

Synthesis and Liquid Crystalline Properties of New Schiff Bases *N*-[4-(4-*n*-Alkanoyloxybenzoyloxy)benzylidene] -4-Cyano-, 4-Hydroxy-, 4-Thio- and 4-Nitroanilines

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Abstract: Series of elongated Schiff base esters containing three aromatic rings with hexadecanoyl moiety as one of the terminal carbon chain and various substituents R (R = CN, OH, SH, and NO₂) 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 all of these compounds exhibit mesomorphic properties except compound with R = SH. Although compounds with R = OH and NO₂ show nematic phases, compound containing cyano substituent are smectogenic in nature.

Key words: liquid crystal, mesophase, Schiff bases, nematic, smectic.

INTRODUCTION

Liquid crystalline behaviour of an organic compound is essentially dependent on its molecular architecture, in which a slight change in its molecular geometry brings about considerable changes in its mesomorphic properties. Detailed studies by liquid crystal researchers have led to empirical rules, one of which includes the effect of the chemical constitution in the formation of nematogenic and smectogenic mesophases (Gray 1962). Most of these studies focus mainly on Schiff's bases since the discovery of 4-methoxybenzylidene-4'-butylaniline which exhibited a nematic phase at room temperature (Kelker and Scheurle 1969).

The mesomorphic properties of aromatic Schiff base esters arising from substituents varying in their polarities have been reported in the previous studies (Yeap *et al.* 2002, 2006a, Ha *et al.* 2009). The different substituents residing at the other end along the long molecular axis of these imines have been known to either promote or suppress the mesomorphic properties (Yeap *et al.* 2006a, Ha *et al.* 2009). In our present laboratory work, a series of two aromatic ring imine *o*-*n*-hydroxy-*p*-hexadecanoyloxybenzylidene-*p*-substituted-anilines has been isolated and their liquid crystalline properties have been thermally and optically characterized (Yeap *et al.* 2004, 2006b). Subsequent to this study, three aromatic rings imine esters with higher molecule length-breadth ratio than the previous core system (two aromatic rings system) have been synthesized from the reaction of 4-(4-*n*-alkanoxybenzoyloxy)benzaldehyde with a series of analogue anilines possessing substituents R = H, F, Cl, Br, OCH₃, CH₃ and C₂H₅ have also been carried out of which the reaction led to the formation of mesogens showing SmA (where R = F, Cl and Br) and nematic (N) phases (where R = H, OCH₃, CH₃ and C₂H₅) (Yeap *et al.* 2006c).

In order to accomplish the investigation upon the mesomorphism of the series consisting three aromatic rings core system, we continued with the other substituents (*p*-CN, *p*-OH, *p*-SH and *p*-NO₂) positioned along the molecular long axis.

MATERIALS AND METHODS

Materials:

4-Aminophenol, 4-aminothiophenol, 4-aminobenzonitrile and 4-hydroxybenzoic acid were obtained from

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Merck (Germany). 4-Hydroxybenzaldehyde was purchased from Acros Organics (USA). Whilst 4-nitroaniline and thionyl chloride were purchased from Riedel-de Haen (Germany), triethylamine was obtained from Fluka Chemie (Switzerland).

Instrumentation:

Analytical data were performed on Perkin Elmer 2400 LS series CHNS/O analyzers. Electron impact mass spectra (EI-MS) were recorded by Hewlett Packard 5989A Mass Spectrometer operating at 70eV ionizing energy. FT-IR data were recorded on a Perkin Elmer 2000-FTIR spectrophotometer. NMR spectra were recorded in CDCl₃ on a Bruker 400 MHz Ultrashield Spectrometer.

The phase transition temperatures for the investigated compounds were determined using a differential scanning calorimetry (Shimadzu DSC-50) which adopted a scanning rate of 2°C/min. The optical microscopy studies were carried out with a Carl Zeiss polarizing microscope equipped with a Mettler FP52 hot stage. Phase identification was made by comparison of the observed texture with those reported in the literature (Demus and Richter 1978).

