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Polar Alkoxy Group and Pyridyl Effects on the Mesomorphic Behavior of New Non-Symmetrical Schiff Base Liquid Crystals

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Abstract: A series of non-symmetrical Schiff base liquid crystals were prepared and investigated. Schiff bases of p-alkyloxy aniline derivatives and 4-phenyl pyridine-4'-carbaldehyde were synthesized. The terminal alkoxy groups substituting aniline are of varied chain length, namely C6, C8, and C16. The structures of the compounds were confirmed via ¹H NMR and ¹³C NMR spectroscopy. Different mesophases of the samples were thermally and optically characterized by differential thermal analysis (DSC) and polarized optical microscopy (POM). All samples revealed enantiotropic smectic B (SmB) and smectic A (SmA) mesophases. The results obtained were further correlated with the density functional theory (DFT) theoretical calculations. The results are compared to a series of compounds bearing biphenyl moiety in their mesogens. The thermal stabilities of the different mesophase reduced upon the increment of the alkoxy chain length. The temperature ranges of both the smectic mesophases of new compounds bearing the 4-phenyl pyridine moiety are generally expanded higher than the other series. In addition, the total mesophase range is greater in the new compounds when compared to their biphenyl analogues. The DFT results were investigated in terms of the molecular geometries and the frontier molecular orbitals as well as the charge distribution mapping to show and illustrate the difference in the mesomorphic properties.

Keywords: liquid crystal; schiff base; biphenyl; 4-phenyl pyridine; DFT

1. Introduction

A unique state of matter called the Liquid crystalline state gained much importance and attracted considerable attention both in the basic sciences and technological applications because of a variety of advanced applications including digital displays, sensors, liquid crystal displays (LCDs), high-performance polymers, transporting of electron, ion or molecule and drug-delivery systems, and hybrid composites [1–5]. Rod-like liquid crystalline materials called calamitic mesogens (possessing a rigid core with two or more aromatic rings linked by connecting groups and flexible terminal chains), have attracted remarkable attention over recent decades due to their ability to display a wide range of technologically important liquid crystal phases [6–9]. With a variety of structures of rod-like molecules, they display some potential applications by changing their physical properties including dielectric anisotropy ($\Delta\epsilon$), birefringence (Δn), rotational viscosity and mesophase range for liquid crystal compounds [10–13].

It was observed that the mesomorphic properties of thermotropic calamitic LC are mostly influenced by the nature of terminal chains including alkyl, alkyloxy, perfluorinated

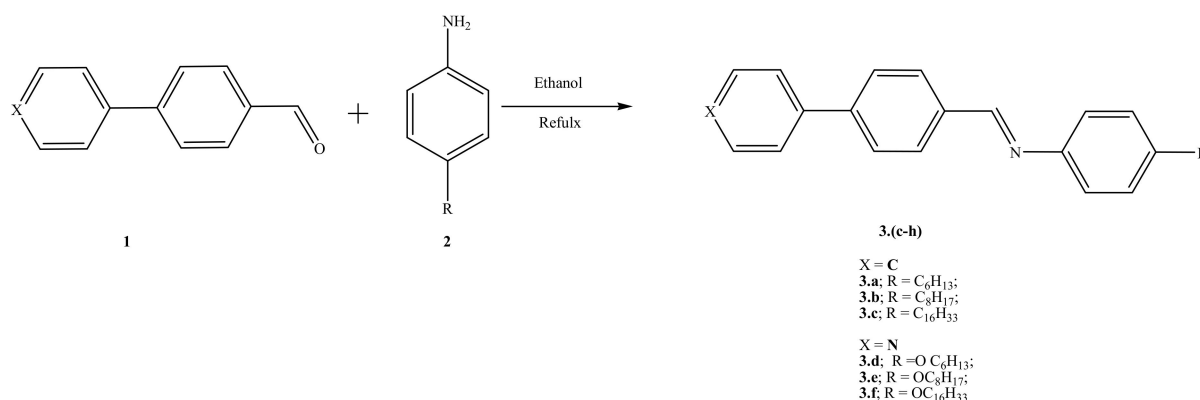
chain, ester or acyl group, or introduction of heteroatom into terminal chains [14–17]. Recently, a huge number of structurally varied thermotropic liquid crystals consist of polar heteroatoms/heterocyclic systems were designed and synthesized [17–19]. A variety of materials synthesized based on five and six membered heterocyclic rings comprising one, two, or three nitrogen atoms gave rise to attracting mesomorphic properties. The enhanced attractive forces and layer formation properties due to molecular stacking and packing of these liquid crystals are attributed to the position of nitrogen atoms and the availability of their lone pair of electrons. The inclusion of a heteroatom or heterocyclic unit induces substantial effects such as polarizability, enhanced lateral and/or longitudinal dipole moment, increased intermolecular interaction, and impact the mesophase stability, phase transition temperatures and introduction of transverse dipole moment, often stimulating negative dielectric anisotropic properties due to the existence of lone-pair electrons on heteroatoms of rings [20]. The mesomorphic compounds with five-membered heterocyclic units such as 1,3,4-oxadiazole [21–23], 1,2,4-oxadiazole [24,25], isoxazole [26,27], 1,3,4-thiadiazole [28,29], and thiophene [30–32] showed interesting mesomorphic properties. Recently, several structurally diverse liquid crystals based on pyridine were prepared and studied for their mesomorphic properties [33–35].

