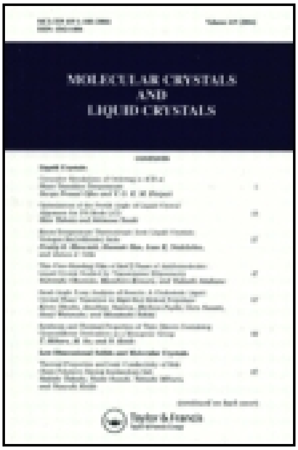

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Nematic and Smectic a Phases in Ortho-Hydroxy-Para-Hexadecanoyloxbenzylidene-Para-Substituted Anilines

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Nemantic and Smectic a Phases in *Ortho*-Hydroxy-*Para*-Hexadecanoyloxbenzylidene-*Para*-Substituted Anilines

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Four Schiff base esters containing the different substituents of R=CN, OH, SH, and NO_2 were synthesized, and the physical characterization was carried out along with spectroscopic techniques (FT-IR and NMR). Thermal properties were analyzed by using differential scanning calometry (DSC), and their liquid crystal textures were observed under polarized optical microscope. All compounds thus obtained exhibit mesomorphic properties of which the alignment of molecules are inclined to either nematic, N (R=SH), or smectic, SmA (for R=CN, OH, and NO_2). The unidentifiable subphases in crystal region were recorded in all compounds except that with R=OH. The presence of a lateral hydroxyl group has been claimed to contribute to the enhanced molecular ordering, leading to a higher clearing temperature.

Keywords: clearing temperature; molecular ordering; *ortho*-hydroxy-*para*-hexadecanoyloxybenzylidene-*para*-substituted anilines; Schiff base esters; thermal stability

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INTRODUCTION

A considerable number of Schiff bases derived from salicyaldehyde have been reported in the past few decades because they can give rise to either thermochromism or photochromism in the solid state [1,2]. Studies on these photochromic compounds have increased ever since the potential applications of photochromic materials emerged in various areas such as the control and measurement of radiation intensity and in optical computer and display systems. In view of the importance and the usefulness of these compounds, chemists were prompted to generate the derivatives by introducing different substituents into the existing molecular system. The presence of an *ortho* hydroxyl group, for instance, has been regarded as one of the important elements favoring the existence of intramolecular hydrogen bonding ($O{-}H\cdots N$ and $O\cdots H{-}N$) and also the tautomerism that accounts for the formation of either enol-imino or keto-amino tautomer [3].

In our recent study, a series of *p*-n-octadecanoyloxybenzylidene-*p*-substituted anilines has been isolated from the reactions of stearic acid and various *p*-n-hydroxybenzylidene-*p*-substituted anilines [4,5]. The attempt to form this series of Schiff base esters has been initiated by using the anilines containing *p*–CN, *p*–OH, *p*–NO_2, and *p*–COOH. Subsequent to this study, the Schiff base esters obtained from the reaction of palmitic acid with a series of the analogous anilines possessing substituents R=H, F, Cl, Br, OCH_3, CH_3, and C_2H_5 have been carried out, of which the reactions led to the formation of mesogens showing SmA (where X=H, F, Cl, Br and OCH_3) and SmC phases (where R=CH_3 and C_2H_5) [6].

To accomplish the investigation of the mesomorphism of the series consisting of palmitic acid as the elongated tail, we continued with the other substituents (*p*–CN, *p*–OH, *p*–NO_2, and *p*-SH) positioned along the molecular long axis. The molecular structure of the title compounds were characterized by elemental analysis, mass spectrometry, Fourier transformed infrared spectroscopy (FT-IR), and NMR techniques. Their liquid crystal properties were investigated by using differential scanning calorimetry (DSC) and polarized optical microscopy (POM).

