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Synthesis, physical and mesomorphic properties of Schiff's base esters containing *ortho*-, *meta*- and *para*-substituents in benzylidene-4′-alkanoyloxyanilines

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Three series of Schiff's base esters, 2-hydroxy-4-methoxybenzylidene-4′-alkanoyloxyaniline, 2-hydroxy-3-methoxybenzylidene-4′-alkanoyloxyaniline and 3-methoxy-4-alkanoyloxybenzylidene-4′-alkanoyloxyaniline, which possess mono- and di-substituted moieties at both ends of the molecules have been synthesized and their mesomorphic properties investigated along with physical characterization (elemental analysis, mass spectrometry, Fourier transform IR and high resolution NMR). The effect of lateral methoxy and polar hydroxy groups on the mesomorphism of the title compounds was studied, based on the thermal properties and textural analysis. The results indicate that compounds with the larger number of carbons in the alkyl chain prefer smectic phase formation and possess higher transition temperatures and molecular polarizability along the long axis. Further analysis shows that the greater shielding effect (through the formation of intramolecular interaction) leads to lower molecular broadening and results in higher clearing points. Increase in melting point due to the lengthening of the alkyl chain is associated with the increase in van der Waals attraction between the molecules. These compounds exhibit nematic, smectic (SmA and SmC) phases depending on the type and position of the substituents.

1. Introduction

The mesomorphic behaviour of an organic compound is basically dependent on its molecular architecture in which a slight change in the molecular geometry brings about considerable change in its mesomorphic properties. Detailed studies by liquid crystal researchers have led to empirical rules which include the effect of chemical constitution in the nematogenic and smectogenic mesophases [1]. Most of these studies have been focused on Schiff's bases ever since the discovery of 4-methoxybenzylidene-4′-butylaniline (MBBA) which exhibits a room temperature nematic phase [2]. Over the past few decades, low molar mass Schiff's base esters have been investigated extensively. In these studies the influence of a terminal alkyl chain upon the liquid crystalline properties [3, 4] and the possibility of enhancing the rigidity of the Schiff's base core system through metal complexes formation [5–7] have been claimed as favourable pathways to improve the mesogenic properties.

We have recently reported the synthesis and mesomorphic properties of Schiff's base esters, *p*-*n*-octadecanoyloxybenzylidene-*p*-subtituted anilines [8] and *o*-*n*-hydroxy-*p*-*n*-hexadecanoyloxybenzylidene-*p*-subtituted anilines [9] derived from the esterification of fatty acids of palm oil with 4-hydroxybenzylideneanilines. The introduction of a lateral polar hydroxyl group into the aldehyde fragment has subsequently been studied and is known as an essential parameter leading to an increase in molecular polarizability as well as to an increase in the clearing temperature [9].

In order to explore further the factors which govern the thermal stability of liquid crystals with a Schiff's base core, and the relationship with its molecular structures, we are prompted to carry out the investigation in a more comprehensive manner wherein lateral methoxy and polar hydroxy groups are introduced into the aldehyde fragment of benzylideneaniline

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compounds through the preparation of the three new homologous series: 2-hydroxy-4-methoxybenzylidene-4′-alkanoyloxyaniline (series **A**), 2-hydroxy-3-methoxybenzylidene-4′-alkanoyloxyaniline (series **B**) and 3-methoxy-4-alkanoyloxybenzylidene-4′-alkanoyloxyaniline (series **C**). The molecular structures of the title compounds were characterized by elemental analysis, mass spectrometry, Fourier transform infrared spectroscopy (FTIR) and NMR techniques. Their liquid crystal properties were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

2. Experimental

2.1. *Characterization*

Structure identification of compounds of series **A**, **B** and **C** was established on the basis of elemental analysis, mass spectrometry and spectroscopic methods (IR and NMR). The elemental analyses of all the compounds were found to be satisfactory and are depicted in table 1. The molecular ion peak obtained from the experimental EI-MS data as shown in table 1 are in good agreement with the theoretical values. The results of IR and NMR spectral data of all the compounds were also found to be consistent with the proposed structure. The relevant IR and NMR data associated with the occurrence of diagnostic peaks and resonance in all the compounds are shown in the experimental section.

