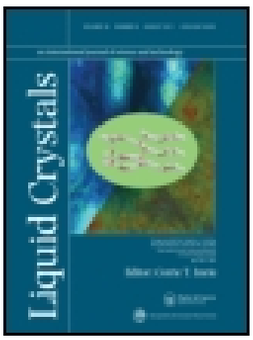

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Mesomorphic study and DFT simulation of calamitic Schiff base liquid crystals with electronically different terminal groups and their binary mixtures

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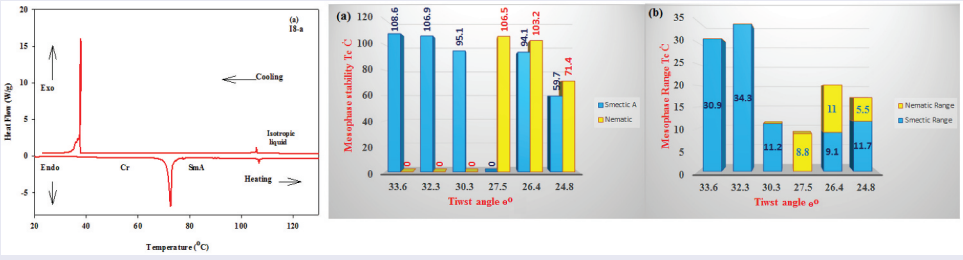
ABSTRACT

Two series of Schiff bases liquid crystals with electronically different terminal substituents, 4-(alkoxy) phenylimino)methyl)benzonitrile (**In-a**) and *N*-(4-(hexyloxy)benzylidene)-4-(alkoxy)benzenamine (**In-6**), were synthesise. Their molecular geometries were elucidated via FT-IR, ^{1} H-NMR and elemental analysis. Mesomorphic and optical properties were investigated by differential scanning calorimetry (DSC) and polarised optical microscopy (POM). The effect of electronic nature of in the attached terminals, extra-conjugation E- withdrawing (CN) and E-donating (hexyloxy), is investigated. All members of the investigated compounds were enantiotropically mesomorphic comprising mono or dimorphic phases depending on the electronic and complexity nature of attached terminals. Computational parameters of both series were related with the experimental findings of the mesophase stability and the length of alkoxy chains to investigate the effect of the terminals on the stability of possible architectures. Density functional theory (DFT) calculations revealed that all investigated members are non-co-planar with twist angles between the rings around the CH = N linkage. The relations of the experimentally mesophase range and stability of the enhanced phases with simulated parameters were studied to conclude that these factors contributed in different extent to affect the mesomorphic behaviour. The binary phase diagrams were constructed between **In-6** components and achieved very low melting temperatures at their eutectic mixtures.



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Schiff base liquid crystals; mesomorphic; computational calculations; molecular geometry; binary mixtures

1. Introduction

Azomethine linkers have been widely employed in the synthesis of numerous liquid crystalline architectures [1–11]. Calamitic (rod-like) Schiff base liquid crystals enhance nematic and/or smectic mesophases [12].The steric packing considerations play an effective role in the transition state of the soft materials [12]. Thus, anisotropic calamitic or discotic molecular structures are used to be fundamental prerequisite for the preparation of conventional thermotropic liquid crystalline compounds. Mesomorphic activities of calamitic compounds are mainly dependent on their molecular shape, in which minor change in the molecular structure offers great changes in their mesomorphic characteristics. Most researches are focused on azomethines since the discovery of nematogenic 4-methoxybenzylidene-4′-butylaniline at room temperature [13].

In order to broaden the mesomorphic range and increment the thermal stabilities, an effective strategy for modification the geometrical structure of compounds may be effective [14–16]. Therefore, considerable attentions have been paid to the calamitic thermotropic liquid crystals [17] with terminal substituents [18,19]. In general, the kind and the size of terminal groups can offer great changes in mesomorphic behaviour [20,21]. Moreover, it was found that, the change of the length of terminal chains or its electronic nature, the core rigidity of structural compound altered, and consequently, the linearity of the compounds changed to some extent due to the greater number of

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configurations of the chains that lead to variable terminal and parallel interactions [22,23], molecular shape and excluded volume also have pronounce effect on the mesomorphic properties [24,25]. Further, the mesomorphic behaviour of liquid crystalline materials is strongly dependent on the mesogenic core and the competitive parallel and terminal intermolecular interactions, and this is most often accounted for in terms of molecular shape [23]. Recently, it was observed that the molecular architecture tends to be more oriented in a parallel arrangement as the length of the terminal substituent increases [26]. Additionally, the terminal chains offer the heliconical and twist-bend nematic phases [27,28] and chiral mesophases [29]. Many terminals have been prepared in the generation of mesomorphic materials, but the most general route [30] is to use either alkyl/alkoxy chain or a small compact polar substituent [31–34].

Computational investigations are excellent tools in pre-preparation designing new attracted architectures that could be interesting to many researchers [22,30,31,33–41]. In recent, the density functional theory (DFT) demonstrates to be an effective tool for estimation of the thermal and geometrical parameters of liquid crystalline materials [42].

Going further in our investigation concerning azomethine derivatives, new two ring calamitic compounds based on Schiff base central moeity were prepared and invesyigated via experimental and theoritical approches. The two homologes sets are namely 4-(alkoxy)phenylimino)methyl)benzonitrile (**In-a**) and *N*-(4-(hexyloxy)benzylidene)-4-(alkoxy)benzenamine (**In-6**) and with different terminal substituents, CN and OC_6H_{13} groups were investigated. The study is aimed to illustrate their mesomorphic behaviour and correlated the outcome results with the theoritically simulated DFT parameters. Finally, in order to achieve low melting points liquid crystals, a study of the binary mixtures of **In-6** established from two systems having different proportionated alkoxy chain lengths.

2. Experimental

2.1. Materials

4-hexyloxybenzaldehyde, 4-cyanobenzaldehyde, 4-hexyloxyaniline, 4-octyloxyaniline and 4-hexadecyloxyaniline were purchased from Sigma Aldrich (Germany). Ethanol was purchased from Aldrich (Wisconsin, USA).

2.2. Synthesis

In-a and **In-6** were prepared according to the following scheme:

Synthesis of *N*-(4-(subistituted)benzylidene)-4-(alkoxy)benzenamine **In-a** and **In-6** [1].

Equimolars of 4-substitutedbenzaldehyde (4.1 mmol) and 4-alkoxyaniline (4.1 mmol) in ethanol (10 ml) were refluxed for two hours. The reaction mixture was allowed to cool, and the separated product filtered. The obtained solid was recrystallised from ethanol.