EXPERIMENTAL

4-Aminophenol, 4-aminobenzonitrile, 4-aminothiophenol, and 4-dimethylaminopyridine (DMAP) were obtained from Merck (Germany). Dicyclohexylcarbodiimide (DCC) was purchased from

TABLE 1 Phase Transitions and Transition Enthalpy Changes for Compounds **6–9** upon Heating and Cooling

Compounds	Phase transitions, C (corresponding enthalpy changes, kJmol^{-1})	Heating Cooling
6	Cr$_1$ 59 (21) Cr$_2$ 81 (29) SmA 140 (7) I	
	I 141 (6) SmA 57 (28) Cr	
7	Cr 149 (66) I	
	I 135 (6) SmA 118 (49) Cr	
8	Cr$_1$ 95 (2) Cr$_2$ 111 (60) I	
	I 111 (2) N98 (24) Cr$_2$ 82 (2) Cr$_1$	
9	Cr$_1$ 52 (4) Cr$_2$ 88 (38) SmA 140 (4) I	
	I 139 (4) SmA 49 (26) Cr$_2$ 29 (3) Cr$_1$	

Note: Cr, Cr$_1$, Cr$_2$, crystal; SmA, smectic A; N, nematic; I, isotropic.

Fluka Chemie (Switzerland). 2,4-Dihydroxybenzaldehyde was purchased from Acros Organics (USA); 4-nitroaniline was obtained from Riedel-de Haen (Germany). Palmitic acid used in this research was provided by Acidchem International Sdn. Bhd. (Malaysia). The purity of the palmitic acid is approximately 99%.

The melting points of the synthesized compounds were measured on Gallenkamp melting-point apparatus. Analytical data were performed on 2400 LS series CHNS/O analyzers. Electron impact mass spectra (EI-MS) were recorded by using Hewlett Packard 5989 A mass spectrometer operating at 70-eV ionizing energy. Samples were introduced by using a direct inlet system with a source temperature of 200°C. IR data were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer in the frequency range 4000–400 cm^{-1} with samples embedded in KBr discs. NMR spectra were recorded in $CDCl_3$ at 298 K on a Bruker 400-MHz Ultrashield spectrometer equipped with a 5-mm broad band inverse (BBI) inverse gradient probe. Chemical shifts were referenced to internal TMS. Thin-layer chromatography analyses were performed by using aluminium-backed silica-gel plates (Merck 60 F524) and examined under short-wave UV light.

The phase-transition temperatures were measured using a Shimadzu DSC-50 at heating and cooling rates of 5°C min^{-1} and -5°C min^{-1}, respectively. The DSC data are shown in Table 1. The optical microscopy studies were carried out with a Carl Zeiss polarizing microscope equipped with a Mettler FP52 hot stage. The textures of the compounds (Fig. 1) were observed using polarized light with crossed polarizers with the sample in thin film sandwiched between a glass slide and cover.