2.2. *Reagents and techniques*

4-Aminophenol and 4-dimethylaminopyridine (DMAP) were obtained from Merck (Germany). 2-Hydroxy-3-methoxybenzaldehye (*o*-vanilin) and 2-hydroxy-4-methoxybenzaldehdye were purchased from TCI Chemical Company (Japan). Dicyclohexylcarbodiimide (DCC) was purchased from Acros Organics (USA), and 3-methoxy-4-hydroxybenzaldehyde was obtained from Fluka Chemie (Switzerland). The lauric acid, myristic acid, palmitic acid and stearic acid used in this research were supplied by Acidchem International Sdn. Bhd. (Malaysia). The purity of the fatty acids was approximately 99%.

Analytical data were obtained on 2400 LS series CHNS/O analysers. Electron impact mass spectra (EI-MS) were recorded on a Hewlett Packard 5989A mass spectrometer operating at 70 eV ionizing energy. Samples were introduced using a direct inlet system with a source temperature of 200°C. IR data were recorded on a Perkin Elmer 2000-FTIR spectrophotometer in the frequency range 4 000–400 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 BBI inverse gradient probe. Thin layer chromatography analyses were perfomed using aluminium backed silica gel plates (Merck 60 F254) and were examined under short wave UV light. Liquid crystalline properties were investigated by polarizing optical microscopy (POM) using a Carl Zeiss polarizing microscope equipped with a Mettler FP52 hot stage. The enthalpies of transitions reported as J g^{-1} were determined from thermograms obtained on a Shimadzu DSC-50, with a scanning rate of $2°\text{C min}^{-1}$.

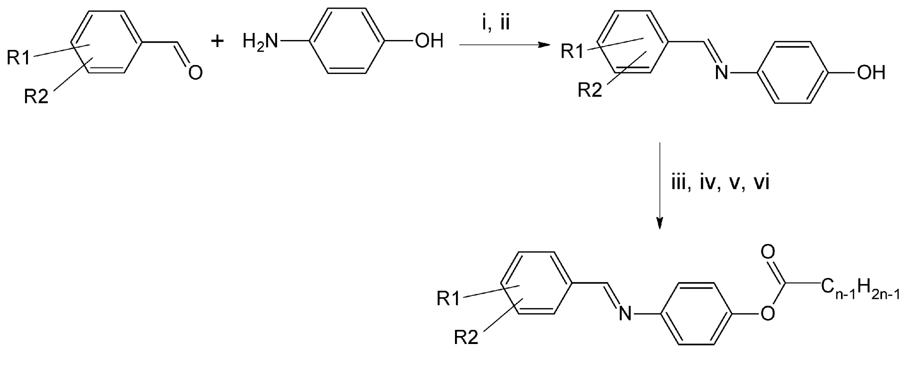
The synthetic route for the formation of series **A**, **B** and **C** compounds is summarized in scheme 1.

2.3. *Preparation of series A compounds*

2-Hydroxy-4-methoxybenzylidene-4′-hydroxyaniline was prepared by mixing equimolar amounts of 2-hydroxy-4-methoxybenzaldehyde and 4-aminophenol (50 mmol

Table 1. Physical data of compounds of series **A**, **B** and **C**.

