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Synthesis and study the liquid crystalline behaviors of double Schiff bases bearing ester linkage as a central core

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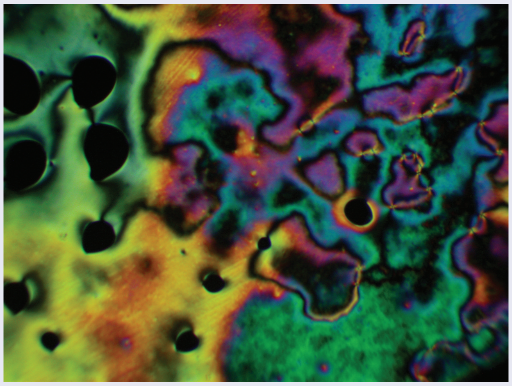
ABSTRACT

Two series of 12 homologues, 4-(((4-substituentphenyl)imino)methyl)phenyl 4-((4-(alkoxy) benzylidene)amino)benzoate (D_n, X = –OCH_3 and E_n, X = –-Br), have been synthesised. The two series have different alkoxy terminal chains (OC_nH2_n+1, n = 3, 4, 6, 7, 9, 12) on one side of their structures while other side in the series (D_n and E_n) was substituted by methoxy and Bromo group, respectively. The structures of the synthesised derivatives have been identified using Fourier transform infrared spectrometry (FT-IR) and nuclear magnetic resonance for H and C (^{1}H-NMR, ^{13}C-NMR) and the elemental analysis (CHN). The texture of liquid crystalline phases of the mesogens has been observed by optical polarised microscopy (OPM) while the details of the thermal transition of compounds were investigated by differential scanning calorimetry (DSC). The obtained liquid crystalline results showed that the derivatives of series (D_n) display a broad range of nematic mesophase (N) while the mesogens of (E_n) series appeared nematic and smectic mesophases. All the studied homologues show a wide range of liquid crystalline mesophases, the stability of mesomorphic behaviour of these compounds was dependent mainly on the length of terminal alkoxy chain (the number of carbon atoms) chain and the effect of substituent groups (OCH_3 and Br).



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Liquid crystals; Schiff bases; mesomorphic properties; ester linkage; imine linkage

1. Introduction

Since the discovery of the liquid crystalline materials by Friedrich Reinitzer in 1988, the goal of scientists has been how to get the best liquid crystalline properties of the compounds that have simple chemical structures with high ranges of these properties. Their goal is concentrated to find an appropriate relationship between the chemical composition of the mesogen and the properties it exhibits, so many researchers have developed the structure–property relation due to relating in many applications especially in the electro-optical fields [1–4]. Also, these materials were applied in different pharmaceutical applications due to increasing their stability and prolonged hydration as well as uses in controlled drug delivery [5]. Recently, the simple structures of the liquid crystals were used as a nano material to develop their application in electro-optical devices [6].

There are many types of LCs materials according to their molecular structure; thermotropic and lyotropic liquid crystals are the main groups of these materials [7,8]. The mesogen behaviours affected by different factors like the shape of molecules and the direction of linkages [9], the number of rings [10], length of terminal chains [11], and the type of terminal substituents [12],

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also the intermolecular interactions between the molecules have an essential influence in the formation of LCs mesophase [13], which is related to the responsibility of arranging the configuration of the mesogenic structure, these factors making the molecules are more rigid cores in calamitic LCs structures [14].

Schiff bases are compounds produced by the dehydration reaction between (C=O) group of aldehydes or ketones with an NH_2 group of amines, these derivatives containing (imine) group (CH=N or C=N), which can be used as a stabiliser, chelating agent, many applications in biological activities and photoconductive media. Also, the Schiff's base linkage is tremendously important in liquid crystal chemistry and has featured in a range of different structures leading to many discoveries of importance. The compounds containing imine linkage have an influential effect on the appearance of liquid crystalline mesophase, it can be seen in the literature many studies related to these compounds, which have been used in many medical and industrial uses [15–31].

Mostly, the design of mesogenic molecules that have linking units as multiple bonds like the imine or ester groups preserves the linearity, rigidity and maintains the conjugation across the structure of the molecules. As well, the presence of ester linkage together with imine groups in the same molecule leads to enhance mesophase stability of these mesogens [32–35]. Continuous to our previous studies in the liquid crystalline properties of different types of organic compounds [36–42], we study in this article the mesomorphic behaviours of new series of double Schiff bases derivatives that bearing ester linkage in the middle of the structure and methoxy and Bromo groups in the terminal side with different alkoxy terminals in the opposite end of the molecules. The data of the mesomorphic properties were studied and discussed the effect of the relation between the chemical structures of the synthesised molecules and their liquid crystalline behaviours.

2. Experimental

2.1. Materials

Ethanol (99.8%), 4-ansidine (99%), 4-hydroxybenzaldehyde (98%), glacial acetic acid (≥99%), sodium bicarbonate (≥99.7%), dichloromethane (≥99.8%), methanol (99.8%),4-bromoaniline (97%), 4-dimethylaminopyrdine (98%) and N,N'-dicyclohexylcarboiimide (99%) were supplied by Sigma-Aldrich. The compounds of 4-alkoxybenzaldehyde (A_n) and 4-((4-alkoxybenzylidene)amino) benzoic acid (B_n) were prepared and characterised previously by Abboud et al., these compounds were used as received without further purification [43].

2.2. Techniques

The nuclear magnetic resonance (^1H and ^{13}C) spectra were recorded on Bruker ultra-shield, 400.22 MHz for protons and 100.65 for carbons in ppm (δ), the DMSO-d_6 and $CDCl_3$ and were used as solvents for the prepared compounds. The Fourier-transform infrared FT-IR spectra were obtained with a Shimadzu spectrophotometer, type 8400S using the attenuated total reflectance (ATR) mode. The microanalytical analysis (C, H and N) for final products (D_n and E_n) was carried out on a Perkin-Elmer-2400 instrument. The thermal behaviours of the final mesogenic derivatives were studied by DSC, type DSC Q2000 in 10 °C/min upon the two cycle heating and cooling. The optical properties of the mesogens and their mesophase textures were investigated by using (PW-BK 5000 PR), built with (HS-400) hot stage.