Molecular modeling study was performed using ACD / ChemsSketch Version 4.5. Geometrical optimization or energy minimization of the molecules was performed in order to gain an appreciation of molecular shape and geometry. The structural conformation obtained was subsequently used in calculating the polarizability of each compound as reported earlier (Yeap *et al.* 2004).

Synthesis of Schiff Bases:

4-(4-n-Hexadecanoyloxybenzoyloxy)benzaldehyde, **1** was prepared by adapting a method previously reported by our group [8]. The imines **6-9** were synthesized by mixing equimolar amounts of compound **1** with the appropriate anilines, both dissolved in absolute ethanol. The reaction mixture was refluxed for three hours with stirring before it was filtered. The solvent was removed from the filtrate by evaporation. The light yellowish crystalline of imines **6-9** thus obtained was recrystallized from ethanol till the constant transition temperatures were obtained. The entire synthetic route is outlined in Scheme 1. The elemental analysis, EI-MS, IR, NMR (¹H and ¹³C) data are summarized as follow:

N*-[4-(4-*n*-hexadecanoyloxybenzoyloxy)benzylidene]- 4-cyanoaniline, **6*

Yield 38%. Found: C, 76.58; H, 7.67; N, 4.79. Cal. For C₃₇H₄₄N₂O₄: C, 76.52; H, 7.64; N 4.82. EI-MS m/z (rel. int %): 580 (1) (M)⁺. IR (KBr): max/ cm⁻¹ 2954, 2917, 2848 (C-H aliphatic), 2227 (C N), 1744 (C=O of C₁₅H₃₁COO- fragment), 1754 (C=O of benzoate), 1632 (C=N), 1602 (C=C aromatic), 1280 (C-O). ¹H NMR (400 MHz, CDCl₃): 0.89-0.92 (t, 3H, CH₃-CH₂-), 1.24-1.45 (m, 24H, CH₃-(CH₂)₁₂-C₂H₄COO-), 1.75-1.84 (m, 2H, -CH₂-CH₂COO-), 2.59-2.63 (t, 2H, -CH₂-COO-), 7.27-7.31 (d, 2H, Ar-H), 7.37-7.40 (d, 2H, Ar-H), 7.41-7.44 (dd, 2H, Ar-H), 7.70-7.72 (dd, 2H, Ar-H), 7.99-8.03 (dd, 2H, Ar-H), 8.26-8.30 (m, 2H, Ar-H), 8.44 (s, 1H, CH=N). ¹³C NMR (100 MHz, CDCl₃): 172.11 (C=O of C₁₅H₃₁COO-), 164.39 (C=O of benzoate), 159.16 (C=N), 109.57, 122.16, 122.45, 122.80, 126.88, 130.94, 132.27, 133.77, 134.23, 154.31, 155.65 and 155.73 for aromatic carbons, 119.37 (C N), 34.82, 32.32, 30.09, 30.06, 29.99, 29.85, 29.76, 29.64, 29.49, 25.24, 23.09 and 14.51 for carbons in the alkyl chain (C₁₅H₃₁COO-).

