(CH₂)₁₆COO) protons. The ¹H NMR spectrum also shows the presence of aromatic protons within the range of δ = 6.70 – 7.37 ppm. Another singlet appeared at δ = 13.71 ppm can be attributed to the hydroxyl (O-H) proton. A singlet peak occurring at δ = 2.41 ppm can be attributed to the presence of methyl group attached to the aromatic ring (Ar-CH₃). The structural information can also be inferred from the ¹³C NMR data (Figure 5), wherein a peak owing to the presence of ester carbonyl (-COO-) was observed at δ = 172.1 ppm, which is in agreement with those analogues earlier reported (Yeap et al., 2002). The appearance of a peak at δ = 161.2 ppm is due to the presence of the carbon in the imine (C=N) group. An additional peak that appears at δ = 21.4 ppm suggested the presence of the methyl group attached to the aromatic ring (Ar-CH₃). The results as inferred from the IR and NMR spectra suggest that the molecular structure for **SB-ME** consist of two aromatic rings bridged by an imine group, which in turn forms an intramolecular hydrogen bonding (Figure 2).

Conclusion

In this paper, we described the synthesis and mesomorphic properties of a homologous series of 3-hydroxy-4-[(4-X-substitutedphenyl)imino]methylphenyl octadecanoate. Different substituents (X) at the para position of the aniline fragment was found to exert an effect on the mesomorphic properties. While compounds with halogen and methoxy substituents (X= F, Cl, Br, OCH₃) exhibited liquid crystal phases, the compounds with less polar substituents, X = CH₃, C₂H₅ are non-mesomorphic derivatives.

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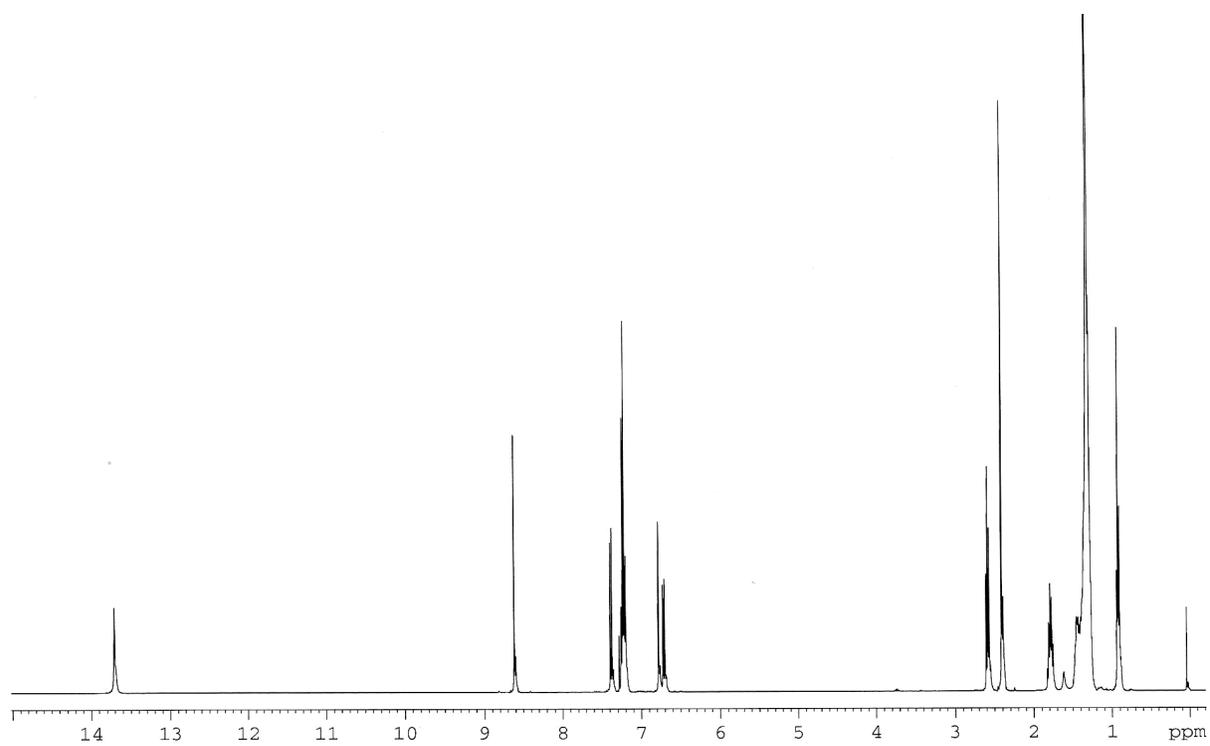