2.3. Preparation methods for compounds (C–E_n)

2.3.1. Procedure for preparation the derivatives 4-(((4-methoxyphenyl)imino)methyl)phenol (C_{OCH3}) and 4-(((4-bromophenyl)imino)methyl)phenol (C_{Br})

An ethanolic solution (25 mL) of 4-hydroxybenzaldehyde (0.0179 mol, 2.196 g) with 10 drops of glacial AcOH as catalyst was added to (0.0179 mol) of amines solution in ethanol (10 mL), (2.214 g) of p-ansidine for prepared the compound (C_{OCH3}) and (3.096 g) of 4-bromoaniline for prepared the compound (C_{Br}). The alcoholic mixture has been refluxed for 6 h [44], the resulting product obtained by the filtration of the cold mixture then it was recrystallised from ethanol.

2.3.1.1. 4-(((4-methoxyphenyl)imino)methyl)phenol (C_{OCH3}).

Yield (90%); mp: 204–206°C; FT-IR (ATR), υ_{max} cm^{-1}: (3200–2350, broad O-H), (2918, 2839, C-H aliph.), (1604, CH=N); ^1H-NMR (400 MHz, $CDCl_3$), δ, ppm: 8.42 (s, 1H, CH=N), 7.80–7.82 (d, *J*= *8.68* ,=CH-ph, 2H, ArH), 7.21–7.24 (d, *J*= *9.04* , =N-ph, 2H, ArH), 6.94–6.96 (d, *J*= *7.08* , H_3CO-ph, 2H, ArH), 6.92–6.93 (d, *J*= *6.96* , ph-OH, 2H, ArH), 5.74 (s, 1H, -OH), 3.85 (s, 3H, -OCH_3).

2.3.1.2. 4-(((4-bromophenyl)imino)methyl)phenol (C_{Br}).

Yield (85%); mp: 190–192°C; FT-IR (ATR), υ_{max} cm^{-1}: (3190–2359, broad O-H), (2920, 2864, C-H aliph.), (1599, CH=N); ^1H-NMR (400 MHz, $CDCl_3$), δ, ppm: 8.37 (s, 1H, CH=N), 7.81–7.83 (d, *J*= *8.68* ,=CH-ph, 2 H, ArH), 7.50–7.52 (d, *J*= *8.80* ,=N-ph, 2H, ArH), 7.09–7.10 (d, *J*= *8.80* , Br-ph, 2H, ArH), 6.92–6.95 (d, *J*= *8.68* , ph-OH, 2H, ArH), 5.46 (s, 1H, -OH,).

2.3.2. Procedure for preparation of the derivatives 4-(((4-methoxyphenyl)imino)methyl)phenyl 4-((4-alkoxybenzylidene)amino)benzoate (D_n)

The derivatives of series (D_n) were prepared by the Steglich esterification approach that was reported by Tomi et al. [45]. The mixture of 4-((4-alkoxybenzylidene) amino)benzoic acid (B_n) (0.001 mol), 4-(((4-methoxyphenyl)imino)methyl)phenol (C_{OCH3}) (0.001 mol, 0.227 g), 4-dimethylamino pyridine (DMAP) (0.001 mol, 0.122 g) and N,N'-dicyclohexylcarboiimide (DCC) (0.001 mol, 0.206 g), was stirred at room temperature in 30 mL of dichloromethane for 5 days. The precipitated by-product of dicyclohexylurea (DCU) removed by filtration then the filtrate washed in a separation funnel with 15 mL of 5% aqueous AcOH, then with 15 mL of 5% $NaHCO_3$ solution and finally with 20 mL of distilled water. The extracted organic layer has been evaporated from the solvent (DCM) to give the esters (D_n). The final products were purified by recrystallisation from methanol. Below is the characteristic data of a representative derivative (D_3) of this series, see the data of all compounds of the series in the supplementary information section.

2.3.2.1. 4-(((4-methoxyphenyl)imino)methyl)phenyl 4-((4-propoxybenzylidene)amino)benzoate (D_3). Yield (55%); FT-IR (ATR), υ_{max} cm^{-1}: (2939, 2877, C-H aliph.), (1247, 1159, C–O–C asym. and sym.), (1735, C=O), (1622, CH=N); ^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm: 8.52 (s, 1H, N=CH), 8.41 (s, 1H, CH=N), 8.25–8.27 (d, *J* = 8.55 Hz, O=C-ph, 2H, ArH), 7.98–8.01 (d, *J*= 8.68 Hz,=CH-ph, 2H, ArH), 7.88–7.90 (d, *J* =8.92Hz, =CH-ph, 2H, ArH), 7.36–7.38 (d, *J* = 8.68 Hz, ph-O-C, 2H, ArH), 7.28–7.30 (d, *J* = 6.72Hz, ph-N=, 2H, ArH), 7.26–7.28 (d, *J* = 5.75 Hz, ph-N=, 2H, ArH), 7.01–7.03 (d, *J* = 8.80 Hz, ph-alkoxy, 2H, ArH), 6.96–6.98 (d, *J* = 8.80 Hz, H_3CO-ph, 2H, ArH), 4.02–4.05 (t, 2H, OCH_2), 3.87 (s, 3H, -OCH_3), 1.85–1.92 (m, 2H, CH_2), 1.08–1.11 (t, 3H, CH_3); Elemental analysis: for $C_{31}H_{28}N_2O_4$ (492.57 g/mol) calculated: C, 75.59; H, 5.73; N, 5.69, found: C, 75.68; H, 5.88; N, 5.75.