4-(Hexyloxy)phenylimino)methyl)benzonitrile, **I6-a** [1].

Yield: 92.0%; mp 77.0°C, ^{1} H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 0.5 H), 8.47 (s, 0.5 H), 8.04–7.87 (m, 1.4 H), 7.42 (d, *J* = 8.7 Hz, 0.8 H), 7.23–7.16 (m, 2.2 H), 7.02 (d, *J* = 8.8 Hz, 1.4 H), 6.91–6.83 (m, 2.2 H), 3.99 (t, *J* = 6.6 Hz, 1.2 H), 3.95 (t, *J* = 6.2 Hz, 0.8 H), 1.97–1.65 (m, 2 H), 1.65–1.16 (m, 6H), 0.93 (t, *J* = 4.7 Hz, 3 H). ^{13} C NMR (101 MHz, $CDCl_3$) δ 190.57, 156.85, 132.28, 125.58, 124.01, 122.24, 116.51, 116.30, 115.89, 115.46, 115.06, 68.37, 31.59, 29.17, 25.70, 22.62, 14.08. Elemental analyses: Found (Calc.): C, 78.40 (78.40); H, 7.23 (7.24); N, 9.12 (9.14).

4-(Octyloxy)phenylimino)methyl)benzonitrile, **I8-a**

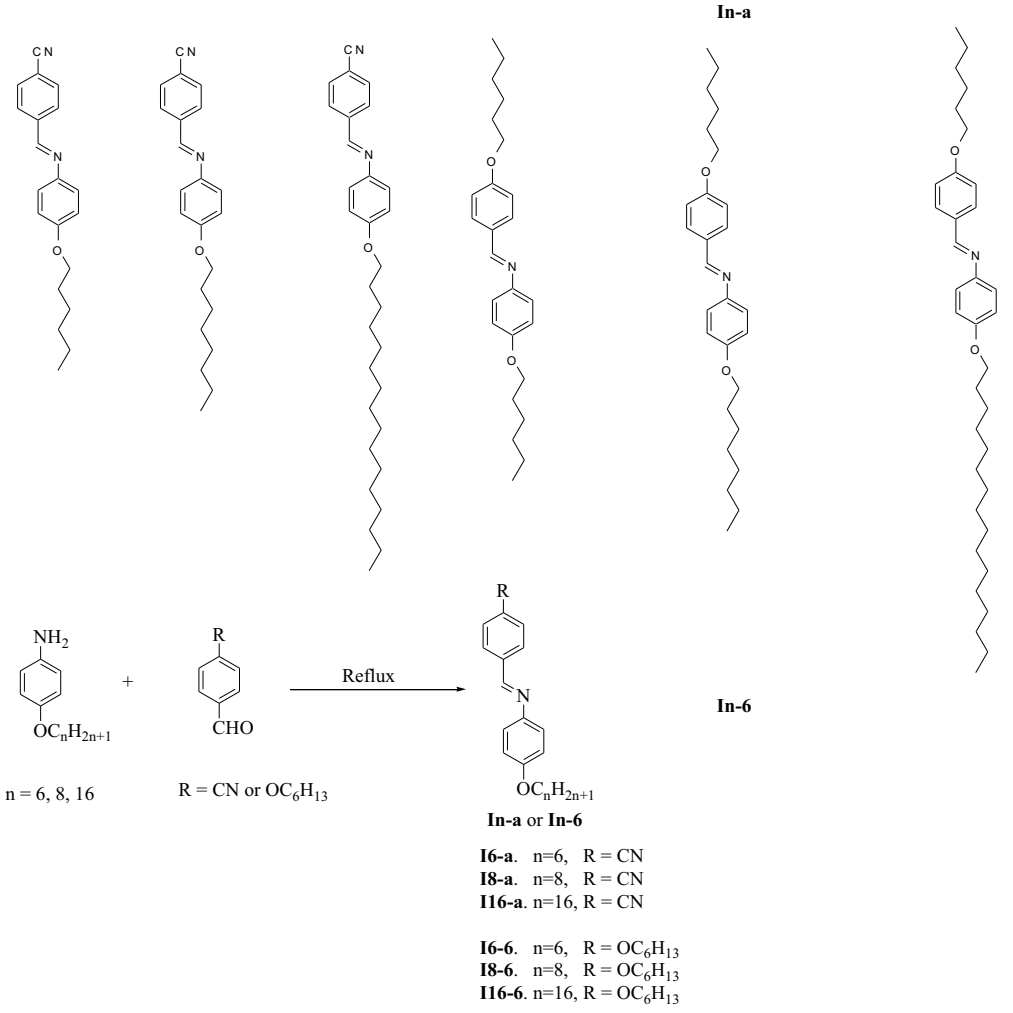
Yield: 97.0%; mp 73.0°C, ^{1} H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 0.5 H), 8.46 (s, 0.5 H), 8.07–7.79 (m, 1.4 H), 7.49 (d, *J* = 8.7 Hz, 0.8 H), 7.24–7.12 (m, 2.2 H), 7.05 (d, *J* = 8.7 Hz, 1.4 H), 6.89–6.80 (m, 2.2 H), 4.09 (t, *J* = 6.6 Hz, 1.2 H), 3.94 (t, *J* = 6.7 Hz, 0.8 H), 1.99–1.67 (m, 2 H), 1.69–1.01 (m, 10 H), 0.96 (t, *J* = 5.9 Hz, 3 H). Elemental analyses: Found (Calc.): C, 78.98 (79.00); H, 7.83 (7.84); N, 8.35 (8.38).

4-(Hexadecyloxy)phenylimino)methyl)benzonitrile, **I16-a**

Yield: 95.0%; mp 84.0°C, ^{1} H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 0.6 H), 8.47 (s, 0.4 H), 8.10–7.86 (m, 1.3 H), 7.43 (d, *J* = 8.7 Hz, 0.8 H), 7.23–7.16 (m, 2.2 H), 7.02 (d, *J* = 8.8 Hz, 1.4 H), 6.91–6.83 (m, 2.2 H), 4.10 (t, *J* = 6.7 Hz, 1.2 H), 3.94 (t, *J* = 6.6 Hz, 0.8 H), 1.99–1.64 (m, 2 H), 1.65–1.59 (m, 26 H), 0.93 (t, *J* = 4.7 Hz, 3 H). ^{13} C Elemental analyses: Found (Calc.): C, 80.64 (80.67); H, 9.46 (9.48); N, 6.25 (6.27).

2.3. Computational and molecular modelling

The theoretical calculations were carried out by Gaussian 09 software [43]. DFT/B3LYP method and 6–31 G (d,p) basis set was selected for calculations. The geometries were optimised by minimising the energies with respect to all geometrical parameters without imposing any molecular symmetry constraints. The structures of the optimised geometries have been drawn with Gauss View [44].



