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New two rings Schiff base liquid crystals; Ball mill synthesis, Mesomorphic, Hammett and DFT studies

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### Abstract

New analogues series of two rings Schiff base comprising different terminal polar substituents changed between N(CH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>O, H, Cl, F, CN and NO<sub>2</sub> were prepared using conventional heating and a ball-milling method. An alkoxy chain substituent contributes one end of their molecular structure. Mesomorphic and optical properties as well as their thermal stability were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and elemental analysis were carried out to elucidate and confirm the molecular structures of the synthesized compounds. The mesophase type and stability of the prepared compounds are rationalized based on the varying Van der Waal volume and polarizability of the terminal groups as well as the intermolecular interactions. After compiling all resulting experimental data and discussing it in the performance of Hammett and Density functional theoretical estimated parameters, it found that the molecular structure and the dipole moment as well as the polarizability of the prepared compounds are highly affected by the electronic nature of the terminal substituent X rather than its volume. Moreover, the mesophase type and its stability were explained in the term of the DFT data and Hammett as well as Van der Waal's volume of the terminal substituents.

**Keywords:** Calamitic liquid crystals, Schiff base, Hammett, DFT, Geometrical structure, Ball mill synthesis.

#### 1. Introduction

During the last few decades, liquid crystals containing Schiff base (or azomethine) linkage have received massive amounts of attention from the discovery of the room temperature-liquid crystal, 4-methoxybenzylidene-4'-butylaniline [1]. Recently, it has been reported that the Schiffs base mesogenic core liquid crystals are known to drive smectic phase formation and has resulted in the discovery of a new family of smectic phases [2, 3]. In the designing of new thermotropic liquid crystals the choosing of a mesogenic core, terminal groups and a flexible chain are the essential specifications [4]. To secure the fact that the molecules have structural linearity and large molecular polarizability a para-substituted phenyl ring is used. [5] Ball milling is a modern environmentally-friendly method and is a mechanical method widely-used to granulate minerals into extremely fine particles and for the preparation or changing of inorganic solids, [6-9] several organic transformations have been achieved by using the ball-milling technique [10-13] including reductions [14] condensations [15, 16] and oxidations [17, 18]. Ball milling is useful for the quick and efficient synthesis of various imines [19, 20]. Generally, the common synthesis by condensation of primary amines with carbonyl compounds in solution needs acid catalysis, elimination of solvent and produced water after the isolation of the product. As a result of the increasing interest that many of the above reactions can be done in a single step with quantitative yields by different states of matter such as gas-solid, liquid-solid or solid-solid reactions [21-24] This approach showed very good performance in comparison to many of the traditional methods in terms of yield, reaction conditions, and time. It has been reported that calamitic low molar mass liquid crystal compounds with two aromatic rings and one or more terminal substituent, i.e. 4-methoxybenzylidene-4'-butylaniline (MBBA), are able to show nematic mesophase at room temperature [25-28]. Furthermore, the polarity effects of the small compact size terminal substituents on the mesomorphic behaviours have been more attention recently [29-35]. Polar substituents, possessing strong dipole moments, have the ability to promote mesomorphic properties [36]. The increased dipole moment enhances

the stability of the lattice and melting temperatures [37]. Lowering the transition temperatures of the mesophase and extension of its temperature range has always been an important aim of studies for many practical applications. One approach to achieve that is mixing compounds with various molecular structures and properties in binary systems [38-46]. Recently, several low molar mass thermotropic Schiff base liquid crystals have been reported and investigated [47-56] Generally, the central linkages and the terminal groups of the liquid crystalline compound play important role for the formation, thermal stability, type, and stability range of the mesophases. [57-65].Thus, the mesogenic portion, terminal groups and flexible chains are the important points in building new mesomorphic compounds. [4] Moreover, studying theoretical calculations for predicting the molecular geometry affects on the thermal properties and connecting them with experiment data is one of our interest [34, 56, 66-76].

Continuing our interest, the goal of the present studies firstly, was to prepare new linear two rings Schiff base liquid crystals through two different ways, conventional and ball-milled methods. Secondly, was to investigate their mesomorphic, thermal and optical behavior with respect to different polarity/size of terminal substituents. Moreover, some parameters estimated from density functional theory (DFT) calculations and Hammett parameters of the attached substituents as well as Van der Waal volume of the terminal X were used to explain the obtained experimental results.