Furthermore, several liquid crystalline compounds with connecting units including imine, ester, ether, and azo to connect various aromatic rings were prepared and studied for their liquid crystal behavior [36–40]. Since the discovery of 4-methoxybenzylidene-4'-butylaniline at room temperature nematogen [41], much attention has been focused by the researchers as the introduction of Schiff base unit (-CH=N-) promote the stability of mesophase by maintaining the linearity and rigidity. Recently, several thermotropic mesogens based on Schiff base with low molar mass have been synthesized, characterized and investigated [32,42,43].

Mesomorphic behavior of rod-like liquid crystal compounds is essentially reliant on the shape of molecule depending on molecular conformation [44,45]. Even a minor alteration in the structure of mesogens results in changes in their mesomorphic properties significantly. Moreover, the formation of mesophase, type of phase and its thermal stability largely dependent on the central connecting unit and the terminal groups/chains attached to mesogenic compounds [44,46]. Consequently, in the design of new mesogenic compounds the linking unit, terminal groups and flexible hydrocarbon chains are crucial.

2. Materials and Methods

All chemicals were purchased from TCI Company, Japan. Their purity is higher than 98%. Schiff bases were prepared and recrystallized twice from ethanol/water mixture and were checked to be TLC pure, Scheme 1.



Scheme 1. Synthesis of N-arylidene-4-alkyloxbenzenamine **3a–f** (samples **3.a**, **3.b** and **3.e** are reported in Reference [47]).

Synthesis of *N*-Arylidene-4-alkyloxybenzenamine (3a–f)

Alkyloxybenzaldehyde (4.1 mmol) and 4-arylamine (4.1 mmol) equimolar equivalents were dissolved in ethanol (10 mL) and refluxed for two hours. The mixture was filtered after cooling to room temperature. TLC analysis showed that the obtained solid was washed with cold ethanol and recrystallized twice from hot ethanol to yield pure compounds.

(*E*)-*N*-(4-(Hexyloxy)phenyl)-1-(4-(pyridin-4-yl)phenyl)methanimine (3.d)

Yield = 97%, IR (KBr, cm^{-1}): 3041, 2952, 2851 (C-H), 1625 (CH=N), 1597, 1539, 1511, 1408, 1361, 1270, 1183, 1118, 887, 822, 808, 721; ^1H NMR (400 MHz, CDCl_3 , δ ppm): 0.93 (t, $J = 7.2$ Hz, 3H), 1.34–1.39 (m, 4H), 1.45–1.52 (m, 2H), 1.78–1.85 (m, 2H), 3.99 (t, $J = 6.4$ Hz, 2H), 6.96 (dd, $J = 6.8$ Hz, 2H), 7.29 (dd, $J = 6.4$ Hz, 2H), 7.57 (dd, $J = 4.4$ Hz, 2H), 7.77 (d, $J = 8.0$ Hz, 2H), 8.01 (d, $J = 8.4$ Hz, 2H), 8.55 (s, 1H), 8.71 (dd, $J = 4.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 14.10, 22.65, 25.76, 29.28, 31.63, 68.29, 115, 121.57, 122.33, 127.35, 129.24, 137.12, 140.33, 144.30, 147.46, 150.42, 157.00, 158.17.

(*E*)-*N*-(4-(Octyloxy)phenyl)-1-(4-(pyridin-4-yl)phenyl)methanimine (3.e)

Yield = 95%, IR (KBr, cm^{-1}): 3045, 2951, 2852 (C-H), 1621 (CH=N), 1594, 1533, 1505, 1402, 1361, 1275, 1181, 1117, 889, 822, 804, 721; ^1H NMR (400 MHz, CDCl_3 , δ ppm): 0.91 (t, $J = 6.8$ Hz, 3H), 1.31–1.37 (m, 8H), 1.45–1.52 (m, 2H), 1.78–1.85 (m, 2H), 3.99 (t, $J = 6.8$ Hz, 2H), 6.96 (dd, $J = 6.8$ Hz, 2H), 7.29 (dd, $J = 6.8$ Hz, 2H), 7.57 (dd, $J = 4.4$ Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 8.02 (d, $J = 8.4$ Hz, 2H), 8.55 (s, 1H), 8.71 (dd, $J = 4.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 14.16, 22.70, 26.08, 29.28, 29.32, 29.41, 31.85, 68.30, 115.00, 121.57, 122.33, 127.35, 129.24, 137.13, 140.34, 144.31, 147.46, 150.42, 157.00, 158.17.