2.3.3. Procedure for preparation of the derivatives 4-(((4-bromophenyl)imino)methyl)phenyl 4-((4-(alkoxy)benzylidene)amino) benzoate (E_n)

These derivatives have been prepared by the same procedure for the series (D_n) using 4-(((4-bromophenyl)imino)methyl)phenol (C_{Br}), (0.001 mol, 0.277 g) instead of the compound (C_{OCH3}). Below, is the characteristic data of a representative derivative (E_3) of this series, see the data of all compounds of the series in the supplementary information section.

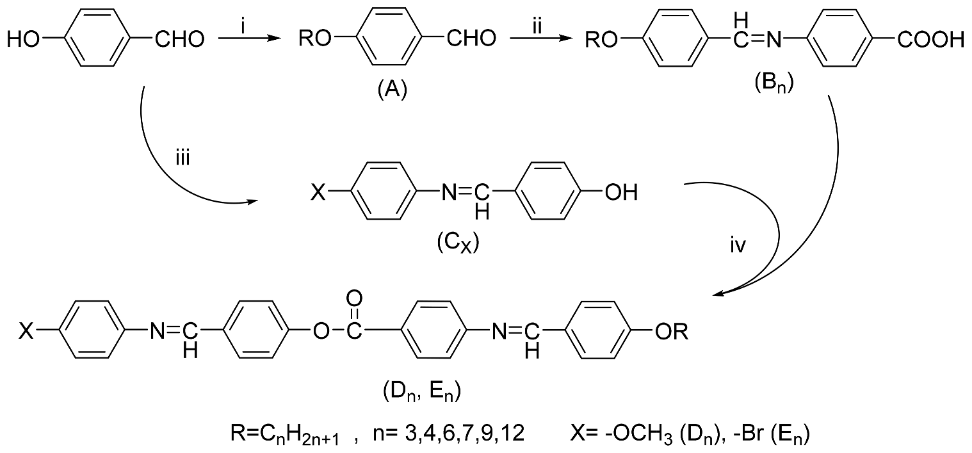
2.3.3.1. 4-(((4-bromophenyl)imino)methyl)phenyl 4-((4-propoxybenzylidene)amino)benzoate (E_3). Yield (47%); FT-IR (ATR), υ_{max} cm^{-1}: (2972, 2872, C-H aliph.), (1253, 1165, C–O–C asym. and sym.), (1718, C=O), (1627, CH=N); ^{1}H-NMR (400 MHz, $CDCl_3$), δ, ppm: 8.66 (s, 1H, N=CH), 8.53 (s, 1H, CH=N), 8.18–8.20 (d, *J*= 7.81 Hz, O=C-ph, 2H, ArH), 8.04–8.07 (d, *J*= 8.55 Hz,=CH-ph, 2H, ArH), 7.92–7.94 (d, *J*= 8.68 Hz, =CH-ph, 2H, ArH), 7.60–7.62 (d, *J*= 9.14 Hz, ph-O-C, 2H, ArH), 7.47–7.49 (d, *J*= 8.06 Hz, ph-N=, 2H, ArH), 7.39–7.41 (d, *J*= 8.19 Hz, ph-N=, 2H, ArH), 7.25–7.27 (d, *J*= 8.43 Hz, Br-ph, 2H, ArH), 7.09–7.11 (d, *J*= 8.32 Hz, ph-alkoxy, 2H, ArH), 4.05–4.08 (t, 2H, OCH_2), 1.73–1.81 (m, 2H, CH_2), 0.98–1.02 (t, 3H, CH_3); Elemental analysis: for $C_{30}H_{25}BrN_2O_3$ (540.10 g/mol) calculated: C, 66.55; H, 4.65; N, 5.17, found: C, 66.61, H, 4.71, N, 5.22.

3. Results and discussion

3.1. Synthesis

The synthetic route for preparing the compounds of the series (D_n) and (E_n) is described in Scheme 1. The first precursors of Schiff bases (B_n) have been prepared by the condensation reaction between 4-alkoxybenzaldehyde (A_n) and 4-aminobenzoic acid in an acidic medium. On the other hand, the other precursors of Schiff bases (C_{OCH3}, C_{Br}) were prepared by the reaction of 4-hydroxybenzaldyde with p-ansidine and 4-bromoanilie, respectively. According to the results of ^{1}H-NMR and FT-IR spectroscopies for the compounds (C_x), the singlet signal at (8.42) and (8.37) ppm in ^{1}H-NMR and the peak around (1604 cm^{-1}) and (1599 cm^{-1}) for compounds C_{OCH3} and C_{Br} respectively in FT-IR spectra corresponded to the stretching vibration of the imine bond (CH=N), the appearance of these signals in the ^{1}H-NMR and FT-IR spectra were good index about formation these compounds (C_x).

The final step in Scheme 1 conducted by condensation the compounds (B_n) with (C_x) using the Steglich esterification method in the presence of DMAP as a catalyst and DCC as a condensation agent in dry dichloromethane at room temperature to obtain the final esters (D_n) and (E_n) with yields in about 47–60%. The chemical structure of these compounds was identified by FT-IR, ^{1}H and ^{13}C-NMR; also, their chemical compositions were checked by elemental analysis. The FT-IR spectra show a strong sharp stretching peak between 1718 and 1737 cm^{-1} that refer to a (C=O) group for the ester compounds in the derivatives (D_n) and (E_n), also the FT-IR charts. Figure S1 shows an obvious increase in the extent of (C-H) stretching



Scheme 1. Reactions and reagents: (i) K_2CO_3, DMF, n-alkyl halides; (ii) 4-aminobenzoic acid, 1,4-dioxane, glacial acetic acid; (iii) ethanol, glacial acetic acid, (p-ansidine for C_{OCH3} and 4-bromoaniline for C_{Br}); (iv) DCC, DMAP, DCM.

bands. These signals were clear evidence for a successful coupling reaction between compounds (B_n) and (C_x). Furthermore, The (^1H) nuclear magnetic resonance spectrum of these series showed a presence of two singlet signals corresponding to the two imine groups, the new doublet of doublet signals for aromatic protons of new benzene rings and the signals of aliphatic protons corresponding to alkoxy chains in the tail of these derivatives (D_n) and (E_n). In addition to the above results, the obtained results of the elemental analyses and ^{13}C-NMR signals were good provident to elucidate the chemical structure of these esters (see experimental part). Figure S2 shows some examples of ^1H-NMR and ^{13}C-NMR spectra for the final products.