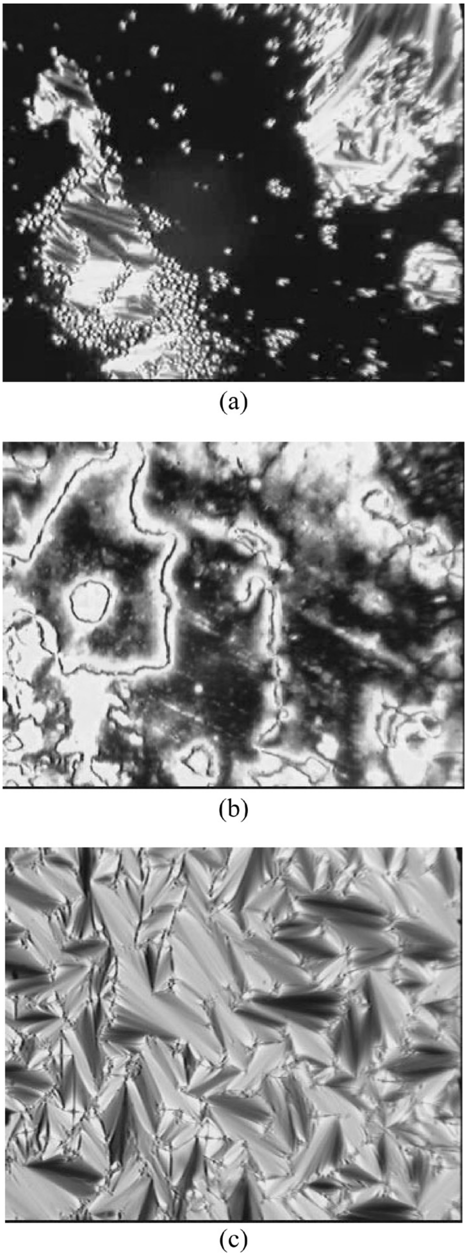


FIGURE 1 (a) Optical photomicrograph of compound **7** exhibiting smectic A with focal conic fan and homeotropic (dark area) textures; (b) optical photomicrograph of compound **8** exhibiting nematic phase with schlieren texture; (c) optical photomicrograph of **9** exhibiting smectic A with fan-shaped textures.

Synthesis

Synthesis of o*-n-Hydroxy-*p*-n-hexadecanoyloxybenzaldehyde, 1*

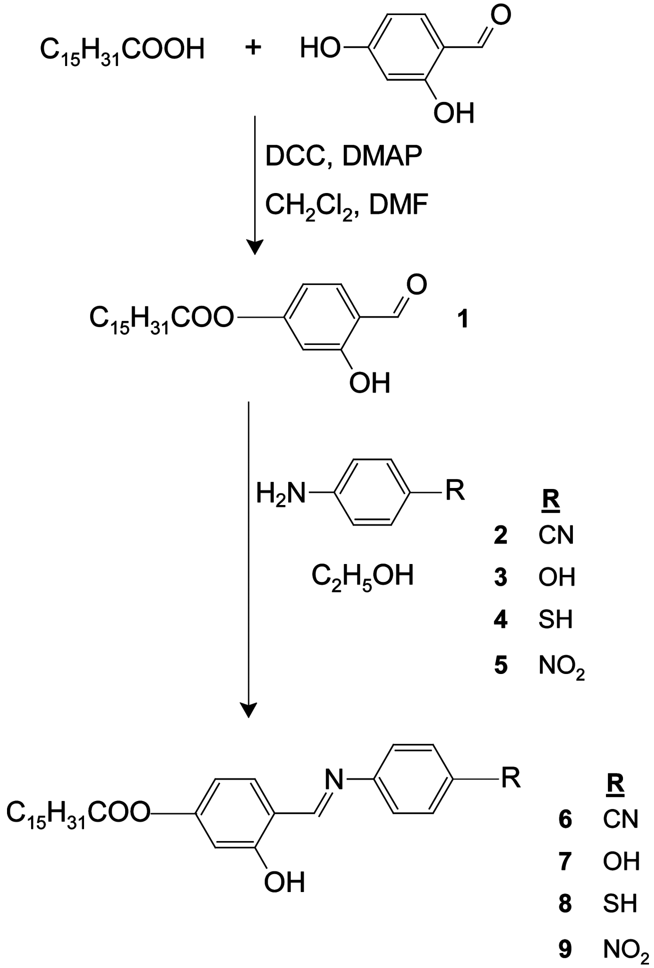
This compound was synthesized via modified reaction described by Sudhakar et. al. [7]. 2,4-Dihydroxybenzaldehyde (20 mmol), palmitic acid (20 mmol), and DMAP (2 mmol) were dissolved in a 60-mL mixture of dichloromethane (CH_2Cl_2) and dimethylformamide (DMF) and stirred at 0°C. To this solution, 20 mmol of DCC dissolved in 20 mL of CH_2Cl_2 was added dropwise, stirred at 0°C for 1 h, and then stirred at room temperature for 3 h. Finally, the reaction mixture was filtered, and CH_2Cl_2 was removed from the filtrate by evaporation. The grey solid thus obtained was recrystallized with n-hexane, whereupon the pure compound was formed. IR (KBr), 3441 cm^{-1} (OH), 2954, 2918, 2850 cm^{-1} (CH aliphatic), 1760 cm^{-1} (C=O ester), 1690 cm^{-1} (CHO).