(*E*)-*N*-(4-(Hexadecyloxy)phenyl)-1-(4-(pyridin-4-yl)phenyl)methanimine (3.f)

Yield = 91%, IR (KBr, cm^{-1}): 3038, 2955, 2847 (C-H), 1618 (CH=N), 1595, 1534, 1501, 1405, 1365, 1277, 1182, 1115, 887, 822, 804, 720; ^1H NMR (400 MHz, CDCl_3 , δ ppm): 0.90 (t, $J = 6.4$ Hz, 3H), 1.28 (m, 26H), 1.73–1.85 (m, 2H), 4.00 (t, $J = 6.4$ Hz, 2H), 6.96 (dd, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 5.6$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 8.0$ Hz, 2H), 8.56 (s, 1H), 8.71 (d, $J = 5.6$ Hz, 2H).

^1H NMR and ^{13}C NMR results (Figures S1–S5) are given in the Supplementary Materials as following: Figure S1: ^1H NMR of compound (OC6) 3.d; Figure S2: ^{13}C NMR of compound (OC6) 3.d; Figure S3: ^1H NMR of compound (OC8) 3.e; Figure S4: ^{13}C NMR of compound (OC8) 3.e; Figure S5: ^1H NMR of compound 3a (OC16) 3.f.

The phase changes in the materials were determined by means of differential scanning calorimetry (DSC), DSC-60A, Shimadzu, Japan. The size of samples was in the range of 2–3 mg. Samples were encapsulated in Al pans and were heated or cooled in inert atmosphere (dry nitrogen atmosphere). Measurements were accomplished at 10.0 $^{\circ}\text{C}/\text{min}$. Samples were heated from room temperature to 200 $^{\circ}\text{C}$ and cooled back to room temperature at the same heating. The transition temperatures for the various phase changes were gained from the endothermic peak minima of enthalpy. The accuracy of temperature recording was better than 1.0 $^{\circ}\text{C}$.

3. Results and Discussion

3.1. Synthesis and Characterization

The ^1H NMR of compounds showed that the terminal methyl group protons were observed as a triplet at δ 0.91 ppm whereas the protons of methylene group directly attached to the aromatic ring observed at δ 2.99 ppm as a triplet. The appearance of singlet at δ 8.55 ppm corresponding to imine linkage proton ($-\text{CH}=\text{N}-$) confirmed the formation of Schiff base for prepared compounds. The protons near the nitrogen of the pyridine ring were observed as a doublet most upfield at δ 8.71 ppm. The rest of the aromatic and aliphatic protons were observed as per the substitution pattern of compounds. In the ^{13}C NMR spectra of new compounds, the terminal methyl carbon was observed most upfield δ 14.10 ppm while methylene carbon directly attached to oxygen were observed at δ 68.29 ppm. The carbon of the imine linkage was appeared most downfield at δ 158.17 ppm whereas two carbons in vicinity to nitrogen of pyridine ring were observed at δ 150.42 ppm.

The rest of the carbons were observed as per the substitution pattern and in agreement with the structures of the new compounds.

3.2. Mesomorphic Behavior

Transition temperatures and the corresponding associated enthalpy changes of the prepared compounds were measured by DSC and displayed in Table 1. The DSC thermograms of the three new alkoxy derivative (3.d, 3.e and 3.f) are presented in Figure 1a–c. All the prepared compounds exhibited dimorphic enantiotropic mesomorphic characteristics whereby the corresponding endotherms were regarded as following according to the increase in temperature: crystalline to smectic B (Cryst.-SmB), SmB to smectic A (SmB-SmA) and SmA-isotropic (SmA-I) transitions. The SmB and SmA mesophases were specified by the existence of the standard Schlieren and focal-conic fan textures.

Table 1. Phase transitions: temperatures (T , °C) and enthalpies (ΔH , kJ/mol) for the prepared compounds 3.a–f. The abbreviations Cr-SmB, SmB-SmA, SmB-I, SmA-I, SmA-N, and N-I refer to the crystalline to smectic B, smectic B smectic A, smectic B to isotropic, smectic A to isotropic, smectic A to nematic and nematic to isotropic transitions, respectively. ΔH refers to the enthalpy changes in kJ/mol for the different phase transitions.