3.2. *Optical properties*

The liquid crystalline behaviours for the final esters (D_n) and (E_n) were examined by (OPM) observations and (DSC) experiments, all the derivatives of the series (D_n) which has X = –OCH_3 shown a liquid crystalline mesophase with nematic phase, while the esters of the series (E_n), which has X = –Br shown a nematic and smectic mesophases. The temperatures used in the DSC technique did not rise to near the isotropic points of esters to avoid the slight decomposition observed in the (OPM) near their melting points. So, due to these observations, the transition from (LC) phase to the isotropic point for these two series did not register in the (DSC) thermograms.

The LCs properties of the precursors (B_3, B_4, B_6, B_7, B_9 and B_{12}) were used in this work have been studied by Abboud et al. [43]. The results showed that all of these Schiff bases have liquid crystalline properties due to their molecular polarity and the geometry of the molecules. These compounds showed a mesomorphic tendency at a high isotropic temperature of about (230–280°C) in the heating scan depending on the longitude of the alkoxy group, also, the mesomorphic range of these imines was recorded between 70 and 100°C. When compared these results with the mesomorphic behaviour of the derivatives synthesised in this study, it was found that the mesomorphic ranges of the imine-esters in the current study were more than those registered for the imines prepared previously. The increase in the liquid crystalline ranges for the derivatives in the current study (D_n an E_n) is due to the influence of the added the second imine moiety and the ester linkage in their chemical structures which caused a decrease in the melting points of these compounds compared to the presence of carboxylic group in the chemical structure of the acids (F_1–F_{11}) [43]. Also, the presence of ester linkage makes the molecule more polarity and polarisability which lead to an increase in the range of mesophase [35], these newly added linkages (imine and ester) in addition to the phenyl ring were an effect of increasing the conjugation along with the molecules which

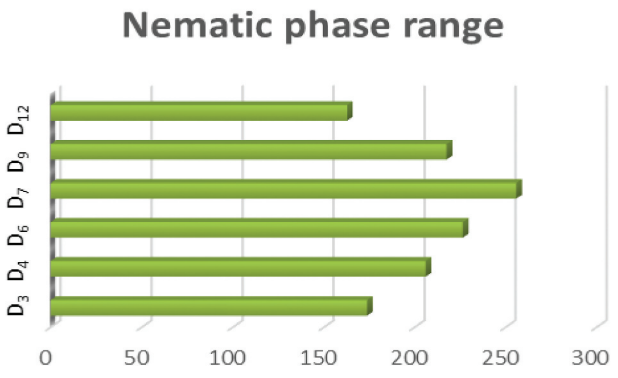


Figure 1. (Colour online) The range of Nematic phase for the mesogens in series D_n.

Table 1. Phase transition temperatures (T, °C), phase transition enthalpy changes (ΔH, kJ mol^{-1}), entropies (ΔS, J mol^{-1} K^{-1}), and the LCs mesophase range (T, °C) of the compounds (D_n) in first heating and cooling cycles from DSC\ examination.

Symbols	Phase transitions T (°C) (ΔH, kJ mol^{-1}) (ΔS, J mol^{-1} K^{-1}) on first heating	Phase transitions T (°C) (ΔH, kJ mol^{-1}) (ΔS, J mol^{-1}K^{-1}) on first cooling	LCs mesophase range (T, °C)
D_3	Cr-N 143.47 (33.97) [81.46] N-I 316[a]	-	172.53
D_4	Cr_1-Cr_2 124.07 (5.97) [15.04] Cr_2-N 140.91 (25.26) [61.01] N-I 347[a]	I-Cr_3 164.31 (−2.26) [−5.17] Cr_3-Cr_4 98.09 (−2.06) [−5.54] Cr_4-Cr_5 56.42 (−3.04) [−9.23]	206.09
D_6	Cr_1-Cr_2 104.61 (1.69) [4.47] Cr_2-Cr_3 132.47 (4.97) [12.25] Cr_3-N 143.44 (11.63) [27.91] N-I 370[a]	I-Cr_4 157.79 (−0.83) [−1.93] Cr_4-Cr_5 12 (−2.30) [−5.81] Cr_5-Cr_6 109.34 (−3.55) [−9.27] Cr_6-Cr_7 59.70 (−3.20) [−9.61]	226.55
D_7	Cr_1-N 105.12 (28.40) [75.08] N-I 361[a]	I-Cr_2 56.5 (−19.30) [−58.56]	255.88
D_9	Cr_1-N 124.365 (39.48) [99.31] N-I 342[a]	I-Cr_2 58.19 (−15.03) [−45.36]	217.63
D_{12}	Cr_1-Cr_2 101.91 (11.18) [29.81] Cr_2-N 121.495 (26.97) [68.33] N-I 284.405 (0.71) [0.31]	I-Cr_3 82.665 (−11.33) [−31.84] Cr_3-Cr_4 74.125 (−1.29) [−3.73]	162.91

Abbreviations: Cr_{1-7}, = crystal phases; N = nematic phase; I = isotropic phase; (a) = observed only on OPM.