Compound	Formula	Molecular mass	M^+(relative intensity %)	% Required (% found) C	H	N
A12	$C_{26}H_{35}NO_4$	425.56	425.60(4)	73.38 (73.45)	8.29 (8.25)	3.29 (3.35)
A14	$C_{28}H_{39}NO_4$	453.61	453.65(5)	74.14 (74.11)	8.67 (8.70)	3.09 (3.13)
A16	$C_{30}H_{43}NO_4$	481.66	481.65 (3)	74.81 (74.87)	9.00 (8.96)	2.91 (2.97)
A18	$C_{32}H_{47}NO_4$	509.72	509.80 (1)	75.40 (75.42)	9.29 (9.35)	2.75 (2.78)
B12	$C_{26}H_{35}NO_4$	425.56	425.25 (28)	73.38 (73.42)	8.29 (8.31)	3.29 (3.30)
B14	$C_{28}H_{39}NO_4$	453.61	453.30 (11)	74.14 (74.08)	8.67 (8.66)	3.09 (3.05)
B16	$C_{30}H_{43}NO_4$	481.66	481.35 (10)	74.81 (74.78)	9.00 (9.02)	2.91 (2.95)
B18	$C_{32}H_{47}NO_4$	509.72	509.50 (5)	75.40 (75.36)	9.29 (9.30)	2.75 (2.74)
C12	$C_{38}H_{57}NO_5$	607.86	608.75 (<1)	75.08 (74.95)	9.45 (9.52)	2.30 (2.37)
C14	$C_{42}H_{65}NO_5$	663.97	664.75 (<1)	75.97 (76.06)	9.87 (9.81)	2.11 (2.13)
C16	$C_{46}H_{73}NO_5$	720.08	720.90 (<1)	76.73 (76.75)	10.22 (10.15)	1.95 (1.97)
C18	$C_{50}H_{81}NO_5$	776.18	777.10 (<1)	77.37 (77.29)	10.52 (10.57)	1.80 (1.83)



where n = 12, 14, 16 and 18

Compounds	**R1**	**R2**
An	2-OH	4-OCH_3
Bn	2-OH	3-OCH_3
Cn	3-OCH_3	4-$C_{n-1}H_{2n-1}COO$-

Scheme 1. The synthesis of series **A**, **B** and **C**. Reagents and conditions, (i) absolute C_2H_5OH, (ii) reflux 5 h, (iii) CH_2Cl_2, (iv) DCC and DMAP, (v) $C_{n\text{-}1}H_{2n\text{-}1}COOH$, (vi) stir at room temperature for 3 h.

each), both dissolved in 70 ml absolute ethanol. The reaction mixture was heated under reflux for 5 h and the precipitate formed on cooling to room temperature (300 K) was filtered. The solid residue was recrystallized from absolute ethanol.

The purified 2-hydroxy-4-methoxybenzylidene-4′-hydroxyaniline (20 mmol), lauric acid (20 mmol) and DMAP (2 mmol) were dissolved in 60 ml of dichloromethane and the mixture stirred at 0°C. To this solution, 20 mmol of DCC dissolved in 20 ml of dichloromethane was added dropwise while stirring at 0°C for 1 h, and then stirring at room temperature for another 3 h. Finally, the mixture was filtered and excess solvent was removed from the filtrate by evaporation. The yellow solid (compound **A12**) thus obtained was recrystallized from ethanol until the transition temperatures remained constant. The other compounds of series **A**, including **A14**, **A16** and **A18** were prepared using the same procedure as described for compound **A12**, replacing the lauric acid by myristic acid, palmitic acid and stearic acid, respectively (scheme 1). The elemental analysis and EI-MS data of all the compounds are listed in table 1. The IR, ^{1}H and ^{13}C NMR spectral data of compound **A12**, given below, are typical for all series **A** compounds.