Scheme 1. Synthesis of *N*-(4-(subistituted)benzylidene)-4-(alkoxy)benzenamine **In-a** and **In-6.**

3. Results and Discussion

Molecular formulae of the prepared compounds were confirmed via their elemental analyses, FT-IR data, and NMR spectroscopy. The results were consentient with the expected structures.

3.1. Mesomorphic and molecular geometry studies

Mesomorphic and optical properties of the synthesised series (**In-a** and **In-6**) were investigated and their details results of the transition temperatures and enthalpies, as derived from DSC measurements, are tabulated in **Table 1**.

Table 1. Phase transition temperatures (°C), (enthalpy of transition **ΔH**, kJ/mole), and normalised entropy of transition, **ΔS/R** for compounds **Ina** and **In-6.**

Compound	$T_{Cr\text{-}SmA}$	$T_{Cr\text{-}N}$	$T_{SmA\text{-}N}$	$T_{SmA\text{-}I}$	$T_{N\text{-}I}$	$\Delta S_{SmA\text{-}N}/R$	$\Delta S_{SmA\text{-}I}/R$	$\Delta S_{N\text{-}I}/R$
I6-a	77.7 (31.41)	-	-	108.6 (0.71)	-		0.22	
I8-a	72.6 (26.94)	-	-	106.9 (0.82)	-		0.26	
I16-a	83.9 (41.38)	-	-	95.1 (0.92)	-		0.30	
I6-6	-	106.5 (30.71)	-	-	115.3 (1.28)			0.40
I8-6	94.1 (32.72)	-	103.2 (2.21)	-	114.2 (2.10)	0.71		0.65
I16-6	59.7 (40.71)	-	71.4 (2.91)	-	76.9 (2.73)	1.02		0.94

Cr-I denotes transition from solid to the isotropic phase.
Cr-SmA denotes transition from solid to the SmA phase.
Cr-N denotes transition from solid to the N phase.
SmA-N denotes transition from SmA to the N phase.
SmA-I denotes transition from SmA to the isotropic phase.
N-I denotes transition from Nematic to the isotropic phase.
* $\Delta S/R$ denotes normalised entropy of transition.

DSC curves of the prepared compounds **I8-a** and **I6-6** during heating/cooling scans are given as examples in Figure 1. As shown from **Figure 1**, both compounds showed two endotherms peaks of the crystal–mesophase and mesophase–isotropic transitions upon heating and cooling scans. The POM showed focal conic fan characteristic for the SmA phase and spread schlieren for the N phase (**Figure 2**). In order to ensure the stability of the prepared compounds, DSC measurements were performed for two heating – cooling cycles. All thermal analyses of these compounds were recorded from the second heating scan. Additionally, DSC measurements were confirmed by the POM texture observations. **Figure 1–2** indicate that these compounds exhibit enantiotropic monomorphic properties. In order to evaluate the effect of terminal flexible groups on the mesophase behaviour of prepared derivatives, graphical representation of DSC transition temperatures was depicted in **Figure 3**. As estimated from Table 1 and **Figure 3**, all investigated compounds in each series (**In-a** and **In-6**) are enantiotropic with thermal stability and mesomorphic temperature range as well as different type. This mesomorphic behaviour is dependent on the kind of terminal groups. Moreover, their melting points (Cr–mesophase) have irregular trends. Also, the results revealed to **I8a** in the first set has the lowest melting temperature (Cr-SmA = 72.6°C) and **I16-6** in the second system has the lowest meting point (Cr-SmA = 59.7°C). For **In-a** set, all members of group are monomorphic exhibiting smectogenic mesophase (SmA phase). Moreover, the SmA stability transitions were linearly decreases with the terminal alkoxy chain length (n = 6–16). While their mesophase range (ΔT_{SmA}) decreases in the order: **I8-a** > **I6-a** > **I16-a**. The second series **In-6**, which has proportionated terminal alkoxy groups, possesses monomorphic and dimorphic phases depend on their terminal alkoxy chain connected to the Ar-CH = N- [45]. Compound **I6-6** enhanced only nematic phase (N) with nematogenic range, ΔT_N = 8.8°C. While, compounds **I8-6** and **I16-6** are dimorphic exhibiting SmA and N mesophase with mesomorphic ranges 20.1 and 17.2°C, respectively. As could be concluded, the type of the terminal group significantly affects the type of the enhanced mesophase, the presence of highly electron withdrawing CN-group of the cyano derivatives **In-a** increases the dipolemoment as will be discussed later, compared with almost electronically symmetric dialkyl derivatives **In-6**. The high dipole moment of **In-a** with respect to **In-6** permits the strong tendency of the cyano-terminated

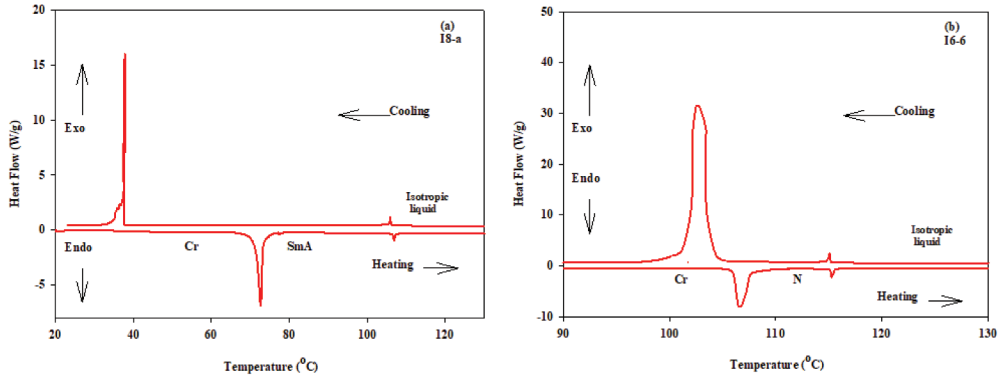


Figure 1. (Colour online) DSC thermograms of (a) compound **I8-a;** and (b) compound **I6-6** upon heating and cooling scans with heating rate 10°C/min.