 $\mathbf{X} = Me_2N$ , MeO, H, Cl, F, CN, NO<sub>2</sub>

#### 2. Experimental

N-arylidene-4-(hexyloxy)benzenamines (A-G) were prepared according to the following scheme:



#### A- Conventional method

A mixture of the 4-hexyloxyaniline (790 mg, 4.1 mmol) and 4-substituted benzaldehyde (4.1 mmol) in ethanol (10 ml) were refluxed for two hours. The reaction mixture was cooled and filtered and washed with cold ethanol. The obtained solid was purified by recrystallization twice from hot ethanol to give pure compounds.

#### **B-** Ball mill method

*N*-arylidene-4-(hexyloxy)benzenamines (**A-G**) have been synthesized according to the optimum conditions of our pervious method [12]. A mixture of the 4–hexyloxyaniline (790 mg, 4.1 mmol) and 4-substituted benzaldehyde (4.1 mmol) was introduced into stainless steel vials with 56.6 g weight of stainless steel balls [4 (12.7 mm), 4 (6.3 mm), 4 (3.2 mm)] at 20 Hz frequency for 2 min milling time. The obtained paste was purified by recrystallization twice from hot ethanol to give pure compounds.

### 3. Results and discussion

#### 3.1 Methods of preparation

The synthesis of N-arylidene-4-(hexyloxy)benzenamines (A-G) have been accomplished by two methods, the first method is the conventional method under reflux conditions in ethanol for two hours. The other method is the ball milling method under

solvent free conditions for very short reaction time (2 mins). The reaction proceeded effectively to afford the final product in excellent product yields (92-98%). The equimolar amounts of hexyloxyaniline and substituted benzaldehydes have been subjected to milling under our previous optimum conditions [12]. The reactants have been subjected into 250 cm<sup>3</sup> stainless steel vials with 56.6 g weight of stainless steel balls [4 (12.7 mm), 4 (6.3 mm), 4 (3.2 mm)] then the reaction proceeded at 20 Hz for 2 mins to afford quantitative amounts of the final products. To the best of our knowledge there is no report for the synthesis of liquid crystals under ball milling conditions, so this reaction could be considered as the first real synthesis of liquid crystalline materials under solvent free ball mill method.

Obviously from the NMR spectroscopy the reaction proceeded under both methods to give a mixture of two geometrical isomers (E and Z) their ratio depends on the electronic nature of the terminal substituent (see supplementary data). The investigation of such effects on the stability of the obtained isomers could be an important point for future perspectives either theoretically or experimentally.

#### 3.2. Mesophase behavior

Temperatures of transition and associated enthalpies, as measured by DSC, and phases identified by polarized optical microscopy (POM), for synthesized compounds A-G are tabulated in **Table 1**. DSC thermograms upon cooling for all prepared derivatives A-G are depicted in **Figure 1** as a representative example. The dependence of mesophase transition temperatures and their ranges of stability on the terminal substituents are depicted in **Figure 2**. Data in **Table 1** and **Figure 2** revealed that the analogous derivatives A-G are mesomorphic except the C (X=H) and G (X=NO<sub>2</sub>) compounds. For electron donating groups, compound **B** analogue is dimorphic showing smectic A (SmA) and nematic phases (N) montropically while compound **B** (X=OCH<sub>3</sub>) is purely nematogenic which exhibiting only monotropic nematic phase with small range of stability. Conversely, all members of electron withdrawing groups are mesomorphic exhibiting suitable range of stability except the terminal nitro-substituent (G) is non-mesomorphic. Cl substituted compound (D) observed dimorphic phases upon heating and cooling exhibiting semectic A and nematic mesophases. CN derivative (F) is purely smectogenic possessing enantiotropic SmA phase while **E** analogues (F-substituent) is