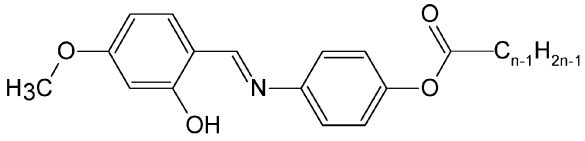
A12: Yield 54%. IR (KBr) (cm^{-1}): 3476 (OH), 2954, 2918, 2850 (C–H aliphatic), 1747 (C=O of ester), 1626 (C=N), 1596 (C=C aromatic). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.90–0.94 (t, 3H, $-CH_3$), 1.25–1.46 (m, 16H, $-CH_2-$), 1.75–1.82 (quintet, 2H, $-OOC-CH_2-C\underline{H}_2-$), 2.56–2.60 (t, 2H, $-OOC-C\underline{H}_2-$), 3.85 (s, 3H, $-OCH_3$), 6.49–6.53 (m, 2H, Ar–H), 7.12–7.15 (m, 2H, Ar–H), 7.24–7.28 (m, 3H, Ar–H), 8.51 (s, 1H, CH=N), 13.59 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ (ppm) 14.47 ($-CH_3$), 23.06–34.78 ($-CH_2-$), 55.80 ($-OCH_3$), 101.53, 107.54, 113.53, 122.20, 122.82, 133.97, 146.49, 149.58, 164.19, 164.48 (Ar–C), 162.02 (C=N), 172.62 (C=O of ester).

2.4. *Preparation of series B compounds*

Compounds of series **B** were prepared following the same scheme as described for series **A** (scheme 1). The elemental analysis and EI-MS data of all the compounds are listed in table 1. The IR, ^{1}H and ^{13}C NMR spectral data of compound **B12**, given below, are typical for all series **B** compounds.

B12: Yield 65%. IR (KBr) (cm^{-1}): 3435 (OH), 2954, 2917, 2849 (C–H aliphatic), 1756 (C=O of ester), 1614 (C=N), 1595 (C=C aromatic). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.82–0.92 (t, 3H, $-CH_3$), 1.22–1.45 (m, 16H, $-CH_2-$), 1.74–1.82 (quintet, 2H, $-OOC-CH_2-C\underline{H}_2-$), 2.52–2.59 (t, 2H, $-OOC-C\underline{H}_2-$), 3.93 (s, 3H, $-OCH_3$), 6.86–6.90 (t, 1H, Ar–H), 6.98–7.03 (m, 1H, Ar–H), 7.00 (s, 1H, Ar–H), 7.13–7.16 (m, 2H, Ar–H), 7.27–7.31 (m, 2H, Ar–H), 8.60 (s, 1H, CH=N), 13.56 ppm (s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.53 ($-CH_3$), 23.09–34.77 ($-CH_2-$), 56.58 ($-OCH_3$), 115.29, 119.00, 119.46, 122.46, 122.94, 124.25, 146.10, 148.86, 150.00, 151.75 (Ar–C), 163.11 (C=N), 172.66 (C=O of ester).

Table 2. Transition temperature (°C) and associated enthalpy changes (J g^{-1}, in parentheses) of series **A** upon heating and cooling. The values in *italics* are taken during cooling. Cr=crystal; SmA=smectic A; N=nematic; I=isotropic.



where n =12, 14, 16 and 18

Compound	Cr	→	SmA	→	N	→	I
A12	•	96.8 (93.9)	—	—	•	110.7 (2.2)	•
	•	*93.9* (*93.9*)	—	—	•	*110.4* (*2.7*)	•
A14	•	99.9 (105.7)	—	—	•	109.3 (2.6)	•
	•	90.9 (114.2)	—	—	•	*108.9* (*3.1*)	•
A16	•	102.8 (114.2)	—	—	•	108.1 (3.9)	•
	•	*96.9* (*126.3*)	—	—	•	*107.1* (*4.1*)	•
A18	•	105.2 (142.2)	•	106.4[a]	•	107.0[a]	•
	•	*95.0* (*140.0*)	•	*106.5* (*8.2*)	•	*106.8*[a]	•

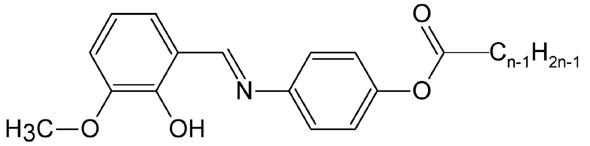
[a] POM data

2.5. *Preparation of series C compounds*

Compounds of series **C** were prepared by similar methods to those described for compounds of series **A** and **B** (scheme 1), except that double amounts of DMAP (4 mmol), DCC (40 mmol) and fatty acid (40 mmol) were used for series **C**. The elemental analysis and EI-MS data of all the series **C** compounds are listed in table 1. The IR, ^{1}H and ^{13}C NMR spectral data of compound **C12**, given below, are typical for all series **C** compounds.