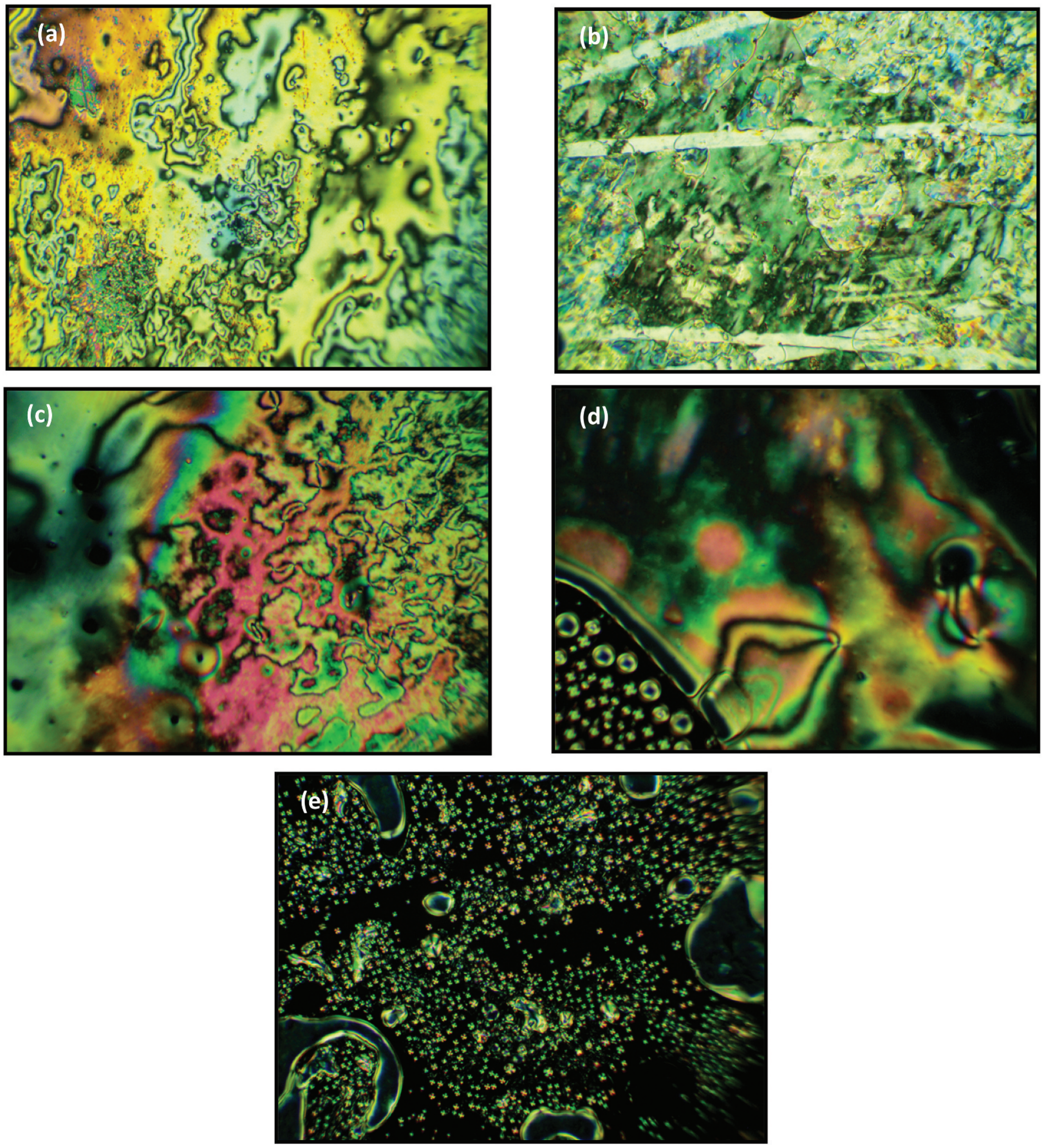


Figure 2. (Colour online) (a) The transition from crystal to Schlieren texture of nematic phase for compound (D_3) on first heating 280°C; (b) Schlieren texture of Nematic phase for compound (D_6) on first heating at 298°C; (c) Schlieren texture of Nematic phase for compound (D_9) on first heating at 317°C; (d) Schlieren texture of Nematic phase for compound (D_{12}) on first heating at 260°C; (e) Nematic texture for compound (D_{12}) on first heating at 304°C.