Compound	°C	kJ/mol	°C	kJ/mol	°C	kJ/mol	°C	kJ/mol	°C	kJ/mol
	$T_{\text{Cr-SmB}}$	$\Delta H_{\text{Cr-SmB}}$	$T_{\text{SmB-SmA}}$	$\Delta H_{\text{SmB-SmA}}$	$T_{\text{SmB-I}}$	$\Delta H_{\text{SmA-I}}$	$T_{\text{SmA-N}}$	$\Delta H_{\text{SmA-N}}$	$T_{\text{N-I}}$	$\Delta H_{\text{N-I}}$
3.a (C6)	86.2	28.09					128.0	—	135.0	—
3.b (C8)	95.1	76.02	130.0	3.03			132.2	1.77	134.5	0.46
3.c (C16)	110.9	119.75	112.7	3.78	118.6	3.71				
3.d (-OC ₆)	121.8	35.78	149.9	3.23	170.1	5.61				
3.e (-OC ₈)	113.9	21.23	146.0	2.37	168.1	3.76				
3.f (-OC ₁₆)	112.3	24.62	143.3	2.13	166.6	3.42				

It is worth noting that this study presents a continuation of our systematic work in which we investigate the effect of conjugation length on the mesomorphic behavior on model examples of LCs. In a recent article, we have investigated the effect of introducing 4-phenyl pyridine moiety on LC molecules terminated with alkyl group [48]. The mesophases of new compounds were verified by observing their textures through POM (Figure 2). Observation of mesomorphic behavior of the new compounds bearing the 4-phenylpyridyl mesogens (3.d–f) under the POM showed enantiotropic dimorphic mesomorphism. After heating from crystalline phase to isotropic liquid and again cooling it from its isotropic liquid phase to crystalline phase, all new compounds verify the presence of two mesophases both via POM and DSC thermograms (Table 1). First, SmB phase texture (Figure 2a) appears after melting, and later it turned out to SmA phase (Figure 2b) at elevated temperatures. The SmB and SmA mesophases were identified by the appearance of the standard Schlieren and focal-conic fan textures. All observed LC mesophase textures agree with the literature both with respect to their textures and the associated enthalpy changes recorded by DSC measurements (ΔH values lies between 2.13 and 5.61 kJ/mol).