C12: Yield 44%. IR (KBr) (cm^{-1}): 2954, 2919, 2850 (C–H aliphatic), 1752 (C=O of ester), 1626 (C=N), 1600 (C=C aromatic). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.88–0.93 (t, 6H, $-CH_3$), 1.24–1.43 (m, 32H, $-CH_2-$), 1.73–1.85 (quintet, 4H, $-OOC-CH_2-C\underline{H}_2-$), 2.56–2.62 (m, 4H, $-OOC-C\underline{H}_2-$), 3.94 (s, 3H, $-OCH_3$), 7.11–7.16 (m, 3H, Ar–H), 7.22–7.25 (d, 2H, Ar–H), 7.34–7.37 (dd, 1H, Ar–H), 7.68 (d, 1H, Ar–H), 8.41 (s, 1H, CH=N). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.49 ($-CH_3$), 23.07–34.82 ($-CH_2-$), 56.43 ($-OCH_3$), 110.99, 122.11, 122.61, 123.42, 123.53, 135.34, 143.13, 149.36, 149.79, 152.13 (Ar–C), 159.89 (C=N), 171.94 (C=O of ester), 172.79 (C=O of ester).

Table 3. Transition temperature (°C) and associated enthalpy changes (J g^{-1}, in parentheses) of series **B** upon heating and cooling. The values in *italics* are taken during cooling. Cr=crystal; I=isotropic.



where n = 12, 14, 16 and 18

Compound	Cr	→	I
B12	•	72.2 (96.4)	•
	•	*63.4* (*103.6*)	•
B14	•	82.1 (108.6)	•
	•	*77.8* (*108.9*)	•
B16	•	83.1 (115.2)	•
	•	*81.3* (*116.4*)	•
B18	•	85.6 (121.8)	•
	•	*83.9* (*122.2*)	•

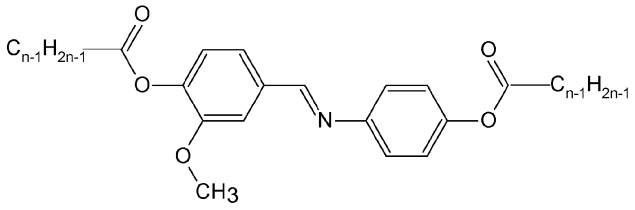
3. Results and discussion

The phase transition temperatures and associated enthalpy changes obtained from DSC analysis over heating and cooling cycles for compounds in series **A**, **B** and **C** are given in tables 2, 3 and 4, respectively.

3.1. *Series A (2-Hydroxy-4-methoxybenzylidene-4′-alkanoyloxyanilines)*

From table 2, it is clear that upon heating, all the compounds exhibit endotherms characteristic of the crystal–mesophase and mesophase–isotropic transitions at temperatures greater than the melting temperature (T_m). Observation by POM during heating and cooling showed the presence of the nematic phase in all the compounds. A representative optical photomicrograph of compound **A16** exhibiting the nematic phase with schlieren texture is shown in figure 1 (*a*). For the compound with the highest number of carbons in the alkyl chain (**A18**), an additional phase with fan-shaped texture, figure 1 (*b*), was observed after the formation of

Table 4. Transition temperatures (°C) and associated enthalpy changes (Jg^{-1}, in parentheses) of series **C** upon heating and cooling. The values in *italics* are taken during cooling. Cr_1, Cr_2, crystal; SmC, smectic C; I, isotropic.