monomorphic showing monotropic SmA phase. The stability of the mesophase is influenced by an increase in the polarity and/or polarizability of the mesogenic core of the molecule. Thus the electron-donating ( $N(CH_3)_2$  and  $CH_3O$ ) and electron-withdrawing (Cl, F, and CN) groups enhance the mesophase stability over their unsubstituted analogues (H). Moreover, the low clearing enthalpy associated with compounds A, B  $(X = N(CH_3)_2$  and  $CH_3O)$  is presumably associated with its enhanced molecular biaxiality [67, 77]. In case of  $NO_2$  substituent may be the high molecular packing prevent the formation of the mesophase. It was reported that [78], the stability and types of the mesophase formation are mainly dependent upon the dipole moment of the mesogenic part of the molecule which dependent on the attached terminal polar group and the steric one that varies according to the position and volume of the substituent. Moreover, the introduction of terminal polar substituent with different size and polarity into this type of two ring systems of Schiff base linkage, with suitable terminal alkoxy group, may be effective approaches to offer and improve the mesophase formation and or/ stability of phase transition phenomena depending on its position as well as its donating, as in  $N(CH_3)_2$ , or withdrawing, as CN, power of the substituent. Thus, the introduction of a substituent into a terminal position of a liquid crystalline compound would have two opposing effects: (a) a decrease in the mesophase stability due to steric effect of terminal group [79-83] and (b) an increase or decrease in its polar anisotropy due to its polarizing effect molecule, the dipole moment will depend on the position and polarity of the group [84, 85]. Furthermore, it is clear that terminal groups play an important role in the influence the melting points of the prepared materials.

Table 1: Phase transition temperatures (°C), (enthalpy of transition  $\Delta H$ , kJ/mole), normalized entropy of transition  $\Delta S/R$  and  $\sqrt{T_C}$  (K<sup>1/2</sup>), for compounds A-G

Comp.	X	T <sub>Cr-I</sub>	T <sub>Cr-SmA</sub>	T <sub>Cr-N</sub>	T <sub>SmA-N</sub>	T <sub>SmA-I</sub>	$T_{ m N-I}$	<b>⊿S</b> /R	$\sqrt{T_C}$
Α	$N(CH_3)_2$	-	110.6	-	91.1*	-	94.3*	1.85	19.17
			(30.72)		(3.04)		(1.45)		
В	CH <sub>3</sub> O	-	-	104.7	-	-	101.0	1.91	19.34
				(37.76)			(1.60)		
С	Н	60.5	-	-	-	-	-	-	-
		(36.48)							

D	Cl	-	89.9	-	97.0	-	105.6	3.37	19.46
			(32.90)		(4.01)		(2.96)		
Ε	F	-	84.4	-	-	66.9*	-	3.88	18.44
			(34.63)			(2.16)			
F	CN	-	77.3	-	-	108.6	-	2.61	19.54
			(30.27)			(2.36)			
G	NO <sub>2</sub>	90.9	-	-	-	-	-	-	-
		(35.34)							

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.

\* denotes to monotropic phase transition.



Figure 1: DSC thermograms of compounds prepared (A-G) upon cooling scan with rate 10  $^{\circ}$ C /min.



Figure 2: DSC transitions for all synthesized series A-G.



Figure 3: POM texture of (a) nematic phase of **B** at 99.0  $^{\circ}$ C upon cooling; (b) Smectic A phase of **F** at 106.0  $^{\circ}$ C upon heating.

Mesophase behaviour of calamitic mesogens is impact the molecular-molecular interactions that essentially depends on the molecular geometry of compounds, polarizability of the terminal polar substituent X, as well as the stereo electronic properties of the whole molecule. Moreover, the shape of the liquid crystalline

compounds resulting from the introducing of polar substituent is also an important factor affecting many characteristics [86, 87]. From this point, in the present studied analogues, molecular association of the calamitic molecules, and consequently their mesophases stability ( $T_{\rm C}$ ) and types of mesophase formation depends mainly on the lateral adhesion of linear molecules that could be increase with the increase of the alkoxy chain length (n). Moreover, the end-to-end interactions differ according to the polarity and size of the polar substituent X. The higher molecular polarizability contributed by CN stabilizes the mesophase and consequently enhanced the  $T_{\rm C}$  value. The terminal substituent (X) in the molecules can be placed in the order of enhancing the mesophase stability as:  $\rm CN > Cl > CH_3O > N(CH_3)_2 > F > H \approx NO2$ . However, the order of enhancing the mesophase range as:  $\rm CN > N(CH_3)_2 > F > Cl > CH_3O > H \approx NO2$ .