N*-[4-(4-*n*-hexadecanoyloxybenzoyloxy)benzylidene]- 4-hydroxyaniline, **7*

Yield 18%. Found: C, 75.66; H, 7.91; N, 2.43. Cal. For C₃₆H₄₅NO₅: C, 75.63; H, 7.93; N 2.45. EI-MS m/z (rel. int %): 571 (1) (M)⁺. IR (KBr): max/ cm⁻¹ 3399 (O-H), 2954, 2916, 2848 (C-H aliphatic), 1747 (C=O of C₁₅H₃₁COO- fragment), 1730 (C=O of benzoate), 1626 (C=N), 1603 (C=C aromatic), 1285 (C-O). ¹H NMR (400 MHz, CDCl₃): 0.90-0.94 (t, 3H, CH₃-CH₂-), 1.27-1.48 (m, 24H, CH₃-(CH₂)₁₂-C₂H₄COO-), 1.78-1.84 (m, 2H, -CH₂-CH₂COO-), 2.60-2.64 (t, 2H, -CH₂-COO-), 6.87-6.89 (dd, 2H, Ar-H), 7.19-7.22 (dd, 2H, Ar-H), 7.27-7.30 (m, 2H, Ar-H), 7.35-7.37 (d, 2H, Ar-H), 7.97-7.99 (d, 2H, Ar-H), 8.25-8.28 (dd, 2H, Ar-H), 8.50 (s, 1H, CH=N). ¹³C NMR (100 MHz, CDCl₃): 172.10 (C=O of C₁₅H₃₁COO-), 164.32 (C=O of benzoate), 157.57 (C=N), 116.29, 122.33, 122.50, 122.77, 127.07, 130.22, 132.23, 132.34, 145.30, 153.36, 154.71 and 155.54 for aromatic carbons, 34.82, 32.31, 30.08, 30.06, 30.03, 29.98, 29.83, 29.74, 29.63, 29.48, 25.23, 23.07 and 14.49 for carbons in the alkyl chain (C₁₅H₃₁COO-).

N*-[4-(4-*n*-hexadecanoyloxybenzoyloxy)benzylidene]- 4-thioaniline, **8*

Yield 15%. Found: C, 73.55; H, 7.71; N, 2.40. Cal. For C₃₆H₄₅NO₄S: C, 73.56; H, 7.72; N 2.38. EI-MS m/z (rel. int %): 587 (1) (M)⁺. IR (KBr): max/ cm⁻¹ 2952, 2917, 2849 (C-H aliphatic), 1744 (C=O of C₁₅H₃₁COO- fragment), 1731 (C=O of benzoate), 1623 (C=N), 1602 (C=C aromatic), 1281 (C-O). ¹H NMR (400 MHz,

CDC₁₃): 0.88-0.93 (t, 3H, CH₃-CH₂-), 1.27-1.48 (m, 24H, CH₃-(CH₂)₁₂-C₂H₄COO-), 1.77-1.82 (m, 2H, -CH₂-CH₂COO-), 2.60-2.64 (t, 2H, -CH₂-COO-), 3.15 (s, 1H, SH), 7.14-7.17 (d, 2H, Ar-H), 7.26-7.29 (m, 2H, Ar-H), 7.33-7.37 (m, 4H, Ar-H), 7.97-8.00 (d, 2H, Ar-H), 8.25-8.29 (dd, 2H, Ar-H), 8.48 (s, 1H, CH=N). ¹³C NMR (100 MHz, CDCl₃): 172.07 (C=O of C₁₅H₃₁COO-), 164.15 (C=O of benzoate), 159.15 (C=N), 122.36, 122.44, 122.59, 127.00, 130.46, 130.97, 132.24, 132.41, 134.33, 150.16, 153.66 and 155.55 for aromatic carbons, 34.82, 32.31, 30.09, 30.06, 30.05, 29.99, 29.85, 29.76, 29.64, 29.49, 25.23, 23.09 and 14.52 for carbons in the alkyl chain (C₁₅H₃₁COO-).