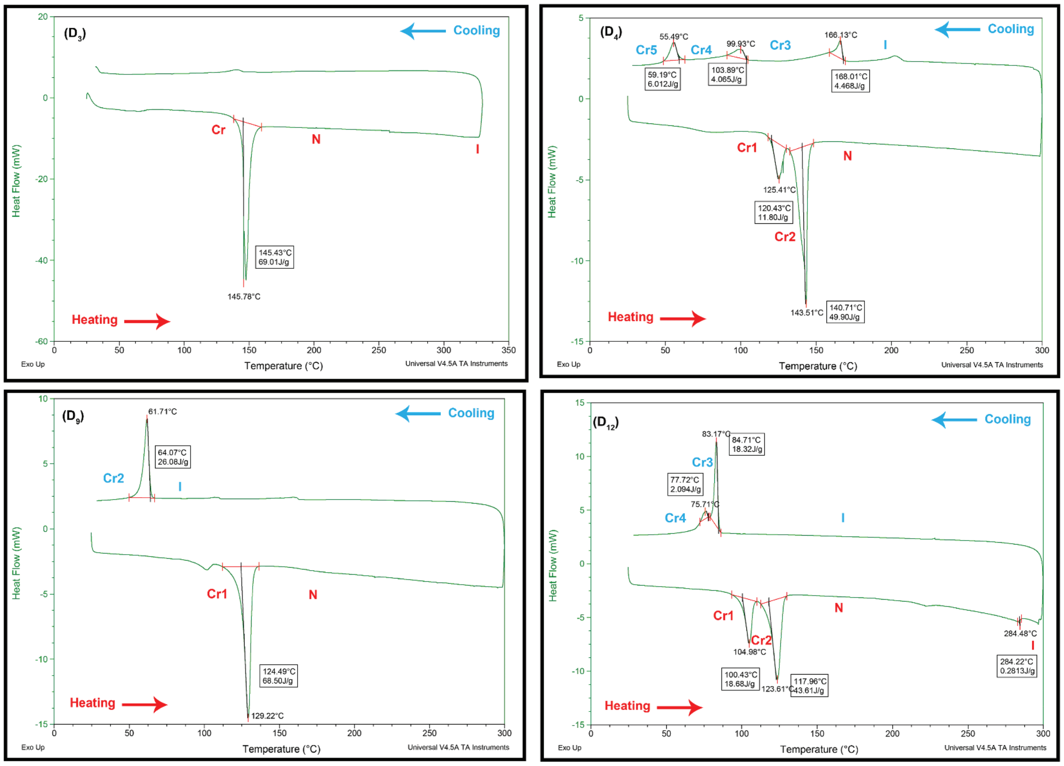


Figure 3. (Colour online) The DSC thermographs for compounds (D_3, D_4, $D_{9,}$ and D_{12}).

influenced on the liquid crystalline ranges of these compounds. Mostly, the mesophase properties of the rod-like mesogen are mainly affected by molecular-molecular interactions that rely on the geometry of molecules and the type of polar substituents [46].

3.2.1. *Optical properties of series (D_n)*

In the first heating cycle of the (DSC) experiments for All derivatives of (D_n), the (Cr_1–N) peak has been shown, also, an additional peak in only two compounds in this series (D_4, D_6) were shown which correspond to (Cr_1–Cr_2) transition. This series shows a high range of mesophase where it is increased with the increasing the length of alkoxy group except the compounds (D_9, D_{12}), which show a slight decrease in the nematic mesophase range as shown in Figure 1. The substituent of a strong electron-donating group (-OCH_3) on the para-position in the terminal phenyl group plays a pivotal role in the consistence of the N phase [47]. The details of temperatures (T, °C), enthalpy changes (ΔH, kJ mol^{-1}), entropies (ΔS, J mol^{-1} K^{-1}), and the LCs mesophase range (T, °C) of all homologues in series (D_n) are illustrated in Table 1. The mesophase textures of the (OPM) images at certain temperatures for compounds in this series are in agreement with the data collected from DSC. The selected photomicrographs from OPM are illustrated in Figures 2 and 3, respectively.

3.2.2. *Optical properties for series (E_n)*

The six derivatives of the (E_n) series show two mesomorphism textures with nematic and smectic phases, some textures as examples of mesophases observed through OPM have been illustrated in Figures 4 and 5, respectively, which agreed with the transition data collected from DSC. The mesomorphic behaviour of this series differs from the previous series (D_n) in the appearance of the smectic phase (SmA and SmC), this variation is due to the presence of polar group (–Br) that cause increasing the molecular polarity and play a considerable role in the stability of the mesophase [33]. All data obtained from DSC: temperatures, enthalpy changes, entropies and LCs mesophase range for all compounds in series

E_n are summarised in Table 2.

The effect of terminal chain length for the alkoxy group on the stability of mesophase has been shown in Figure 6. It can be seen from this chart that the range of the transition (N-I) was decreased gradually from (n = 7), this behaviour was confirmed and discussed by Imrie et al. [48]. Otherwise, increasing a terminal