#### 3.3. Tc and polarizability anisotropy of the $C_{ar}$ -X bonds

The relationship between the polarizability anisotropy ( $\Delta \alpha_X$ ) of bonds to small compact terminal substituent ( $C_{ar}X$ ) and the mesophase stability ( $T_C$ ) was studied by van der Veen [88]. The relation has the form:

$$\boldsymbol{T}_{\mathrm{C}} \propto \left(\Delta \alpha_{\mathrm{M}} + \Delta \alpha_{\mathrm{X}}\right)^2 \tag{1}$$

where  $T_{\rm C}$  is measured in Kelvin. The term  $\Delta \alpha_{\rm M}$  is the anisotropy of the polarizability for all the molecular structure except the terminal substituent, X. Equation (1) can be put in the form [89]:

$$\sqrt{T_{\rm C}} \propto (\Delta \alpha_{\rm M} + \Delta \alpha_{\rm X}) = a \cdot \Delta \alpha_{\rm M} + a \cdot \Delta \alpha_{\rm X}$$
 (2)

where "*a*" is the proportionality constant. Thus, if  $\sqrt{T_{\rm C}}$  is plotted against  $\Delta \alpha_{\rm X}$  for any series of liquid crystalline compounds, a straight line is expected, the slope of which equals "*a*" and intercept equals " $a \Delta \alpha_{\rm M}$ ". Consequently,  $\Delta \alpha_{\rm M}$  will be given by:  $\Delta \alpha_{\rm M} = \text{intercept/slope}.$ 

The values of  $\sqrt{T_C}$  (see **Table 1**) are plotted as a function of  $\Delta \alpha_X$ , for the series **A-G** in **Figure 4**. As shown in **Figure 4**, linear correlation was estimated for all mesomorphic compounds, whereby the slope and the intercept, and consequently  $\Delta \alpha_M$ , were calculated by the least squares method and resulted positive values. It was found that  $\sqrt{T_C}$  increases

linearly with the polarizability anisotropy,  $\Delta \alpha_X$ , of the C<sub>ar</sub>–X bond for the investigated series (**A-G**), suggesting that the proper choice of the terminal polar groups with different polarity and size play an important role in the stability of the mesophase. Furthermore, the presence of terminal substituents with different polarity and volume are more essential to enhancement the polarizability of the imino linkage by positive inductive effect (+I), and, consequently the polarizability anisotropy of the whole molecular structure [84].



**Figure 4:** Dependency of the mesophase stability ( $\sqrt{T_{\rm C}}$ ) on the polarizability anisotropy ( $\Delta \alpha_{\rm X}$ ) of the terminal substituent (X) for series A-G.

#### 3.3. DFT calculations

#### 3.3.1. The geometrical structure

Gaussian 09 software was used for DFT calculations for the studied compounds [90]. DFT/B3LYP methods using 6-31G (d,p) basis set was selected for the calculations. The geometries were optimized by minimizing the energies with respect to all geometrical parameters without imposing any molecular symmetry constraints. The structures of the optimized geometries had been drawn with Gauss View [91]. Also, calculations frequencies were carried out by the same level of theory. The frequency calculations showed that all structures were stationary points in the geometry optimization method with none imaginary frequencies.

In order to investigate the effect of substituents on many properties, the relationship between Hammett substituent constants ( $\sigma$ ) and variable parameters such as  $\lambda_{max}$  of UV-Vis absorption spectra, the energy gap between the FMO, liquid crystalline mesophase stability ......etc has been studied. Hammett substituent coefficient ( $\sigma$ ) is one of the

major tools that are used to evaluate the electronic effect of the substituents upon the reaction rate [92]. The results revealed that all compounds are having non-planar geometry. Generally, the deviation from linearity being variable depends upon the type of the compound. The twist angle between the two phenyl rings, which predicted from DFT calculations, is highly affected by the electronic effect of the terminal substituent X, **Figure 5, Table 2**. However, all calculations of the optimum and stable molecular structure of compounds under investigation have been performed for individual molecules in gas phase, consequently, the calculated twist angles could be different in condensed phases such as liquid crystals and crystals [93].