Figure 4. ^1H NMR spectrum of SB-Me.

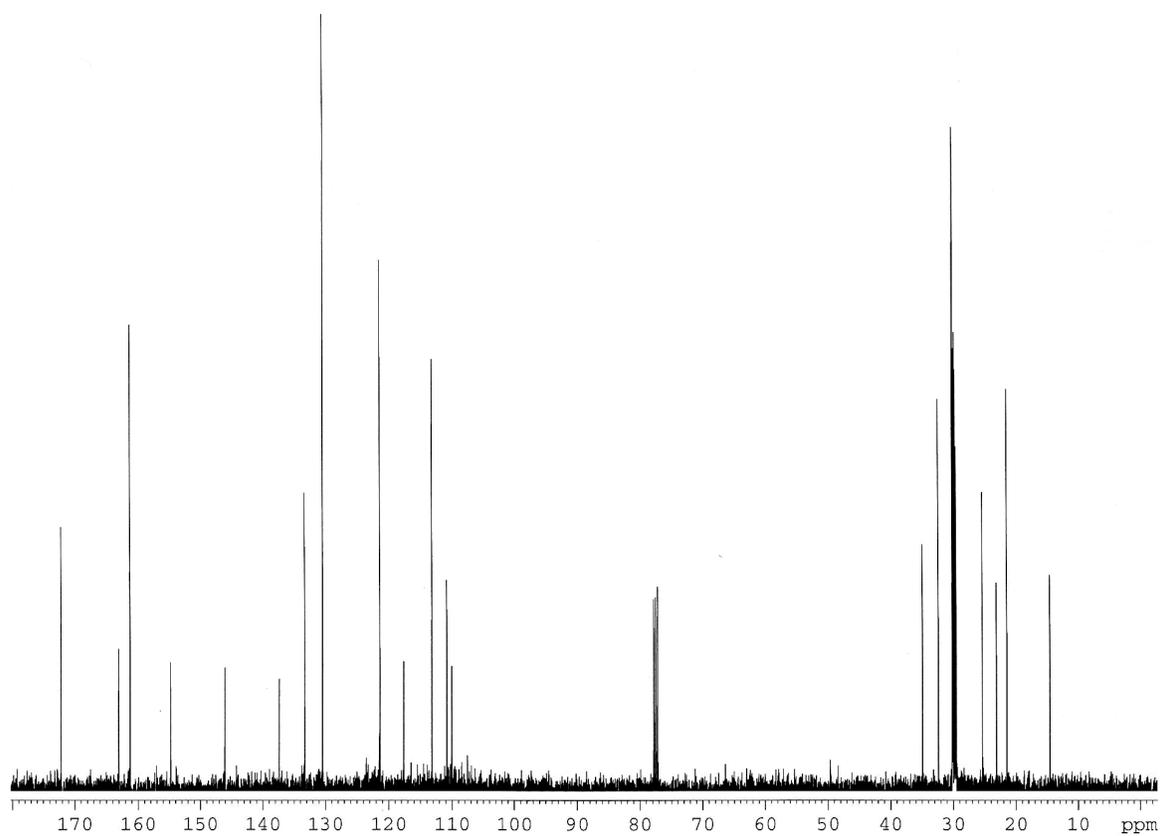


Figure 5. ^{13}C NMR spectrum of SB-ME.

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