***N*-[4-(4-*n*-hexadecanoyloxybenzoyloxy)benzylidene]- 4-nitroaniline, 9**

Yield 12%. Found: C, 72.00; H, 7.42; N, 4.64. Cal. For C₃₆H₄₄N₂O₆; C, 71.97; H, 7.38; N 4.66. EI-MS m/z (rel. int %): 600 (<1) (M)⁺. IR (KBr): max/ cm⁻¹ 2954, 2916, 2848 (C-H aliphatic), 1747 (C=O of C₁₅H₃₁COO- fragment), 1732 (C=O of benzoate), 1624 (C=N), 1604 (C=C aromatic), 1280 (C-O). ¹H NMR (400 MHz, CDCl₃): 0.90-0.94 (t, 3H, CH₃-CH₂-), 1.27-1.48 (m, 24H, CH₃-(CH₂)₁₂-C₂H₄COO-), 1.78-1.84 (m, 2H, -CH₂-CH₂COO-), 2.60-2.64 (t, 2H, -CH₂-COO-), 7.26-7.29 (m, 2H, Ar-H), 7.35-7.37 (d, 2H, Ar-H), 7.37-7.40 (dd, 2H, Ar-H), 7.96-7.98 (m, 2H, Ar-H), 8.26-8.29 (dd, 2H, Ar-H), 8.31-8.34 (dd, 2H, Ar-H), 8.50 (s, 1H, CH=N). ¹³C NMR (100 MHz, CDCl₃): 171.86 (C=O of C₁₅H₃₁COO-), 164.22 (C=O of benzoate), 157.83 (C=N), 122.31, 122.35, 122.55, 125.58, 126.64, 130.15, 132.13, 132.44, 145.88, 153.37, 154.39 and 155.60 for aromatic carbons, 34.80, 32.30, 30.08, 30.07, 30.03, 29.97, 29.82, 29.74, 29.63, 29.48, 25.24, 23.07 and 14.49 for carbons in the alkyl chain (C₁₅H₃₁COO-).

The percentages of C, H and N from the elemental analysis agreed with the calculated values for compounds 6-9. The molecular ion peaks (M⁺) obtained from the mass spectrometry analyses were also in accordance with the theoretical values. The diagnostic bands observable via the IR analysis are characteristic of the structure properties of title compounds. All ¹H and ¹³C NMR data further support the identification of each molecule in CDCl₃ of which the assignment of peaks agree with the respective formulation of compounds 6-9.

RESULTS AND DISCUSSION

Phase Transition Behaviour and Liquid Crystallinity of *N*-[4-(4-*n*-hexadecanoyloxybenzoyloxy)benzylidene]-4-cyano-, 4-hydroxy-, 4-thio- and 4-nitroanilines

The phase transitions temperatures, associated enthalpy (*H*) and associated entropy (*S*) values of all the title compounds are summarized in Table 1. First, it should be mentioned that all of the phase transition temperatures evaluated on the basis of texture change is in good accord with those measured by DSC. Enthalpy values of the various transitions agree well with the existing related literature values (Yeap *et al.* 2006c) which in fact has helped in further confirmation of the mesophase type. From Table 1, it is clearly shown that upon heating all compounds exhibit endotherms characteristic of the crystal-mesophase and mesophase-isotropic transitions at temperature greater than melting temperature (T_m) except compound 8. For compound 8, direct melting from crystal-to-isotropic phase was observed under crossed polarizer. No other mesophases upon heating were observed under crossed polarizer and even the supercooling of compound 8 failed to show the emergence of a monotropic mesophase.

Table 1: Transition Temperatures, Associated Enthalpy and Entropy Changes of Compounds 6-9

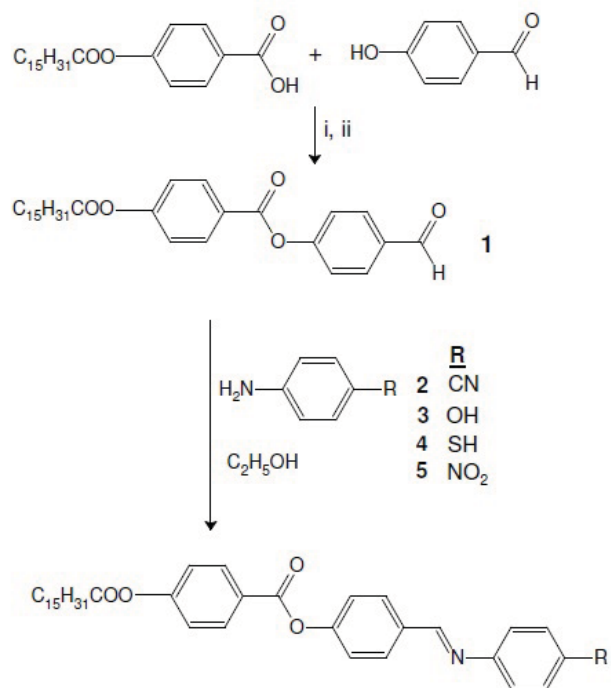
Compound	Transition	T /°C	ΔH/kJ mol ⁻¹	ΔS/(10 ⁻³) kJ K ⁻¹ mol ⁻¹
6	Cr ₁ -Cr ₂	55.4	36.2	110.2
	Cr ₂ -SmA	105.2	10.5	27.8
	SmA-I	218.5	2.1	4.3
7	Cr ₁ -Cr ₂	138.0	8.5	20.7
	Cr ₂ -N	151.0	20.1	47.0
	N-I	206.8	0.9	1.9
8	Cr-I	189.3 ^a	-	-
9	Cr-N	95.7	43.2	117.2
	N-I	215.1 ^a	-	-