Synthesis of Schiff Base Esters, 6–9

The Schiff bases were synthesized by mixing equimolar amounts of compound **1** with the appropriate aniline, both dissolved in absolute ethanol. The reaction mixture was refluxed for 3 h with stirring before it was filtered. The solvent was removed from the filtrate by evaporation. The yellowish crystals were obtained after being recrystallized with absolute ethanol. The entire synthetic route is outlined in Scheme 1. The title compounds were characterized by spectroscopic and elemental analysis data. The elemental analysis, selected mass spectrometric, IR, and NMR (^1H and ^{13}C) data are summarized as follows.

Compound **6**: Yield 22%. Found: C, 75.62; H, 8.45; N, 5.87. Cal. for $C_{30}H_{40}N_2O_3$; C, 75.59; H, 8.46; N, 5.88%. EI-MS m/z (rel. int. %): 476(1) $(M)^+$, 359(1), 280(1), 258(1), 240(3), 239(25), 238(100), 237(18), 228(1), 154(2), 136(6), 129(4), 127(1), 115(1), 111(2), 77(1), 76(3), 69(12), 57(40), 56(8), 55(36), 43(81). IR (KBr), 3426 cm^{-1} (OH), 2954, 2914, 2850 cm^{-1} (C–H aliphatic), 1765 cm^{-1} (C=O of ester), 1624 cm^{-1} (CH=N), 1599 cm^{-1} (C=C aromatic), 1279 cm^{-1} (C–O). ^1H NMR ($CDCl_3$), 0.88–0.92 ppm (CH_3), 1.28–2.61 ppm (CH_2), 6.75–7.75 ppm (Ar–H), 8.61 ppm (CH=N), 12.92 (OH). ^{13}C NMR ($CDCl_3$), 14.52 ppm (CH_3), 23.09–34.84 ppm (CH_2), 110.64–163.04 ppm (Ar–C), 164.47 ppm (C=N), 172.01 (C=O ester).

Compound **7**: Yield 45%. Found: C, 74.50; H, 8.81; N, 2.98. Cal. for $C_{29}H_{41}NO_4$; C, 74.48; H, 8.84; N, 3.00%. EI-MS m/z (rel. int. %): 467(2) $(M)^+$, 271(1), 240(1), 239(1), 231(3), 230(21), 229(100), 228(27), 154(1), 136(3), 129(1), 127(1), 115(1), 111(1), 77(1), 69(7), 57(18), 56(5), 55(19), 43(38). IR (KBr), 3460 cm^{-1} (OH), 2948, 2917, 2847 cm^{-1} (C–H aliphatic), 1739 cm^{-1} (C=O of ester), 1623 cm^{-1} (CH=N), 1600 cm^{-1} (C=C



SCHEME 1 Preparation of Schiff base esters **6–9.**

aromatic), 1272 cm^{-1} (C−O). ^{1}H NMR ($CDCl_3$), 0.90–0.93 ppm (CH_3), 1.31–2.60 ppm (CH_2), 6.69–7.34 ppm (Ar−H), 8.56 ppm (CH=N), 13.58 (OH). ^{13}C NMR ($CDCl_3$), 14.26 ppm (CH_3), 22.94–34.85 ppm (CH_2), 109.99–162.90 ppm (Ar-C), 159.96 ppm (C=N), 172.05 (C=O ester).