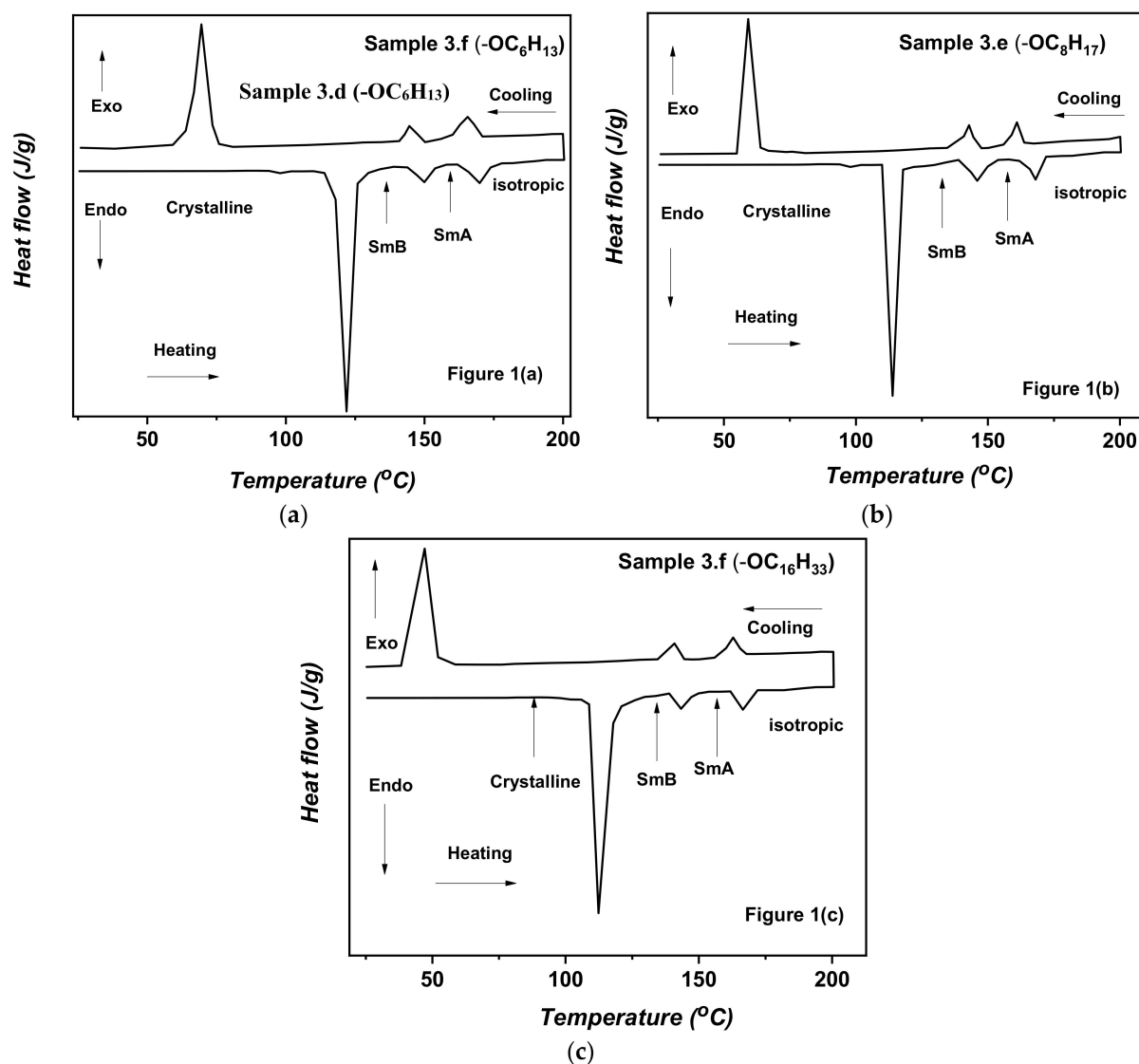


Figure 1. (a–c) DSC thermograms of the new compounds 3.d, 3.e and 3.f during heating and cooling cycles (10 °C min^{−1}).

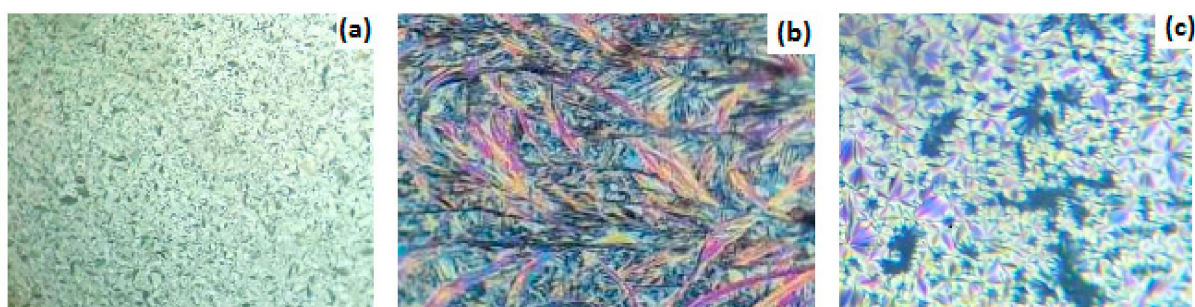


Figure 2. Mesophase textures observed by POM during heating cycle of compound 3.d Smectic B phase at 130.0 °C (a), 3.e Smectic A phase at 158.0 °C (b), 3.f Smectic A phase at 162.0 °C (c).

The effect of variation of the alkyloxy chain length on the mesomorphic behavior of the new compounds is displayed in Figure 3.

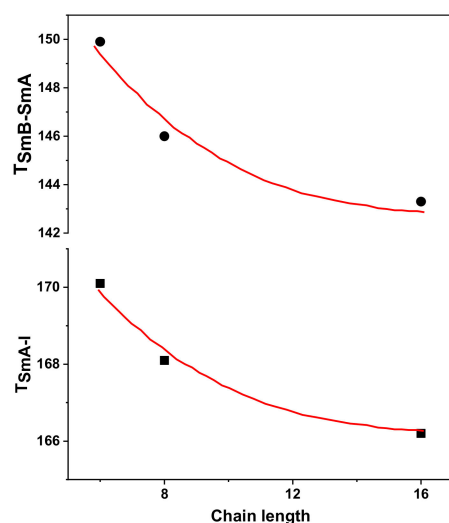


Figure 3. Dependence of the mesophase transition temperatures on the alkoxy chain length.

It is observed that the transition temperatures of SmB/SmA mesophase transition decreases as alkoxy chain length increase. In the same manner, the SmA-I transition temperatures showed similar response upon the increase of the terminal alkoxy group (C6 to C16).

The variation of mesophase temperature ranges of the different observed textures (SmB and SmA) in the new compounds **3.d** to **3.f** is compared to the results obtained for mesomorphic compounds bearing biphenyl moiety and terminated with long chain alkyl groups rather than our new series containing 4-phenyl pyridyl group in their mesogens and terminated with long chains of alkoxy groups. The results are shown in Table 2.

Table 2. Variation of mesophase temperature ranges of the different observed textures for the mesomorphic compounds bearing biphenyl group (alkyl terminated) rather than 4-phenyl pyridine (alkoxy terminated) ends in their mesogens.