Figure 5: Estimated geometrical structure and twist angles of compounds A-G.

Recently, we have reported the relationship between the molecular geometry twist angle and thermal and mesomorphic properties of synthesized Schiff base ester liquid crystals, where the molecular geometry twist angle is highly affected with the electronic nature of the substituent [34]. The relationship between the calculated angles and Hammett substituent coefficient ( $\sigma$ ) [94] of compounds **A-G**, **Figure 6a**, showed that as the Hammett substituent coefficient goes to more positive value the twist angle decreases while the highly electron donating substituent NMe<sub>2</sub> showed the most non-planar compound with twist angle 33.00°. On the other hand, while the substituent X in terminal position there is no effect of Van der Waal volume on the planarity of the prepared compounds and this could be good evidence that the twisting of the two phenyl rings is due to the electronic effect not the steric hindrance one, **Figure 6b**.

Compound	Van der Waal volume	Hammett substituent coefficient (σ)	Twist angle		
Α	37.07	-0.13	33.00		
В	14.37	-0.11	30.92		
С	3.50	0.00	30.32		
D	12.00	0.24	29.68		
Е	5.80	0.06	29.16		
F	14.70	0.67	26.95		
G	16.80	0.79	22.43		

**Table 2.** Hammett substituent coefficient ( $\sigma$ ), Van der Waal volume of terminal X and estimated twist angle of compounds A-G



**Figure 6**: Correlation between the twist angles against (a) Hammett substituent coefficients  $\sigma$  and (b)Van der Waal volume of terminal X of compounds **A-G**.

The calculated thermal parameters, dipole moment and the polarizability of the prepared liquid crystalline compounds A-G are summarized in Table 3. As shown from Figure 7, the dipole moment is highly impacted by the electronic nature of the substituent X. excluding the unsubstituted derivative C, which is more positive Hammett constant and more polar compound. The most electron withdrawing group  $(NO_2)$  showed the highest dipole moment (8.2 Debye). The results of the calculated

dipole moment could illustrate the non mesomorphic properties of the unsubstituted and the nitro derivatives. The terminal neat derivative ,**C**, showed the least polarity with  $\mu = 1.1$  Debye, where this small value of the dipole moment cannot permit a significant interaction neither end to end nor side by side to arrange the molecules in nematic or semectic phases. On the other hand, the large dipole moment resulted by the highest electron withdrawing NO<sub>2</sub>-group could makes a very high lateral interaction that opposes the liquid crystalline mesophase property, thus prevent the mesophase formation. Moreover, the high value of dipole moment of the F- and CNgroups allows a high parallel interaction to enhance a smectic A mesophase, while the lower dipole moment in case of Cl-, MeO, and Me<sub>2</sub>N predominates the terminal interaction to give a nematic mesophase. Such variation in the polarity is expected to be accompanied by a parallel behaviour in the stability of the mesophase. However, the presence of the smectic mesophase in addition to the nematic one could be due to the large Van der Waal volume of the Me<sub>2</sub>N group that permits a favorable space filling and thus enhance the molecular packing of molecules, **Figure 7**.

Table 3. Thermal parameters (Hartree/Particle), Dipole Moment (Debye) and polarizability of compounds A-G.

Parameter	Α	В	С	D	Ε	F	G
E <sub>corr</sub>	0.451539	0.410489	0.378469	0.368535	0.369890	0.376839	0.380132
ZPVE	-1001.32539	-981.92166	-867.43777	-1327.05298	-966.69402	-959.67370	-1071.91841
E <sub>tot</sub>	-1001.300529	-981.898482	-867.417306	-1327.031211	-966.672656	-959.651417	-1071.895335
Н	-1001.299585	-981.897538	-867.416362	-1327.030267	-966.671712	-959.650473	-1071.894390
G	-1001.383911	-981.978376	-867.490811	-1327.108036	-966.748249	-959.729290	-1071.975600
Dipole moment	3.2188	1.7389	1.1403	4.0362	3.4335	6.8760	8.2444
Polarizability α	307.04	278.35	252.00	270.77	253.22	284.89	296.04

ZPVE: Sum of electronic and zero-point energies; Etot: Sum of electronic and thermal energies; H: Sum of electronic and thermal enthalpies; G: Sum of electronic and thermal free energies.