^aPolarized optical microscopy data

Cr1 and Cr2, crystal; SmA, smectic A; N, nematic; I, isotropic.

Surprisingly for compound 6, while cooling slowly from isotropic phase the SmA phase grows as filaments which coalesce to form a focal-conic fan texture on further cooling. The appearance of enantiotropic SmA phase is found to be in conformity with its analogue *o*-*n*-hydroxy-*p*-*n*-hexadecanoyloxybenzylidene-*p*-cyanoanilines (16-CN) as that reported earlier (Yeap *et al.* 2006b). Fig. 1a shows the filament growth pattern

appearing below the isotropic. The filaments grow in length but not in diameter. During this growth process, the filaments buckle quasi-continuously, leading to a snake-like appearance. Of course these filaments are metastable, and eventually coalesce to focal-conic domains (Fig. 1b). Naito *et al.* (1997) have developed a theory in which the filamentary structure is regarded as a smectic A tube, consisting of concentric cylindrical smectic layers. This theory explains our observations, namely that the growth has strong temperature dependence during the cooling process, and that once the filaments have grown straight to a certain length (called the threshold length in the theory) buckling occurs. The filamentary growth is generally seen for binary/ternary mixtures (Pratibha and Madhusudana 1992, Adamczyk 1995), although as here, Arora *et al.* (1989) and Yelamagad *et al.* (2003) have reported it in a single component. It is possible that this type of growth is observed when the system has a 'structural degrees of freedom' (as in mixtures) or 'configurational degrees of freedom' (as in the present system). In the cyano compounds, there is a strong tendency to form an antiparallel dimer due to a strong dipole-dipole interaction and form bilayer arrangements of smectic A phase (Yeap *et al.* 2002, Gray and Goodby 1984). The presence of bilayer arrangements in compound **6** probably induced the filamentary structure wherein each cyano group in a pair is located close to the opposite end of its neighbour wherein the dimerization occurs by interaction of two cyano groups. The lateral interaction between one cyano group of a molecule with another cyano group of another molecule is probably weak. Thus, the intermolecular bonding formed between two cyano groups is very flexible and hence, the filament (or tube) formed from the dimerization will buckle freely leading to a snake-like appearance.



Scheme 1: Synthetic routes towards the formation of intermediates and target compounds **6-9**. Reagent and conditions: (i) SOCl_2 , reflux for 3 hours; (ii) anhydrous CH_2Cl_2 , DMF, $(\text{C}_2\text{H}_5)_3\text{N}$, N_2 atmosphere, reflux for 5 hours.

Observation under POM upon compounds **7** and **9** during melting process exhibit schlieren threaded or marble texture typical of a nematic phase. Figure 2 shows the representative optical photomicrograph of compound **7** exhibiting nematic phase. Compound **7** also showed an endotherm in the DSC thermogram (Table 1) before the crystal-nematic transition at 138°C . The texture observed under the polarizing microscope is indicative of the presence of subphases within the crystal phase ($\text{Cr}_1\text{-Cr}_2$) which resembles the phenomena reported in our recent finding on *ortho*-hydroxy-*para*-hexadecanoyloxybenzylidene-*para*-substituted anilines (Yeap *et al.* 2004, 2006b). The crystal subphases ($\text{Cr}_1\text{-Cr}_2$) was also observed in compound **6**.