Alkyl Chain Length	SmB Range (°C)		SmA Range (°C)	
	Biphenyl	4-Phenyl Pyridine	Biphenyl	4-Phenyl Pyridine
C6	41.8	28.1	–	20.2
C8	34.8	35.1	2.2	22.1
C16	1.8	31.0	5.9	23.3

The increased mesophase stabilities and broadening in the SmA mesomorphic temperature range in the compounds **3d–f** can be rationalized to two different factors. The first factor is the increased pi-pi stacking arising from the extra contribution of the N-atom of the pyridine ring to the total conjugated electrons along the mesogen. The second factor is the presence of two lone pairs of electrons on the oxygen atom of the alkoxy chains which is directly fused to the mesogenic group. The presence of the lone pairs of electrons on the oxygen atom may lead to extra conjugation which in turn increases the length of the mesogenic group (increased pi-pi stacking). Consequently, the mesophase stability is largely increased in alkoxy terminated series of LCs compared to the biphenyl series ended with alkyl chains. This elevation in pi-pi stacking can explain the promoted SmB and SmA mesomorphic order rather than the nematic one even for the sample bearing relatively short hexyloxy chain length (**3.d**). Comparing the effect in the present study with LC having 4-phenyl pyridine and terminated with alkyl groups, the effects of introducing the above explained two factors were more pronounced [48].

3.3. DFT Calculations

Gaussian 9 was used to carry out theoretical DFT computations in the gas phase using DFT and B3LYP 6-311g (d,p) base site. All optimized structures were found to be stable due to the lack of the imaginary frequency. The results of the theoretical calculations of the studied compounds **3.a–f** reveal a non-planar geometry (Figure 4). The phenyl rings, on the other hand, are not coplanar, and the twist angle of the CH=N is affected presence of the pyridine atom that affect the degree of aromaticity conjugated arylidene component. Furthermore, the biphenyl ring and its pyridyl derivative are significantly different in the degree of the aromaticity and consequently the presence of N- heteroatom affects the angle deviated from co-planarity. The twist CH=N angle (θ) = 7.8° for the hexyl derivative **3.a** of the biphenyl and 4.6° for its pyridyl derivative **3.d**. The pyridyl derivative **3.e** (θ) = 7.8° had the higher twist angle, while its longest chain length (C=16) derivative **3.f** had twist angle (θ) = 9.3° . The result of the difference in twist angle of the alkoxy derivatives of the pyridyl and its alkyl derivatives of the biphenyl one could be explained in terms of better conjugation of the π -cloud of aromatic rings with the imino group with the alkoxy one of higher mesomeric resonance effect rather than the hyper conjugated alkyl group, and as a result of the high conjugation, arylidene system is more enforced to be more planar in the case of the alkoxy pyridyl derivatives. While these theoretical molecular geometries may be a good predictor of the preferred molecular structure in the gas phase, the presence of these compounds in liquid crystalline matter condensed phases with a different lowest energy and more elongated species will be favored [49].