Figure 7: Dependence of calculated dipole moments and Hammett substituent coefficient ( $\sigma$ ) of compounds A-G.



Figure 8: Correlation between the calculated polarizability  $\alpha$  against (a) Hammett substituent coefficients  $\sigma$  and (b) Van der Waal volume of terminal X of compounds A-G.

Other factors are the polarizability [78, 95, 96] and Van der Waal volume of the terminal substituent [94] also affect the type of the mesophase as well as the phase stability temperature,  $T_c$ . To illustrate the impact of these factors, firstly, we correlate the calculated polarizability to Hammett substituent coefficient  $\sigma$  (Figure 8a) and the calculated polarizability to Van der Waal volume of the substituent (Figure 8b) then the  $T_c$  values are displayed graphically against Van der Waal volume of the

substituent (**Figure 9a**) and the polarizability of substituent X (**Figure 9b**). The results suggested that the Van der Waal volume and polarizability resulted due to the attachment of the substituent, X, impact the mesophase stability of the compounds under investigation. The higher mesophase stability and mesophase range of NMe<sub>2</sub> and CN derivatives could be attributed to their high polar nature as well as the extra conjugation due to the nitrogen atom donation of the NMe<sub>2</sub> or the presence of the triple bond of CN group in conjugation with the  $\pi$ -cloud, which increases the overall polarizability compared with unsubstituted and halo derivatives. Moreover, the large size of NMe<sub>2</sub> with respect to CH<sub>3</sub>O enhances their molecular packing due to higher space filling. The lower mesophase thermal stability of halo derivative could be due to their lower polarizability as well as smaller size. It could be concluded that comparable effects on the type as well as the thermal stability of the mesophases due to the presence of polarizable atom that affect on the dipole moment and polarizability to enhance the intermolecular attraction between molecules and a bulk terminal groups those facilitate the molecular space-filling at the terminal moiety. [29]



Figure 9: Correlation between the *T*c against (a) Hammett substituent coefficients  $\sigma$  and (b) Van der Waal volume of terminal X

#### 3.3.2. Frontier molecular orbitals and UV-visible spectroscopy

Optical applications of non-linear optical (NLO) liquid crystals are highly affect by the energy difference between the frontier molecular orbitals (FMOs), HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) [97, 98]. Moreover, this energy gap between FMOs is a good tool for prediction of important

parameters such as chemical hardness ( $\eta$ ), global softness (S) and polarizability ( $\alpha$ ). Figure 10 illustrates the calculated ground state isodensity surface plots for the FMOs of A-G. Table 3 summarizes the values of the FMO energy gap and the global softness (S) and the experimental  $\lambda_{max}$ . As shown from **Table 4** and **Figures 10**, **11** the global softness as well as the experimental maximum absorption ( $\lambda_{max}$ ) were affecting by the FMO energy gap and the electronic nature of the terminal substituent. The experimental results of the UV-Vis absorption are constituent with that of the theoretical calculations of the energy gab between the FMO. As the energy gab between the FMO decreases the  $\lambda_{max}$ decreases. The attachment of electron donating substituents (Me<sub>2</sub>N, MeO) of the phenyl ring  $(\mathbf{A}, \mathbf{B})$  produces bathochromic shifts of the band wavelength absorption maximum as compared to the unsubstituted derivative C. The lowest energy FMO electronic transitions of  $n-\pi^*$  electronic transition due to the resonance that present a double bond character of the methoxy and dimethylamino groups enhancing the push-pull character of molecules and consequently, makes red shift (see Figure 12). [99, 100] On the other hand, if  $\sigma$  value is negative, which have electron withdrawing substituent F, Cl, CN and NO<sub>2</sub>, they cause red shift of the  $\lambda_{max}$  of these molecules. The electron donation of the Cl group is higher than that of the F-group of the more electronegative character and so the  $\lambda_{\text{max}}$  of the chloro derivative (**D**) is longer than that of the flouro (**E**). While, the extra conjugation of the CN and  $NO_2$  derivatives (**F**, **G**) decreases the energy gaps of the FMO that causes a bathochromic shift. As shown from Figure 13 a, the relation between the  $\lambda_{\text{max}}$  and the energy gap between the FMO is almost linear except for the NMe<sub>2</sub> (A) this could be explained in the term of the high donation of this group. Moreover, the deviation of the highest electron donation  $NMe_2$  and the highest electron withdrawing  $NO_2$  group from the linear relationship of the  $\lambda_{max}$  with Hammett substituent coefficient ( $\sigma$ ) could be illustrated in term of their high electron nature as well as their large Van de Waal volume Figure 13 b.