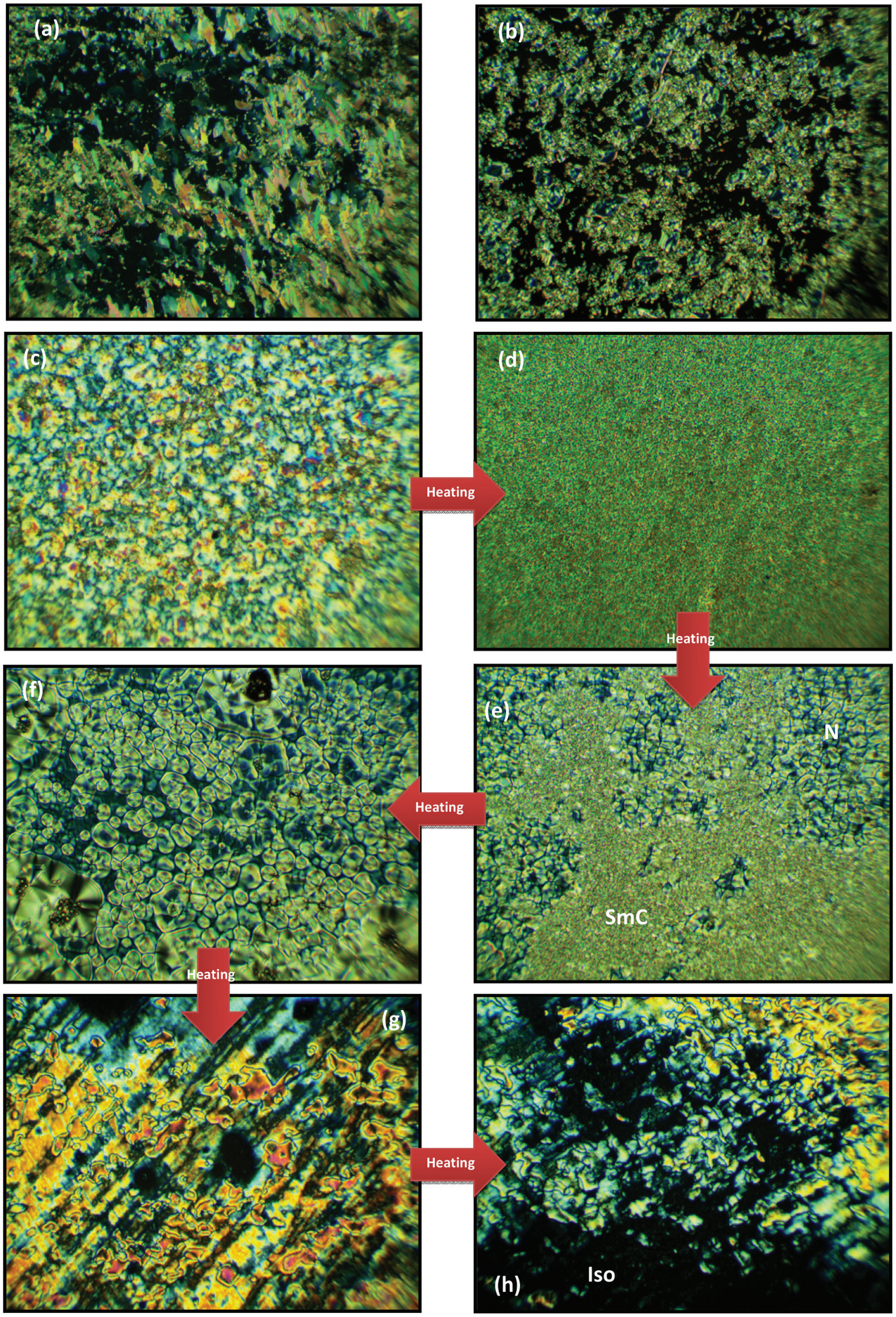


Figure 4. (Colour online) (a) SmA texture of compound (E_4) on first heating 154°C; (b) Nematic texture of compound (E_{12}) on first heating at 184°C, phase transitions from crystal to isotropic point for compound (E_9) on first heating: (c) Crystal texture at room temperature; (d) SmC texture at 155°C; (e) the transition from SmC to Nematic texture at 247°C; (f) Nematic texture at 265°C; (g) the formation of Nematic Schlieren texture at 270°C; (h) the transition from Schlieren texture of Nematic to isotropic phase at 273°C.

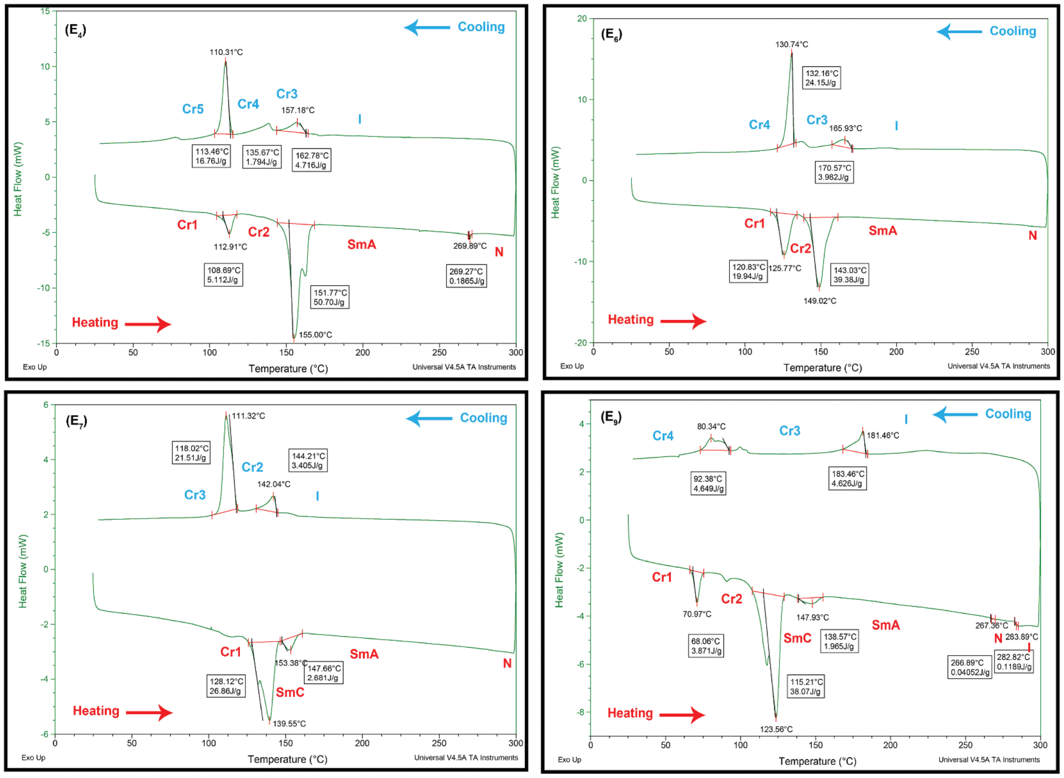


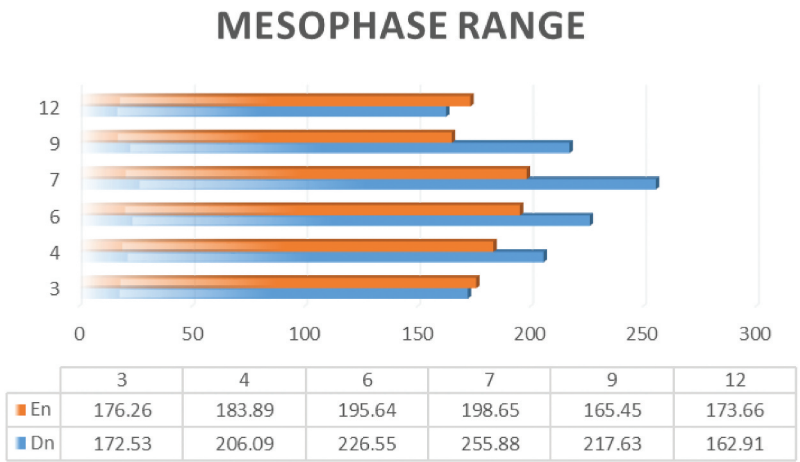
Figure 5. (Colour online) DSC thermographs of compounds (E_4, E_6, $E_{7,}$ and E_9).