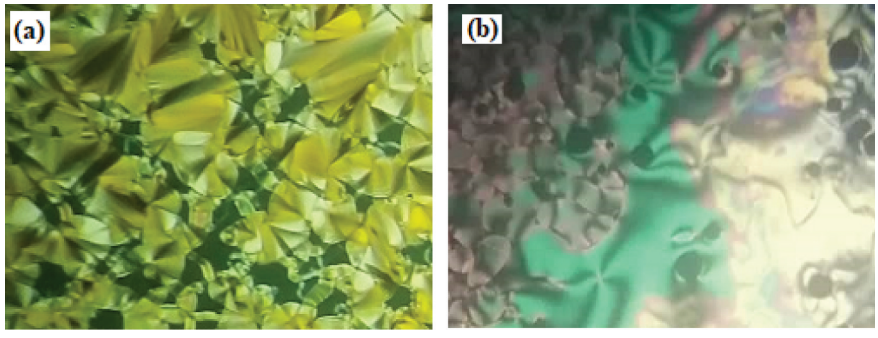


Figure 2. (Colour online) Textures under POM upon heating of (a) SmA phase for compound **I8-a** at 102.0°C and (b) N phase for compound **I6-6** at 110.0°C.

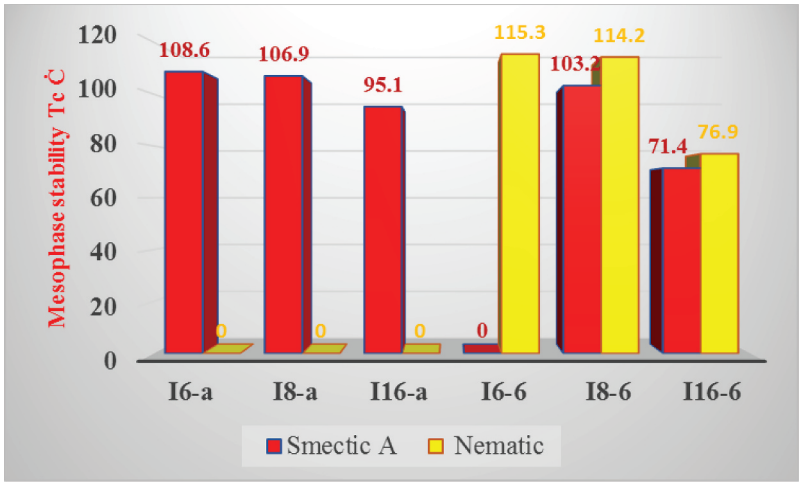


Figure 3. (Colour online) DSC graphical transitions of prepared series **In-a** and **In-6.**

group to exhibit antiparallel association which will drive smectic phase formation as monomorphic phase, while the lower dipolemoment of **In-6** could enhance the formation of the less ordered nematic mesophase.

A comparison was made between the present azomethine series (**In-a** and **In-6**) in order to study the effect of electron as well as the conjugation of the E-withdrawing (CN) group in first set, **In-a**, and the mesomeric E-donating hexyloxy group in the second series **In-6** on the mesophase behaviour. The results revealed that, the thermal stability of **In-6** is higher than **In-a** except the long chain $n = 16$. Since, the enhanced mesophase is dependent on the dipole moment of the molecule; it is remarkably dependent on the polarity of the terminal substituents. Another factor is the molecular architected shape which varies according to the location and kind of the terminal substituent. Mesomeric interactions of the di-alkoxy groups in **In-6** set with the azomethine -CH = N- linkage are prohibited to the extent that the derivatives possess high thermal stability than the CN derivatives, **In-a**. The estimated parameters of both series were related with the experimentally determined values of the mesophase stability and the length of alkoxy chains to study the effect of the terminals nature on the stability of possible architectures. The predicted geometrical structures derived by DFT theoretical calculations (B3LYP 6–31 G (d,p) base site) were shown to be none co-planar compounds with twist angles between the plans passes the aromatic rings around the CH = N bond. It is worthy note that, the twist angle is significantly affected by the length as well as the type of the terminal substituent. It should be observed that even though these DFT calculations will offer a prediction of the preferred molecular geometry in the gas phase, the presence of these compounds in a condensed phase such as a liquid crystalline matter, the lowest energy may be different and more elongated species will be preferred [46].

Moreover, mesomorphic behaviour, either the stability or the type of the enhanced mesophase of liquid crystal materials is intensively dependent on the length of the flexible terminal groups, and this is most often accounted for in terms of molecular shape [23]. In general, the polarity of the attached groups, polarisability, aspect ratio, rigidity and shape of the molecule are considered significant parameters that could be responsible for the stability of the formed mesophases and the type of their textures. These factors contribute in different percentages to affect the mesomorphic behaviour. It is known that, the temperature stability of an enhanced mesophase is improved by any increment in the polarity and/or polarisability of the mesogenic core of the materials, which is affected by the polarity and the complexity of the attached substituent. Further, a strong van der Waals intermolecular attraction, which enforced by the increment of the length terminal alkoxy chains, increases the mesophase stability of the SmA phase by permitting high degree of the lamellar packing. The increment of the alkoxy chain length of strongly enhances the stability of compounds (**Figure 3**). The longer the chain length the higher the van der Waal's intermolecular interaction the more enhanced the transition stability. It is worthy note that the weak dependence of the clearing temperature (≈100°C) for the **In-a** series on increasing the chain length. This data was expected for such series as previously reported of low molar mass liquid crystalline compounds possessing lateral alkyl chains [47]. On the other hand, although there is very small change between the N-I on passing from **I6-6** to **I8-6** (only 1°C), however, a large decrement in the N-I transition temperature and the SmA-N temperatures from **I8-6** to **I16-6** is very surprising. This observation could be illustrated in terms of the large molecular asymmetry of the molecules.

The relationship between the length of the alkoxy chain and the total smectic and nematic mesophase ranges for

the prepared compounds are shown in **Table 2**, **Figure 4**. It obvious from **Figure 4** that the total smectic and nematic mesophase stability decrease with the alkoxy chain length, however, their ranges is the highest for the chain length C = 8 for both series and a significant decrease at the longest chain length C = 16 for the CN terminal group series, on the other hand, the smectic range of the dialkoxy terminal groups increases regularly with the increment of the chain length. These observed data could be explained in terms of the competitive interactions between the parallel and terminal aggregation. At the longer chain length, the van der Waal's interactions increase to show high smectic range with decrement of the less-ordered nematic phase range. Moreover, the competitive intermolecular lateral and terminal molecular interactions could illustrate the absence of the nematic mesophase of the highly polar extra-conjugated cyano derivatives (**In-a**). Furthermore, the extra-conjugation of the CN group enforces the molecules to be more planar of compounds (**In-a**) than that of the hexyloxy group of (**In-6**). Thus, the length of the alkoxy group is highly affected the degree of the twist angle for the same terminal groups. The longer alkoxy chains offer high planarity of molecules **Figure 5**.