Compound **8**: Yield 37%. Found: C, 71.97; H, 8.57; N, 2.92. Cal. for $C_{29}H_{41}NO_3S$; C, 72.01; H, 8.54; N, 2.90%. EI-MS m/z (rel. int. %): 483(3) (M)$^+$, 257(1), 256(2), 247(7), 246(24), 245(100), 244(29), 228(13), 154(4), 136(14), 129(3), 127(3), 115(4), 111(5), 77(5), 69(17), 57(49), 56(15), 55(47), 43(99). IR (KBr), 3429 cm^{-1} (OH), 2951, 2917, 2848 cm^{-1}

(C$-$H aliphatic), 1758 cm^{-1} (C$=$O of ester), 1623 cm^{-1} (CH$=$N), 1609 cm^{-1} (C$=$C aromatic), 1275 cm^{-1} (C$-$O). ^{1}H NMR ($CDCl_3$), 0.90–0.94 ppm (CH_3), 1.26–2.59 ppm (CH_2), 3.50 ppm (SH), 6.71–7.37 ppm (Ar$-$H), 8.59 ppm (CH$=$N), 13.32 (OH). ^{13}C NMR ($CDCl_3$), 14.29 ppm (CH_3), 22.96–34.84 ppm (CH_2), 110.78–162.98 ppm (Ar$-$C), 161.63 ppm (C$=$N), 171.74 (C$=$O ester).

Compound **9**: Yield 20%. Found: C, 70.16; H, 8.14; N, 5.63. Cal. for $C_{29}H_{40}N_2O_5$; C, 70.13; H, 8.12; N, 5.64%. EI-MS m/z (rel. int. %): 496(1) $(M)^+$, 260(3), 259(23), 258(100), 257(8), 228(8), 154(4), 136(4), 129(3), 127(2), 115(2), 111(2), 77(3), 76(5), 69(13), 57(40), 56(9), 55(36), 43(79). IR (KBr), 3444 cm^{-1} (OH), 2952, 2921, 2850 cm^{-1} (C$-$H aliphatic), 1751 cm^{-1} (C$=$O of ester), 1621 cm^{-1} (CH$=$N), 1604 cm^{-1} (C$=$C aromatic), 1275 cm^{-1} (C$-$O). ^{1}H NMR ($CDCl_3$), 0.88–0.92 ppm (CH_3), 1.28–2.61 ppm (CH_2), 6.76–8.34 ppm (Ar$-$H), 8.64 ppm (CH$=$N), 12.85 (OH). ^{13}C NMR ($CDCl_3$), 14.51 ppm (CH_3), 23.08–34.84 ppm (CH_2), 111.10–163.11 ppm (Ar$-$C), 164.85 ppm (C$=$N), 171.98 (C$=$O ester).

The percentages of C, H, and N from the elemental analysis agree with the calculated values for compounds **6–9**. The molecular ion peaks obtained from the mass spectrometric analysis are also in accordance with the theoretical values. The diagnostic bands observable via the IR analysis are characteristic of the structure properties of title compounds including the presence of intermolecular hydrogen bonding between the lateral OH groups among the molecules. All ^{1}H and ^{13}C NMR data further support the identification of each molecule in $CDCl_3$ of which the assignment of peaks agree with the respective formulation of compounds **6–9**.

RESULTS AND DISCUSSION

Phase-Transition Behavior and Liquid Crystallinity of Compounds 6–9

Table 1 clearly shows that upon heating all compounds except compounds **7** and **8** exhibit endotherms, which can be attributed to the crystal–mesophase and mesophase–isotropic transitions at temperature higher than melting temperature (T_m). It is very clear that an endotherm appeared over heating cycle for compound **7** suggests a direct melting from crystal to isotropic phase. However, the thermogram of compound **8** has shown an endotherm before isotropization at 95°C. 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 [6]. Although the clearing points for compounds **6** and **9** represent the transition temperature of SmA-I, the clearing temperature observed for compound **7** at 149°C is merely for the crystal–isotropic phase transition. These phenomena could be ascribed to the increase of the melting point lying above the mesophase–isotropic liquid transition temperatures [8].