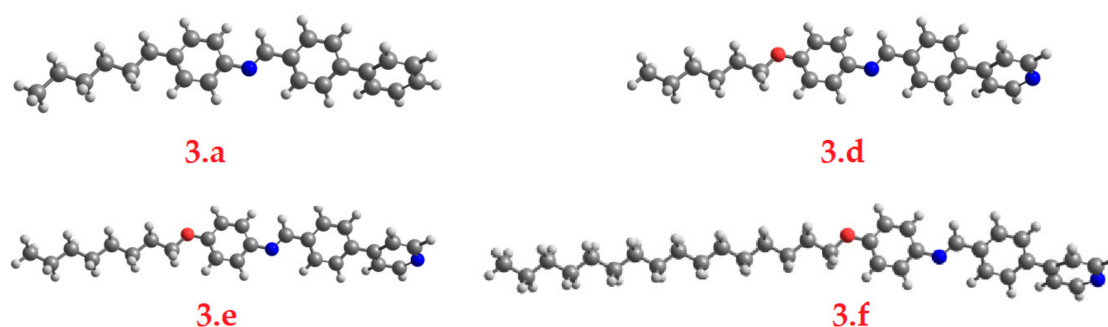


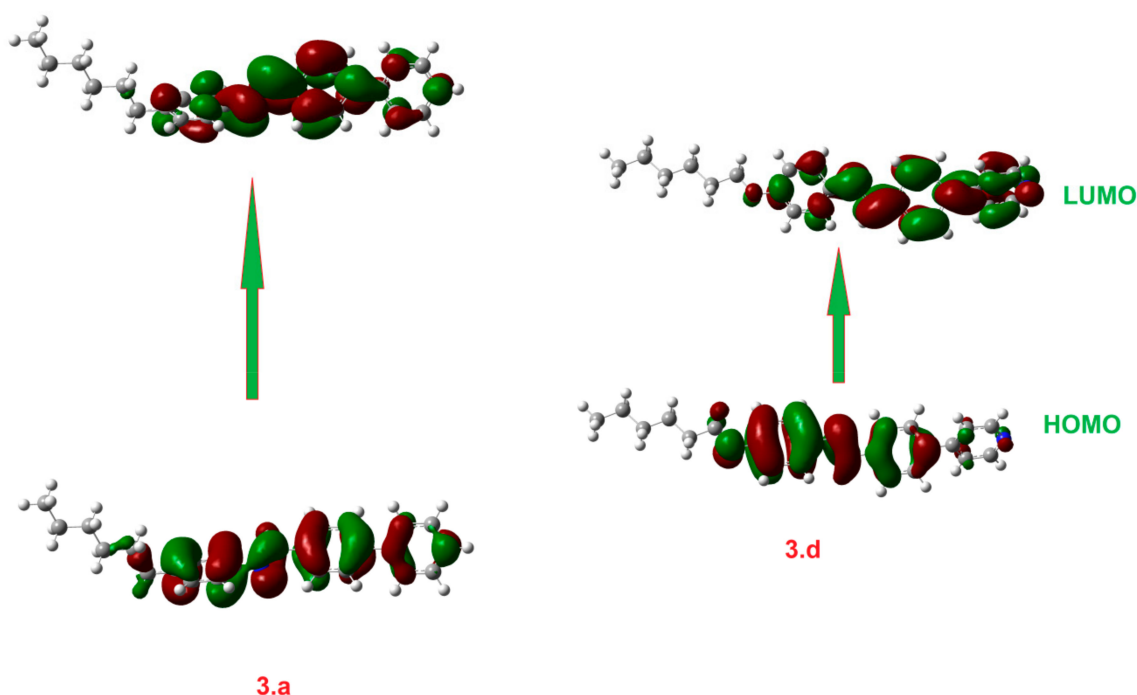
Figure 4. Optimized geometrical structure of the prepared compounds **3.a,d–f**.

3.4. Frontier Molecular Orbitals (FMOs)

The results of the calculated plots of the synthesized compounds frontier molecular orbitals HOMO (highest occupied) and LUMO (lowest unoccupied) are shown in Table 3 and Figure 5. Figure 5 shows how the electron densities of the sites involved in LUMO and HOMO generation are localized on the pyridyl part and its conjugated rings. On the other hand, the electron densities of the FMOs were affected by the degree of conjugated rings affected by the polar alkoxy group as well as the presence of the hetaryl atom. Furthermore, the degree of conjugation and the existence of the N-atom had a substantial impact on the energy levels of the FMOs and the energy gap between them. The presence of a more aromatic ring in the biphenyl derivatives affects the levels of the frontier molecular orbitals. The energy level of the FMOs is dramatically reduced when the N-atom replaces the carbon. Furthermore, the energy difference between the FMOs was significantly altered by the extraconjugation of the alkoxy derivatives **3.d–f** due to the resonance effect. The pyridyl derivative, on the other hand, showed a greater decrease in the energy gap than the phenyl derivative. This was demonstrated by increases in co-planarity in the case of the pyridyl derivative with respect to its phenyl, which resulted in additional more conjugation and a decrease in the FMOs energy gap. On the other hand, there is no difference in the FMOs energy gap and energy difference with the longer chain lengths.

Table 3. FMO Energies e. V. and their values for the prepared compounds **3.a,d–f**.

Compounds	HOMO	LUMO	ΔE
3.a	−5.75	−1.85	3.90
3.d	−5.77	−2.10	3.67
3.e	−5.76	−2.10	3.66
3.f	−5.77	−2.11	3.66

**Figure 5.** The calculated plots for the prepared compounds **3.a,d** of the frontier molecular orbitals.

3.5. Molecular Electrostatic Potential (MEP)

According to molecular electrostatic potential (MEP), the charge distribution map for the synthesized compounds **3.a,d–f** was estimated using the same method of calculations with the same basis sets as shown in Figure 6. Furthermore, the molecular electrostatic potential (MEP) is an important parameter to understand when analyzing the electron density distribution over molecules [49–51]. MEP is also one of the one of excellent tool to predict the intermolecular and/or intramolecular interactions. The existence of the polar N-atom and the connecting CH=N group of the examined compounds had an impact on the localization of the iso-electronic density of the electron rich and electron deficient areas. The Schiff base part CH=N group has the lowest electron density, whereas the terminal alkoxy chain has the maximum electron density. The anticipated charge distribution maps could be used to illustrate how liquid crystals molecular structure assist mesophase behavior change.