Table 2. The predicted thermal, dimensional parameters and aspect ratios of the prepared compounds, **In-a** and **In-6.**

Parameter		I6-a	I8-a	I16-a	I6-6	I8-6	I16-6
T_C, smectic A		108.6	106.9	95.1	-	103.2	71.4
T_C, nematic		-	-	-	115.3	114.2	76.9
ΔT_{SmA}		30.9	34.3	11.2	-	9.1	11.7
ΔT_N		-	-	-	8.8	11.0	5.5
ΔT (mesomorphic range)		30.9	34.3	11.2	8.8	20.1	17.2
T_C (**m**esomorphic stability)		108.6	106.9	95.1	115.3	114.2	76.9
Twist angle (ɵ)		33.6	32.3	30.3	27.5	26.4	24.8
Dipole moment, μ total		6.71	6.91	6.97	1.80	1.86	1.82
Polarisability, α		284.9	309.1	404.3	343.7	368.2	463.4
Dimension Å	**Width (D)**	7.2	7.4	7.8	7.1	7.3	7.7
	Length (L)	24.2	26.8	37.0	31.1	33.7	44.1
Aspect ratio (L/D)		3.4	3.6	4.7	4.4	4.6	5.7

It is reported that the dimensions parameters of the materials as well as the electronic nature of the attached substituents has high effect on the polarisability [48,49]. It is obvious from **Figure 6** that as the chain length of the alkoxy terminal groups increases the polarisability increases; this could be explained in terms of the aspect ratios. As the aspect ratios of the molecule increases the space filling of the liquid crystalline compounds increases and resulted in the enhancement of the polarisability.

The twist angle between the aromatic rings around the -CH = N- linkage are correlated with the mesophase stability and mesophase ranges of the prepared series **In-a** and **In-6** and represented graphically in **Figure 7**. It is clear that, as the twist angle decreases the mesophase stability decreases. Moreover, the mesophase range of the enhanced phases changes irregularly with the decrement of the twist angle. These finding could be approved that the mesophase behaviour is impacted with a cumulative effect of variable parameters not only on one parameter. The parameter such as the aspect ratios, polarisability, dipole moment, chain lengths could share together with different extent to enhance a mesophase with certain behaviour.

The dipole moment is one of the most important factors that could affect the type and behaviour of the formed mesophase. The lower the dipole moment of the dialkoxy compounds (1.8–1.86) and a higher dipole moment of the cyano derivative (6.71–6.97 Debye) may be safely attributed to electronic nature point of view. The variation of the dipole moment with the type of the terminal group

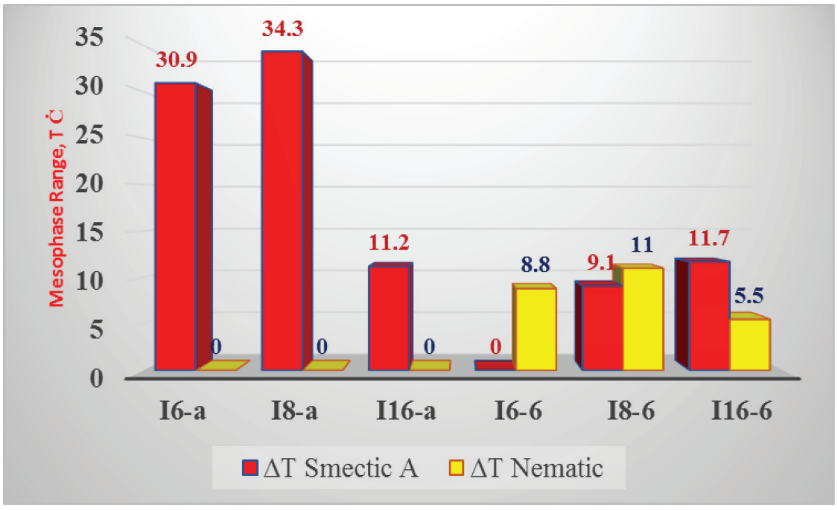


Figure 4. (Colour online) The relationship between the length of the alkoxy chain and the total smectic and nematic mesophase ranges.

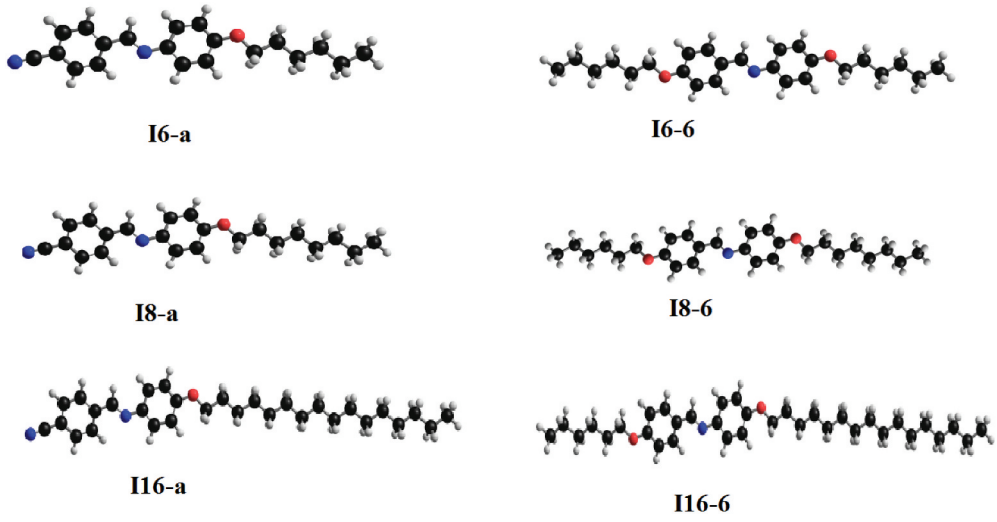


Figure 5. (Colour online) Calculated molecular geometrical the prepared compounds.

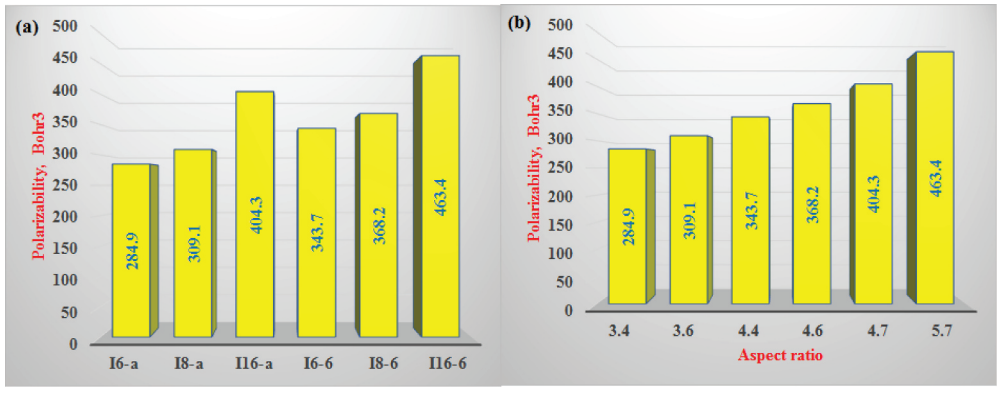


Figure 6. (Colour online) The relationship between the polarisability and (a) the length of alkoxy chains; (b) the aspect ratio (L/D) for all prepared compounds.