**Figure 10:** The calculated ground state isodensity surface plots for frontier molecular orbitals of compounds **A-G** 

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Figure 11: UV–vis spectra of compounds A-G in dichloromethane at 25°C.



Figure 12: Resonating structures of compounds A, B



**Figure 13**: Correlation between the  $\lambda_{max}$  against (a)  $\Delta E(E_{LUMO}-E_{HOMO})$  and (b) Hammett substituent coefficient ( $\sigma$ ) of compounds **A-G**.

Compound	E <sub>HOMO</sub> (a.u)	E <sub>LUMO</sub> (a.u)	$\Delta E(E_{LUMO}-E_{HOMO})$ (a.u)	$S=1/\Delta E$	λ <sub>max exp</sub>
Α	-0.18580	-0.04575	0.14005	7.140307	358.2
В	-0.20267	-0.05620	0.14647	6.827337	333.6
С	-0.20946	-0.06311	0.14635	6.832935	333.2
D	-0.21592	-0.07341	0.14251	7.017051	340.4
E	-0.21389	-0.06877	0.14512	6.890849	334.0
F	-0.22201	-0.08971	0.13230	7.558579	356.4
G	-0.22721	-0.11804	0.10917	9.160026	379.8

Table 4. Molecular orbital energies, hardness  $(\eta)$  and global softness (S) of compounds A-G

#### 3.3.3. Molecular electrostatic potential (MEP)

The charge distribution map for the compounds A-G was calculated under the same basis sets according to molecular electrostatic potential (MEP, Figure 14). The red region (negatively charged atomic sites) was localized on the oxygen atoms and the nitrogen atom of the imino group, while alkyl chains showed the least negatively charged atomic sites (blue regions). As shown from Figure 14, the conformation of the electronic nature of the terminal substituent (X) that affects the orientation of the charge distribution map; this could impact on the type and stability of the mesophase by alteration of the competitive interaction between end-to-end and side-side interaction. Recently, we reported the relationship between the theoretical charge distribution and the experimental mesophase type [101-103]. The alteration of the charge distribution on the molecules due to more electron donation or

electron acceptance could predominate the terminal aggregation to enhance the nematic mesophase or the parallel interaction to give a semectic mesophase. Moreover, the high separation of the charges as in case of the nitro derivative G is a good reason for its non mesomorphic.



Figure 14: Molecular electrostatic potentials (MEP) of compounds A-G.

## 4. Conclusions

A new Schiff base series, *N*-4-substitutedbenzylidene-4-(hexyloxy)benzenamines was successfully synthesized and prepared by ball milling method. Molecular structures were confirmed via elemental analyses, FT-IR, and <sup>1</sup>H and C<sup>13</sup>-NMR spectroscopy. Mesomorphic and optical behaviors of prepared compounds were investigated by DSC, POM and UV- spectroscopy.

The study revealed that:

1- All prepared Schiff base compounds are mesomorphic except the NO<sub>2</sub> and unsubstituted derivatives not exhibited any liquid crystal phases.

2- The molecular structures of the prepared compounds are highly affected by the electronic nature of the terminal substituent X rather than its volume.

3- The mesophase formation and/or stability of the phase depends mainly upon the size and polarity of terminal group as well as the polarizability of whole structure and other parameters that impacted by the terminal substituent, X.

4- The high dipole moment of the  $NO_2$  derivative and the least of the terminally neat compound explain their non mesomorphic behaviors.

5- Finally, the estimated charge distribution varied by the polarity of the terminal substituent, X has high effects on the type and stability of the observed mesophase.

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Figure 1









 $\Delta \alpha_{e} \times 10_{24} / cm_{3}$ 











Figure 9











Wavelength, nm



X = NMe<sub>2</sub>, MeO