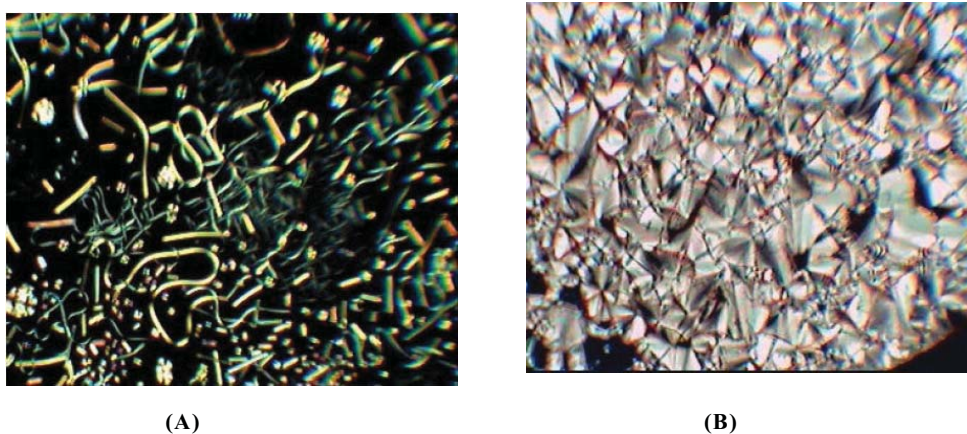


Fig. 1: (a) Optical photomicrograph of the filaments texture observed at 213°C at a cooling rate of 0.1°C min⁻¹ of the SmA phase developing from the isotropic phase, for compound **6**. (b) Optical photomicrograph of compound **6** exhibiting SmA phase with focal-conic fan texture.

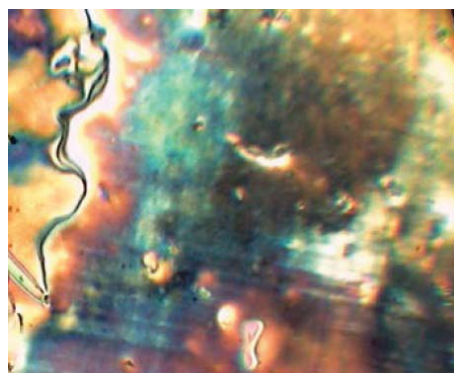


Fig. 2: Optical photomicrograph of compound **7** exhibiting nematic phase.

The mesomorphic properties of compounds **6-9** were compared with the analogue compounds, *o*-*n*-hydroxy-*p*-*n*-hexadecanoyloxybenzylidene-*X*-substituted anilines (**16-X**), in which *X* is the substituent of CN, OH, SH and NO₂ (Yeap *et al.* 2006b). Compounds **6-9** are found to be different from those reported analogue compounds owing to the presence of an additional aromatic ring joined to the benzylideneaniline core system via ester bond. As such, it has been presumed to change the characteristic of the benzylideneaniline skeleton whereby the molecule increases with little or no change in the width. These two factors allow an increase in the anisotropy of the molecule. Thus, the polarizability of the molecules in compounds **6-9** is expected to rise. This has also been confirmed by the polarizability values wherein the calculated polarizability (Table 2) of compound **6**, **7**, **8** and **9** are higher than those values reported in the series of **16-X** of which **16-CN** [(56.92 ± 0.5) × 10⁻²⁴ cm³], **16-OH** [(54.67 ± 0.5) × 10⁻²⁴ cm³], **16-SH** [(57.24 ± 0.5) × 10⁻²⁴ cm³] and **16-NO₂** [(56.58 ± 0.5) × 10⁻²⁴ cm³], respectively. As a consequence, the clearing temperature of compounds **6-9** is comparatively higher than those values reported for the analogue compounds.

Table 2: Polarizability (calculated value) for Compounds 6-9

Compound	Polarizability ($a \pm 0.5 \times 10^{-24} \text{ cm}^3$)
6	69.25
7	67.00
8	69.57
9	68.91

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