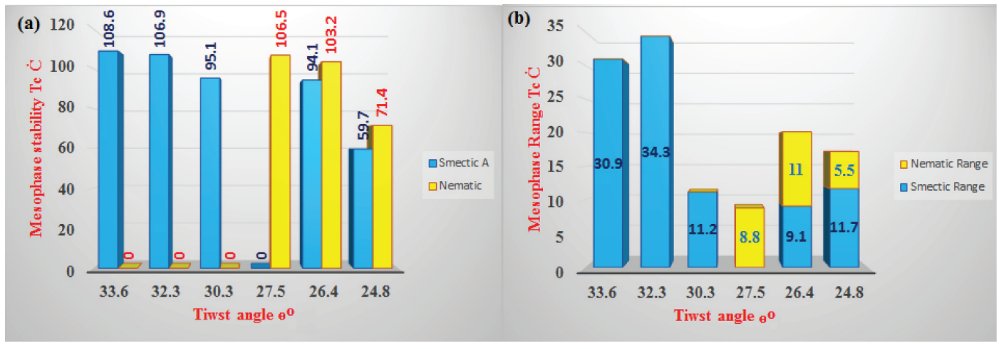


Figure 7. (Colour online) The relationship between the twist angle between the aromatic core and mesophase stability (a) and mesophase range (b) of investigated series.

significantly affected the mesophase behaviour (Figure 8). The lower dipole moment of dialkoxy derivatives (**In-a**) could be an explanation of the formation of the nematic mesophase at the shorter chain lengths as a single mesophase. However, at longer chain length the terminal van der Waal's aggregation could illustrate the enhanced smectic mesophase. On the other hand, the higher dipole moment of the cyano derivatives (**In-a)** permit high degree of lateral interaction to enhance the more ordered smectic mesophase [50]. The lower dipole moment value allows the terminal aggregation rather than the lateral one, which enhances the nematic mesophase. However, the long

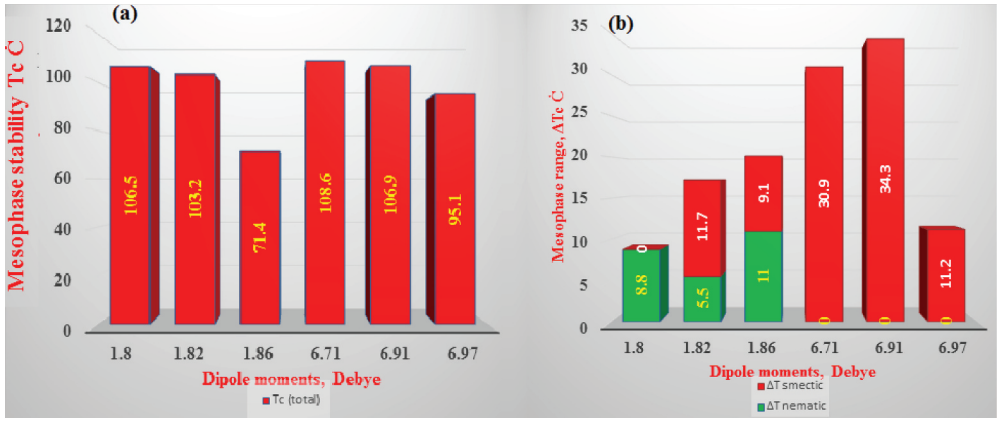


Figure 8. (Colour online) The dependence of the dipole moment on mesophase stability (a) and their mesophase range (b) for the investigated series.

lengths of chains increase the strong van der Waals interaction of the alkoxy chain enforces, besides the high dipole moments, the parallel interaction which facilitates the formation of the smectic mesophase with shrinking of the less ordered nematic one increases.

The transition entropy changes of prepared compounds (ΔS/R) are estimated from DSC measurements and collected in **Table 1**. Small magnitudes of entropy changes are observed in addition to, a systematic trend for both series (**In-a** and **In-6**) with the length of flexible alkoxy groups. In addition to, entropy change values for the **In-a** series are low for a SmA-I transition. It can be concluded about the lower values of estimated entropy changes for conventional low molar mass mesogens may be attributed to the thermal cis-trans isomerisation of the linkage and this is in agreement with previous report [51–54]. Further, the enhanced shape anisotropy of molecules to pack more efficiently in the liquid crystal phase will results higher transition temperatures and effect on the entropy changes [55].

3.2. Frontier Molecular Orbitals and Polarisability

Table 3 and **Figure 9** demonstrates the estimated plots of frontier molecular orbitals HOMO (highest occupied) and LUMO (lowest unoccupied) of both conformers of the prepared compounds, **In-a** and **In-6**. As shown from figures, it is obvious that the electron densities of the sites that shared in the formation of the HOMOs and the LUMOs are localised on the aromatic rings. Moreover, there was no obvious impact of the alkoxy chain length on the location of the electron densities of the FMOs. However, the type of the terminal substituent affects the energy gap between the FMOs. The attachment of the cyano group resulted in extra conjugation of the aromatic part and consequently decreases the FMOs energy gap. This energy difference between the FMOs could be used in the prediction of the ability of electron transformation from HOMO to LUMO during any electronic excitation process. The global softness (**S**) = **1/ΔE** is the parameter expects the polarisability as well as the sensitivity of materials for the photoelectric property.