where n = 12, 14, 16, 18

Compound	Cr_1	→	Cr_2	→	SmC	→	I
C12	•	23.0 (32.8)	•	57.9 (57.5)	—	—	•
	•	*27.0 (37.3)*	—	—	•	*54.1 (13.5)*	•
C14	•	33.8 (8.9)	•	64.5 (96.9)	—	—	•
	•	*38.1 (14.2)*	•	*42.8 (50.2)*	•	*61.6 (18.6)*	•
C16	•	47.6 (10.1)	•	68.4 (103.1)	—	—	•
	•	*54.5 (77.9)*	—	—	•	*64.5 (18.6)*	•
C18	•	60.1 (6.2)	•	73.4 (114.4)	—	—	•
	•	*63.2 (93.7)*	—	—	•	*66.2 (21.4)*	•

the nematic phase on the cooling run. This feature is characteristic of the SmA phase owing to the formation of batonets that coalesce to form the fan-shaped texture.

3.2. *Series B (2-Hydroxy-3-methoxybenzylidene-4′-alkanoyloxyanilines)*

All the derivatives of the series are non-mesogenic. Even the supercooling of these compounds failed to produce a monotropic mesophase. These results indicate that the introduction of the lateral methoxy substituent at the *meta*-position in series **B** compounds is unfavourable for the formation of mesophases, in contrast to series **A** with the methoxy substituent at the *para*-position. One of the probable reasons is that the lateral methoxy substituent at the *meta*-position exerts a molecular broadening influence, reducing the lateral intermolecular force of attraction and thus impeding liquid crystal formation [10].

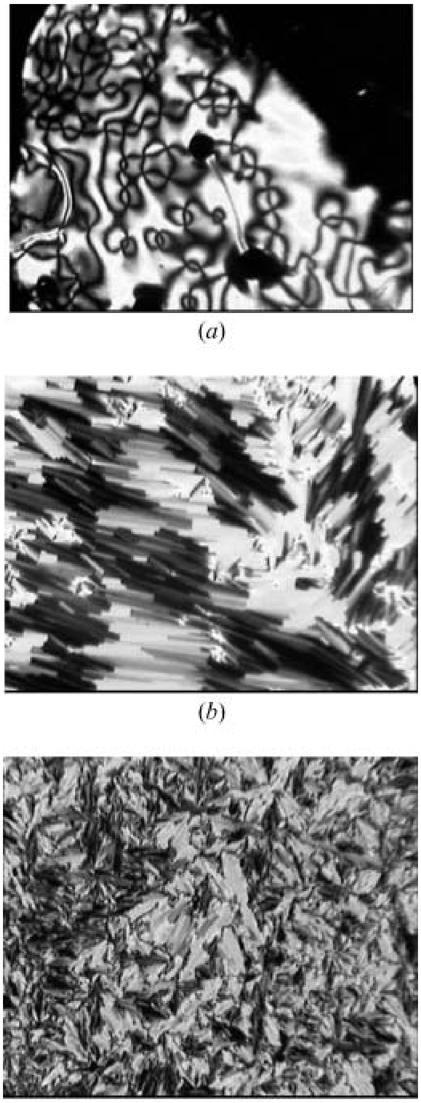
3.3. *Series C (3-Methoxy-4-alkanoyloxybenzylidene-4′-alkanoyloxyanilines)*

The DSC thermograms of compounds **C12**, **C14**, **C16** and **C18** each show an endotherm before isotropization at 23.0, 33.8, 47.6 and 60.1°C, respectively. The texture observed by POM indicates the presence of subphases within the crystal phase (Cr_1–Cr_2), similar to phenomena observed for isoflavone derivatives [11] and other reported Schiff's base esters [9]. It can be inferred from table 4 that the liquid crystal phase was only observed on supercooling, with isotropic–mesophase transitions at 54.1, 61.6, 64.5 and 66.2°C. POM on compounds **C12**, **C14**, **C16** and **C18** confirmed the monotropic feature wherein the SmC phase appeared with broken fan-shaped texture. The smectic character of these compounds was found to be similar to that reported in the literature [12]. As a representative illustration, the optical photomicrograph of compound **C12**, exhibiting the SmC phase with broken fan-shaped texture during cooling is shown in figure 1 (*c*).