Table 2. Phase transition temperatures (T, °C), phase transition enthalpy changes (ΔH, kJmol^{-1}), entropies (ΔS, J mol^{-1} K^{-1}), and the LCs mesophase range (T, °C) of the compounds (E_n) in first heating and cooling cycles from DSC examination.

Symbols	Phase transitions T (°C) (ΔH, kJ mol^{-1}) (ΔS, J mol^{-1}K^{-1}) on first heating	Phase transitions T (°C) (ΔH, kJ mol^{-1}) (ΔS, J mol^{-1}K^{-1}) on first cooling	LCs mesophase range (T, °C)
E_3	Cr-SmA 153.74 (27.83) [65.20] SmA-I 330^a		176.26
E_4	Cr_1-Cr_2 111.195 (2.83) [7.37] Cr_2-SmA 156.105 (28.09) [65.45] SmA-N 270.05 (0.1) [0.19] N-I 340^a	I-Cr_3 154.58 (−2.61) [−6.11] Cr_3-Cr_4 135.67 (−0.99) [−2.43] Cr_4-Cr_5 109.17 (−9.29) [−24.29]	183.89
E_6	Cr_1-Cr_2 125.88 (11.61) [29.09] Cr_2-SmA 150.36 (22.93) [54.13] SmA-N 281^a N-I 323^a	I-Cr_3 164.03 (−2.32) [−5.30] Cr_3-Cr_4 127.23 (−14.06) [−35.11]	195.64
E_7	Cr_1-SmC 136.35 (16.01) [39.10] SmC-SmA 154.08 (1.60) [3.74] SmA-N 315^a N-I 335^a	I-Cr_2 138.21 (−2.03) [−4.93] Cr_2-Cr_3 111.37 (−12.72) [−33.07]	198.65
E_9	Cr_1-Cr_2 70.68 (2.42) [7.03] Cr_2-SmC 118.62 (23.76) [60.66] SmC-SmA 146.48 (1.23) [2.92] SmA-N 268.33 (0.03) [0.05] N-I 284.07 (0.07) [0.13]	I-Cr_3 176.02 (−2.89) [−6.43] Cr_3-Cr_4 82.83 (−2.90) [−8.15]	165.45
E_{12}	Cr_1-SmC 70.34 (20.69) [60.23] SmC-SmA 101.74 (14.65) [39.08] SmA-N 175.185 (0.04) [0.09] N-I 244^a	I-Cr_2 77.77 (−0.81) [−2.31] Cr_2-Cr_3 33.37 (−10.75) [−35.06]	173.66

Abbreviations: Cr_1-Cr_5 = crystal phases; N = nematic phase; SmA, SmC = smectic phase; I = isotropic phase; (a) = observed only on (OPM).

chain almost invariably promoted smectic behaviour [49], the increasing of the length the alkoxy group in series (E_n) from (n = 4 to n = 7) leads to an increase in the range of the (Sm) phase and a decrease in the range of the (N) phase. This conduct may be due to the increase of the alkoxy chain that affects increasing the dipole–dipole interaction between the methylene groups in the molecules, which makes the (Sm) phase more stable due to the aggregation of the molecules may be more regular. This arrangement in the structure



	3	4	6	7	9	12
🟧 En	176.26	183.89	195.64	198.65	165.45	173.66
🟦 Dn	172.53	206.09	226.55	255.88	217.63	162.91

Figure 6. (Colour online) Comparison of mesophase range between the two series (D_n & E_n).

makes the mesogen molecules in this series prefer the (S_m) rather than (N) phase [50]. In the case of compound E_3, the transition (N-I) was not observed may be due to the thermal decomposition that occurs for these compounds near their melting points. As seen the thermodynamic results of the compound (E_4, E_9 and E_{12}) in Table 2, the enthalpy change of the SmA-N transition has very small value because of the interference that occurred between the partial decomposition of the compound and the transition from the smectic phase to the nematic phase. Also, the transition (N-I) in compound (E_9) has small thermodynamic change values because it is known that this transition is to be a very weak first order transition [51].

From the results of Tables 1 and 2, it can be seen that the clearing temperatures of series D_n are higher than those of the corresponding members of the series (E_n). This is completely consistent with the established trend for the efficiency of the methoxy and Bromo groups in promoting mesogenic behaviour. This phenomenon enhanced the view that it is predominantly the effect of substituent size and how it affects the shape of the molecule that influences the clearing temperature. The presence of a polarisable Br atom enhanced the attraction between the molecules in compounds (E_n) while the existence of the bulky methoxy group in compounds of series (D_n) facilitated filling the space in the molecular terminal, led to increasing the thermal stability of the compounds in series (D_n) [52–54].

4. Conclusion

Two new series of ester-Schiff bases derivatives (D_n, X = –OCH_3 and E_n, X = –Br) were synthesised with yields (47–60%) and characterised with FT-IR, ^{1}H-NMR, ^{13}C-NMR and C.H.N. techniques, the relationship between the structure and their mesomorphic attitudes were studied and tested by using POM and DSC. All the derivatives of two series (D_n) and (E_n) show liquid crystal properties with a high range of nematic phase for (D_n) series, and smectic and nematic for (E_n) series. The results show that the polarity of substituents plays an important role in the appearance and the thermal stability of the formation of liquid crystal phases. On the other hand, the mesomorphic results obtained showed that the length of the alkoxy group can be an effect on the range of (N-I) transition.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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