Table 1 also shows that upon cooling, all the compounds exhibit smectic phase except compound **8**. For compound **6**, **7**, and **9**, microscopy studies revealed that on cooling from the isotropic liquid, smectic batonnets were observed during the phase transition from the isotropic to the smectic phase. These batonnets disappeared and changed to a pseudo-isotropic texture (homeotropic alignment). This characteristic behavior of the microscopic textures indicates that the smectic phase observed for compounds **6**, **7**, and **9** can be identified as a smectic A [9]. As the representative illustration, the partial homeotropic alignment for smectic A phase is shown in Fig. 1a wherein the focal conic fan texture and homeotropic texture (dark area) were observed.

The appearance of enantiotropic smectic A phase in compound **6** is found to be in conformity with its analogue *p*-n-octadecanoyloxybenzylidene-*p*-cyanoaniline (**18B-CN**) as that reported earlier [4]. The presence of thermally stable mesomorphic Schiff base esters with the CN substituent can be ascribed to the ability of this compound to form bilayers as reported for the compounds with OH substituent [10]. One of the remarkable features is that the clearing temperature of compound **6** (140°C) is very much higher than that for the earlier reported compound **18B-CN** (107°C) on a heating run. This information indicates that the introduction of a hydroxyl group at the *ortho* position in the aldehyde fragment increases the degree of anisotropy of the molecular polarizability of compound **6** and hence increases the degree of molecular order, causing the smectic phase to be more stable [11].

For compound **7**, the monotropic smectic A observed under the polarized optical microscope is in agreement with the DSC data wherein direct melting (Cr-I) with high enthalpy changes (66 $\mathrm{kJmol^{-1}}$) was observed on the heating run. The small enthalpy changes associated with the mesophase–isotropic transition were not observed. The appearance of smectic A also conforms with its analogue 4-(4-n-hexadecyloxy-2-hydroxy-benzylideneamino)phenol as reported by Sakagami and Takase [12]. Although compound **7** has not shown any mesomorphic behavior during the heating cycle, it possesses the highest clearing point. The presence of thermally stable mesomorphic Schiff base esters with the OH substituent can be ascribed to the lateral intermolecular hydrogen bonding as that reported by Sakagami et al. [13] and Naoum et. al. [14]. The lateral intermolecular hydrogen bonding in compound **7** resulted in the formation of hydrogen bonding between the hydroxyl group and the carbonyl group as that inferred from the IR spectroscopy.

The observation on compound **8** confirms the monotropic feature wherein the schlieren texture (Fig. 1b) appeared during cooling cycle. This feature is characteristic of the nematic phase where the disclination points show 2-brush singularities ($s = \pm 1/2$) [9].

In the previous article, we had reported that the emergence of liquid crystalline properties of *p*-n-octadecanoyloxybenzylidene-*p*-nitroaniline (**18B-NO$_2$**) seemed to be suppressed during heating and cooling cycles [4]. However, the introduction of the lateral hydroxy group as reported for compound **9** has enhanced the mesomorphism of compound **9**, leading to a mesophase containing a fan-shaped texture which, can be classified as SmA phase (Fig. 1c). The smectic character of compound **9** is found to be similar to that reported in the literature [9].

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 compounds **6–9** wherein a comparison was made between the data of compounds **6–9** (Table 1) and their analogues *p*-n-octadecanoyloxybenzylidene-*p*-cyanoaniline (**18B-CN**), -*p*-hydroxyaniline (**18B-OH**) and -*p*-nitroaniline (**18B-NO$_2$**) [4]. The clearing temperature of compounds **6** (140°C), **7** (149°C), and **9** (135°C) are found to be higher than those for compounds **18B-CN** (107°C), **18B-OH** (125°C), and **18B-NO$_2$** (48°C), respectively.

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