3.4. *Influence of structural changes on the mesomorphism of Schiff's base derivatives*

As the number of carbons in the alkyl chain increases from $n=12$ to $n=18$, the clearing temperature decreases following the order: **A12**, $T_c=110.7$°C>**A14**, $T_c=109.3$°C>**A16**, $T_c=108.1$°C>**A18**, $T_c=107.0$°C. The decrease in the clearing temperature is attributed to the dilution of the core induced by the increasing length of the terminal alkyl chain [13]. However, the dilution effect of the core system did not apply to series **B** and **C** compounds, as their clearing temperatures increase as the length of terminal alkyl chain increases. One similarity in the molecular structures of series **B** and **C**, which might give rise to this effect, is the presence of the methoxy group at the *meta*-position of the aldehyde fragment, instead of at the *para*-position of the series **A** compounds. A comparison of the clearing temperatures for the homologous series **A**, **B** and **C** is shown figure 2.

Inspection of the clearing temperatures has also revealed a correlation between the influence of the lateral polar hydroxy group in the series **A**, **B** and **C** (tables 2–4 and figure 2). Figure 2 clearly shows that



(*a*)

(*b*)

(*c*)

Figure 1. (*a*) Optical photomicrograph of compound **A16** exhibiting nematic phase with *schlieren* texture during cooling cycle. (*b*) Optical photomicrograph of compound **A18** exhibiting smectic A fan-shaped texture with narrow and elongated ellipses during cooling cycle. (*c*) Optical photomicrograph of **C12** showing smectic C with broken fan-shaped texture during cooling cycle.

compounds with the *ortho*-hydroxy group (series **A** and **B**) possess higher clearing temperatures than compounds without the *ortho*-hydroxy group (series **C**). There are also compounds in which the lateral substituents are shielded, so that they are less effective in molecular broadening [14]. The compounds of series **A** and **B** may give rise to shielding effects owing to the presence of intramolecular association [7] and hence the polarizability along the long axis of molecule will be larger in such compounds than in unsubstituted analogue [9]. This results in higher clearing temperatures than the corresponding compound without an *ortho*-hydroxy group.

A comparison among the compounds possessing the *ortho*-hydroxy group (series **A** and **B**) revealed that the clearing temperatures of compounds **B12** (72.2°C), **B14** (82.1°C), **B16** (83.1°C) and **B18** (85.6°C) during the heating cycle are lower than those found in the corresponding **A12** (110.7°C), **A14** (109.3°C), **A16** (108.1°C) and **A18** (107.0°C), respectively. This indicates that the lateral methoxy substituent at the *meta*-position in the aldehyde fragment causes a significant supression in the clearing point in comparison with the compounds containing the *para*-methoxy substituent [10].

Another remarkable feature is the melting points of compounds in the series **A** and **C** which increase as the length of alkyl chain increases (figure 2). This could be attributed to the increase of van der Waals attraction as the alkyl chain of these compounds ($O–C=O–C_{n\text{-}1}H_{2n\text{-}1}$) increases from 12 to 14, 16 and 18 [15].

For compounds **A12**, **A14**, **A16** and **A18**, the nematic phase range during heating (table 2) decreases in the order **A12** (13.9°C)>**A14** (9.4°C)>**A16** (5.3°C)>**A18** (0.6°C). This indicates that as the length of the terminal chain increases, the nematic properties decrease, leading to the emergence of the smectic phase. This is due to attraction betweem the long alkyl chains leading to their intertwining, which facilitates the lamellar packing and is essential for the smectic phase. The smectic characteristic was absent in compounds **A12**, **A14** and **A16**, but present in compound **A18** which possesses the longest alkyl chain. It can therefore be proposed that in order to generate the smectic phase in the analogous substituted $C_6H_5CH=NC_6H_5$ compounds, the number of carbons in the alkyl chain ($C_{n\text{-}1}H_{2n\text{-}1}COO–$) must be at least 18 ($n \geqslant 18$).