3.3. Molecular Electrostatic Potential (MEP)

The charge distribution map for SMHBCs the prepared compounds, **In-a** and **In-6** was calculated with the same method at the same basis sets according to molecular electrostatic potential (MEP) (**Figure 10**). The negatively charged atomic sites (the red region) were estimated to be localised on the aromatic rings of the dialkoxy derivatives. However, the attachment of the cyano group instead of the alkoxy group changes the localisation the negatively charged atomic sites. On the other hand, the moieties of the alkoxy chains were predicted to show the least negatively charged atomic sites (blue regions) regardless the nature of the terminal attached group. These finding of the distribution mapping of the charges could be another illustration of the formation of the smectic mesophase as

Table 3. FMO Energies a.u., polarisability, α, and dipole moment μ (Debye) of the prepared compounds, **In-a** and **In-6.**

Parameter	I6-a	I8-a	I16-a	I6-6	I8-6	I16-6
E_{LUMO}	−0.08971	−0.08966	−0.08962	−0.05509	−0.05517	−0.05527
E_{HOMO}	−0.22201	−0.22200	−0.22210	−0.20178	−0.20174	−0.20173
$\Delta E_{HOMO\text{-}LUMO}$	0.132	0.132	0.132	0.147	0.147	0.146
S Softness	7.56	7.56	7.55	6.82	6.82	6.83

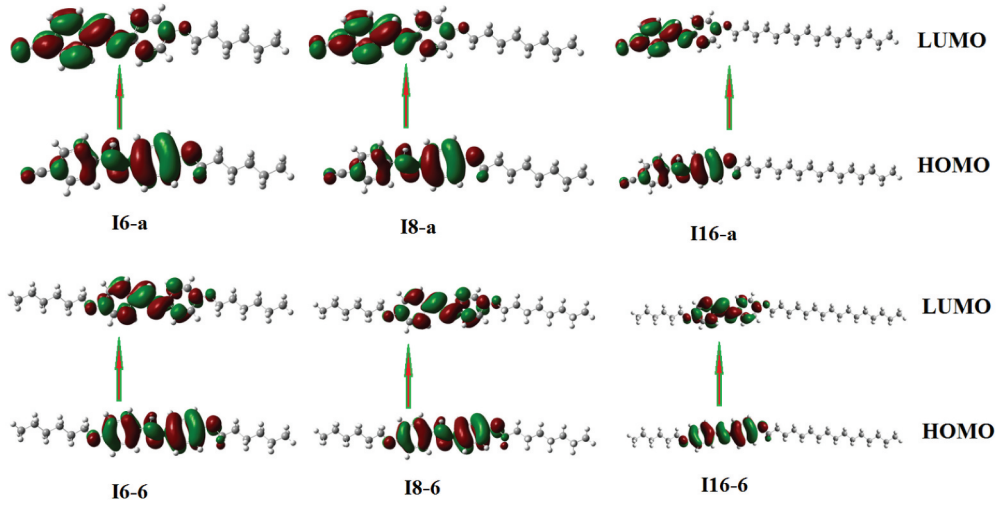


Figure 9. (Colour online) The estimated plots for frontier molecular orbitals of the prepared compounds, **In-a** and **In-6.**

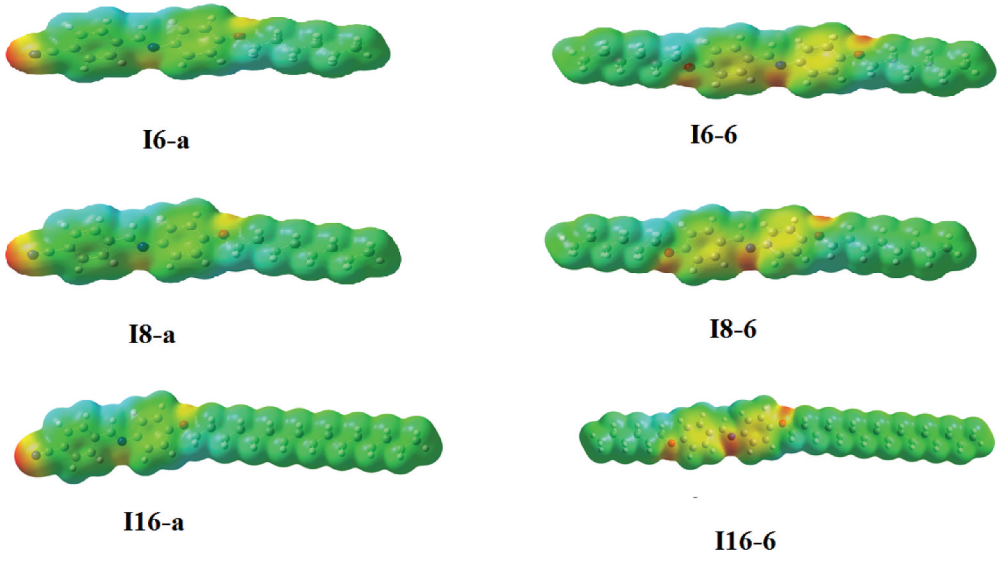


Figure 10. (Colour online) Molecular electrostatic potentials (MEP) for the prepared compounds, **In-a** and **In-6.**

monomorphic liquid crystals for the cyano derivatives and dimorphic phases, smectic and nematic, for the di alkoxy derivatives.

3.4. Binary mixtures

In order to achieve low melting temperatures near to the room temperature, the eutectic mixtures of investigated series **In-6** was investigated. The mixture is exhibiting dialkoxy chains having liquid crystalline properties in their pure state. This is because under such condition, the temperature range of the mesophase is consequently greater for the eutectic mixture than for either pure component.

Binary phase diagrams obtained from measured DSC thermograms (see supplementary data) of the binary mixtures prepared from different homologues of **In-6**, having different length of terminal alkoxy chains, are displayed in **Figure 11**. As can be seen from these diagrams, mixtures constructed from derivatives bearing proportionating terminal chains, **I6-6/I8-6, I6-6/I16-6** and **I8-6/I16-6** showed to exhibit enantiotropic mesophases over all entire composition ranges. In the first system **I6-6/I8-6**, compound **I6-6** is purely nematogenic while, the other compound **I8-6** possesses dimorphic mesophases SmA and N phases. Examining their phase diagram (**Figure 11a**) revealed that, the addition of **I6-6** derivative to **I8-6** is accompanied by an increase in temperature range as