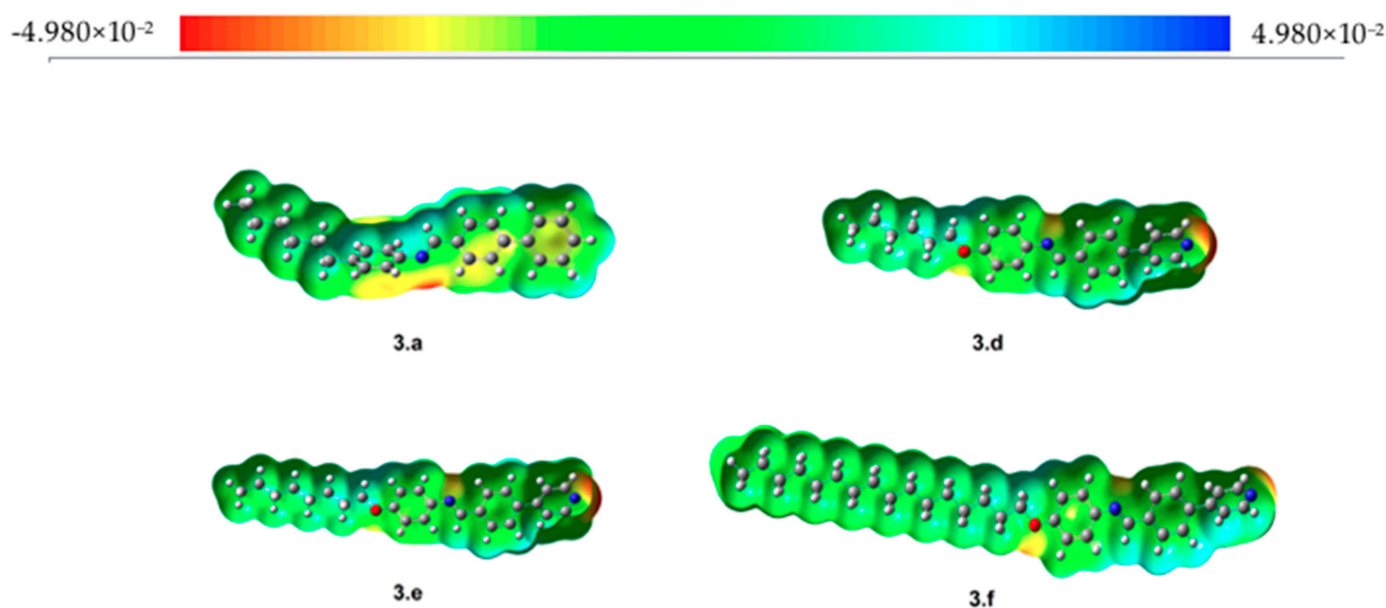


Figure 6. Molecular electrostatic potentials (Hartree) for the prepared compounds 3.a,d–f.

4. Conclusions

A novel series of Schiff base liquid crystals were prepared and investigated. Schiff bases of p-alkyloxy aniline derivatives and 4-phenylpyridine-4'-carbaldehyde were synthesized. The terminal alkoxy groups substituting aniline are of varied chain length, namely C6, C8, and C16. All samples revealed enantiotropic smectic B (SmB) and smectic A (SmA) mesophases. The results are compared to two series of compounds bearing pyridine and biphenyl, respectively, in their mesogens. The thermal stabilities of the different mesophase reduced upon the increment of the alkoxy chain length. The temperature ranges of both the smectic mesophases of new compounds bearing the 4-phenyl pyridine moiety are generally expanded higher than the other two series. In addition, the total mesophase range is greater in the new compounds when compared to their biphenyl analogues. The increased mesophase stabilities and broadening in the SmA mesomorphic temperature range in the new compounds were rationalized to the increased pi-pi stacking arising from the extra contribution of the N-atom of the pyridine ring. A second factor that may contribute effectively is the lone pairs of electrons on the oxygen atom of the alkoxy chains. The presence of the lone pairs of electrons on the oxygen atom imparted extra conjugation and consequently, the mesophase stability increased. The results obtained were in a good agreement with the density functional theory (DFT) theoretical calculations. The result of DFT showed a difference in twist angle as well as the charge distribution maps of the alkoxy derivatives of the pyridyl and its alkyl derivatives and this could explain the difference in the mesomorphic properties.

Supplementary Materials: ^1H NMR and ^{13}C NMR results of the samples 3.d, 3.e and 3.f are given as supplementary materials. They are available at <https://www.mdpi.com/article/10.3390/sym13101832/s1>, Figure S1: ^1H NMR of compound (OC6) 3.d; Figure S2: ^{13}C NMR of compound (OC6) 3.d; Figure S3: ^1H NMR of compound (OC8) 3.e; Figure S4: ^{13}C NMR of compound (OC8) 3.e; Figure S5: ^1H NMR of compound 3a (OC16) 3.f.

Author Contributions: Conceptualization, S.Z.M. and M.H.; methodology, S.Z.M., D.M.A., M.A.A., A.K.A., M.A., K.D.K. and M.H.; validation, S.Z.M. and M.H.; investigation, S.Z.M., D.M.A., K.D.K., M.J. and M.H.; resources, S.Z.M. and M.H.; data curation, S.Z.M.; writing—original draft preparation, S.Z.M. and M.H.; writing—review and editing, S.Z.M., M.J. and M.H.; visualization, S.Z.M.; supervision, S.Z.M. and M.H.; project administration, S.Z.M.; funding acquisition, S.Z.M. All authors have read and agreed to the published version of the manuscript.

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