The compounds of series **C** are specially designed to generate stable smectic compounds; two alkyl side chains are introduced into series **C**, instead of the one alkyl side chain in series **A** and **B**. As can be seen in table 4 and figure 1 (*c*), the smectic phase was present for each compounds of series **C**. All the series **C** compounds exhibited a tilted SmC phase instead of the non-tilted SmA phase found in compound **A18**. In series **C**, the compounds possess two carbonyl groups ($C=O$) in comparison with only one $C=O$ in series **A**. For series **C** compounds, the extra lateral dipolar moment associated with two carbonyl group favours the intermolecular interaction which gives rise to a tilted arrangement of the molecules in the smectic layers [16].

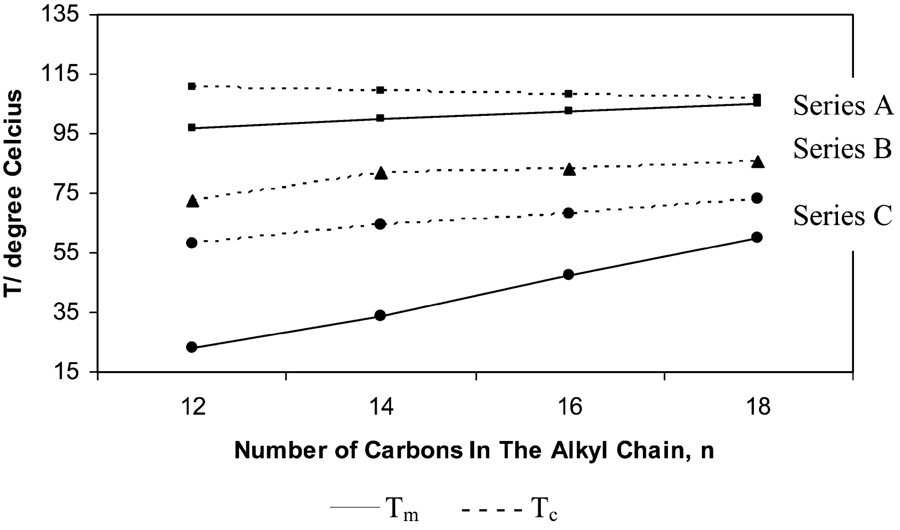


Figure 2. Comparison of the melting (T_m) and clearing temperatures (T_c) for the homologous series **A**, **B** and **C** as a function of number of carbons (n) in the alkyl chain.

4. Conclusion

The present study on mesogenic homologous series (**A**, **B** and **C**) containing a Schiff's base core with lateral methoxy and hydroxy groups indicates that the molecular broadening caused by the *meta*-methoxy group in the aldehyde fragment of 2-hydroxy-3-methoxybenzalidene-4′-alkanoyloxyanilines (series **B**) suppresses the thermal stabilities of mesophases in this series, leading to the formation of non-mesogenic materials. The introduction of the carbon side chain at the *para* position in the aldehyde fragment, and thus the increase of molecular length–breadth ratio, seemed to outweigh the broadening effect caused by the *meta*-methoxy group. In order to generate a smectic phase (SmA or SmC) in the analogous substituted $C_6H_5CH{=}NC_6H_5$ compounds, the number of carbons in the terminal alkyl chain ($C_{n\text{-}1}H_{2n\text{-}1}COO$–) must be at least 18 ($n \geq 18$) of which all compounds in the homologous series **A** exhibited an enantiotropic N phase except for compound **A18** (with $n=18$) which exhibited an enantiotropic SmA phase. Compounds in the homologous series **C**, with both side chains (wherein $2n \geq 24$) along the long molecular axis, exhibited a monotropic SmC phase.

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