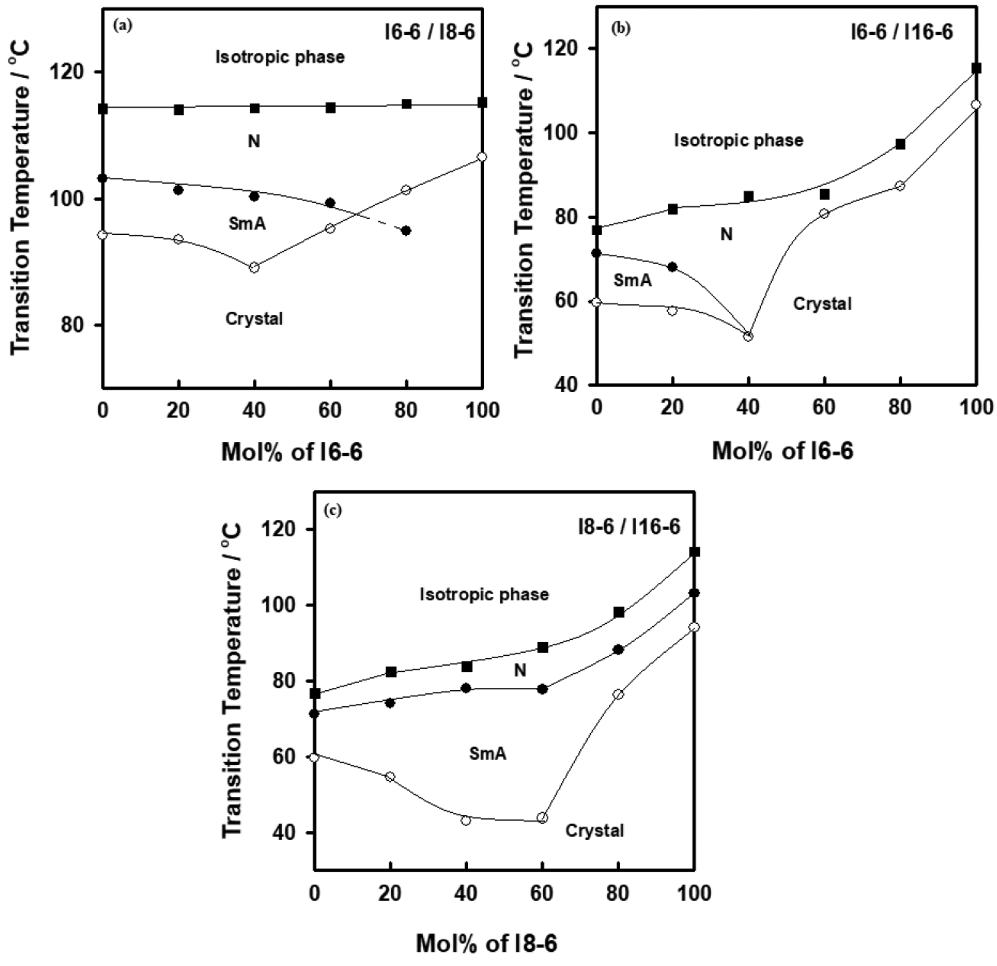


Figure 11. Binary phase diagrams of (a) **I6-6/I8-6**; (b) **I6-6/I16-6**; and (c) **I8-6/I16-6.**

a result of the depression of their melting points upon the mixing. All mixtures of the two components are enantiotropic dimorphic (SmA and N) up to 80 mol% of **I6-6** whereas; the SmA phase stability slightly decreases with the composition until become monotropic and vanishes at 80 mol % of **I6-6**. The disruption of the smectic phase is actually affected by the addition of the component bearing the shorter flexible chain length that decrease lateral adhesion between alkoxy chains that helps the formation of the SmA design [56].The N phase covers all composition range with observation of linear N-I dependency. Eutectic mixture of **I6-6/I8-6** system appeared around 40 mol % of **I6-6** and exhibit eutectic melting temperature at 83.8°C with mesomorphic range 30.5°C. The mesophase stability is mainly depends on the intermolecular attractions, in which the molecular polarity plays a significant role, it has been reported that the dipole moment of any compound is dependent upon the nature of the terminal substituent [57].

In the case of **I6-6/I16-6** binary phase mixture (**Figure 11b**), the addition of **I6-6** to **I16-6** disrupt the formation of the SmA phase of the derivative **I16-6**. The thermal stability of the SmA decreases with increasing of the composition of **I6-6** until vanished at about 40 mol % of **I6-6**. On the other hand in the binary system **I8-6/I16-6**, the addition of one component to the other dose not disrupt the formation of mesophases and dimorphic enantiotropic SmA and N phases are observed to cover all composition mixtures (**Figure 11c**). For both cases **I6-6/I16-6** and **I8-6/I16-6**, their solid mixtures possess the eutectic melting temperatures at 51.5°C and 43.8°C with eutectic compositions 40 and 60 mol % for **I6-6** and **I8-6**, respectively. The mesomorphic ranges for both systems **I6-6/I16-6** and **I8-6/I16-6** at their eutectic compositions are 33.3°C and 45.2°C, respectively. Moreover, a gradual deviation from ideal behaviour (decreasing of N phase stability) is observed regarding clearing temperatures for both systems. Such destabilisation may be attributed to the disruption of the molecular association, due to the dissimilarity of the terminal alkoxy chain length, in the two components as observed in the other binary systems [58,59].

Generally, the mesomorphic properties of rod-like mesogens are impacted by many parameters such as the polarisability, dipole moment, aspect ratio and the competitive interaction between terminal aggregations. Further, the molecular geometry that is affected by the mesomeric configurations also affects the molecular-molecular interactions. In our investigations, the molecular aggregation of calamitic molecules by the lateral attraction of planar molecules that enforced with longer alkoxy-chains (*n*) might be played the main role of the mesophase behaviour. Another factor is the end-to-end association of terminal flexible chains that differs according to mesomeric effects. These factors share in different ratios to affect the mesomorphic properties of pure components as well as their mixtures.

4. Conclusion

Mono-azomethine sets of liquid crystalline materials namely 4-(alkoxy)phenylimino)methyl)benzonitrile (**In-a**) and N-(4-(hexyloxy)benzylidene)-4-(alkoxy)benzenamine (**In-6**), were prepared and their mesomorphic and optical behaviour were investigated by DSC and POM. Computational approaches were established to confirm the experimental results and carried out using DFT calculations.

The following results have been concluded:

- All members of each investigated sets are enantiotropic mesomorphic comprising mono or dimorphic phases dependent on the kind of attached terminals.
- Series **In-a** possessing SmA phase while group **In-6** exhibiting SmA and N phases depending on the length of alkoxy chains.
- The aspect ratios, dipole moment, polarisability of the prepared liquid crystalline derivatives are dependent on the electronic nature of the attached group.
- The effect extra-conjugation E- withdrawing (CN) and E-donating (hexyloxy), effective impact on the mesomorphic characterisations.
- The higher dipole moment of the cyano derivatives than the dialkoxy one illustrates the enhanced smectic phase of the cyano and the nematic phase for the dialkoxy derivatives.
- Binary phase diagrams accomplished between dialkoxy compounds (**In-6)** are achieved very low melting temperatures at their eutectic mixtures.
- There are many factors contributed in different extent to significantly effect on the mesomorphic properties of components in pure and mixed states.

Disclosure statement

Authors declare 'no conflicts of interest'.

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