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Theoretical and Experimental Studies on Liquid Crystals-The Role of Position of Oxygen

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Abstract The present article deals with the theoretical and experimental studies on novel liquid crystals. Theoretical studies on nematic liquid crystals viz. 4-octylphenyl-6-octyloxy-2-naphthoate (NAPHE1), and 6-octyloxy-2-naphthyl-4-octyloxybenzoate (NAPHE2) using the density functional theory (DFT) method has been carried out. The structural and electrochemical properties such as HOMO, LUMO energies, and energy gap (Eg) have been investigated. It has been observed that the energy gap is increased due to the substitution of oxygen. Further, the four Schiff's base compounds are synthesized and characterized by using TM and DSC.

Keywords Liquid crystals, DFT method, TM, DSC

1. Introduction

Liquid Crystals (LCs) are soft condensed matter and now commonplace in displays devices, light modulator, temperature sensor and optical communication networks [1]. These demands are being met by the continuous advances [2] in the theoretical knowledge and the software technologies. This provides an informative database for further computations, and support to the experimental observations [3]. They have the different phases like nematic, smectic and cholesteric are innovative class of functional materials and have attracted the great deal of attention due to their various applications in electro-optics. The liquid crystal characteristics need to be satisfied for many applications such as stability of mesophase range, and existence of phases at a desired temperature [4]. The terminal groups present in a molecule are finding an increasingly influential role because of their polarity. The liquid crystal properties mainly the clearing temperature and enthalpy of transitions are influenced by the end chains. It is well known that physical and chemical properties of the liquid crystal molecules change with the length of alkyl chains [5].

The spectroscopic and structural aspects pose big challenges to the interplay between theories, and experiments, with important implications to the photophysics, and chemistry of the materials containing electron- donating, and electron- withdrawing substituent effects [6]. In general, two types of structural modifications are possible in any chemical system: chain and ring. The present article involves the modification of first type. The Schiff's base liquid crystals occupy a special place, among many chemical systems that are found to exhibit a liquid crystalline nature, as they present scenario with a wide incidence of polymorphism [7]. N (*p*-*n*-alkoxy benzylidene) *p*-*n*-alkyl aniline are popularly known as *n*O.*m* compounds represent an interesting case of liquid crystals owing to the presence of oxygen atom bridging the essential rigid core to the flexible end chains [8]. It is often found that the lower members of homologous series are purely or predominantly nematic, while the higher members, the smectic state encroaches on, and eventually prevents the observation of nematic. Though much of the experimental work has been carried out to infer the details of growth of nematic liquid crystal from isotropic liquid, the scarcely distributed data across the growth of smectic phases from the isotropic liquid are yet to be furnished [9].

The compounds chosen for the present theoretical investigations NAPHE1, and NAPHE2. The structural and electrochemical properties such as Highest Occupied Molecular Orbital, HOMO (H), Lowest Unoccupied Molecular Orbital, LUMO (L) energies, and energy gap ($E_g = E_L - E_H$) have been investigated. Further, experimental investigations on the four synthesized compounds namely; N (*p*-*n*-Octyloxy benzylidene) *p*-*n*-Pentyl aniline (8O.5), N (*p*-*n*-Octyl benzylidene) *p*-*n*-Pentyloxy aniline (8.O5), N (*p*-*n*-Octyloxy benzylidene) *p*-*n*-Pentyloxy aniline (8O.O5) and N (*p*-*n*-Octyl benzylidene) *p*-*n*-Pentyl aniline (8.5) have been carried out. In the homologous series, the Octyl group acts as a boundary between nematic and smectic polymesomorphism. The position of oxygen atom present in the terminal chain varied from either side of the core, on both sides and is removed from the terminal chain. The observed

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values are discussed in the light of earlier data available on Schiff's base *n*O.*m* compounds [10]. An examination of thermodynamic data reveals that NAPHE1, and NAPHE2 molecules exhibit nematic- isotropic transition at 380.2K, and 406.1K [11] respectively.

2. Theoretical and Experimental Details

2.1. Theoretical Details

The first method is based on density functional theory (DFT). An understanding of absorption behavior requires the knowledge of molecular orbitals properties, spectral shifts, and appropriate excited states. Moreover, their photophysics, and chemistry represent a challenge in understanding of the excited states dynamics. The main difficulties against reliable theoretical approaches are concerned with the size of systems, and the presence of strong electron correlation effects. Both the properties are difficult to treat in the framework of the quantum mechanical methods rooted in the Hartree–Fock (HF) theory. The density functional theory (DFT) is successful to evaluate a variety of ground-state properties with accuracy close to that of the post-HF methods [12].

An important factor that determines the accuracy of time-dependent density functional theory (TDDFT) excitation energies is the exchange correlation functional used in the calculation. The use of these hybrid functionals yields good accounts of the vertical excitation energies of the excited states with substantial charge transfer character. In this context, the remarkable structural predictions have been obtained especially, using the 'hybrid' density functionals [13] such as Becke3-Lee-Yang-Parr (B3LYP) [14] combining 'exact exchange' with the gradient-corrected density functionals. As a consequence, there is currently a great interest in extending density functional theory (DFT) to excited electronic states. The time- dependent density functional theory (TDDFT) approach offers a rigorous route to the calculation of vertical electronic excitation energies, and the other spectral characteristics [15].

2.2. Experimental Details

The compounds are prepared by condensation of the corresponding benzaldehyde (0.1mole) and aniline (0.1mole) on refluxing with absolute ethanol in the presence of few drops of glacial acetic acid [16]. After refluxing the reactants for four hours, solvent is removed by distillation under reduced pressure and the pure compound is recrystallized from absolute ethanol at low temperature. The optical textural observations [17] are made with an OLYMPUS DX 50 polarizing microscope equipped with DP 10 CCD display, in conjunction with an INSTEC temperature controller of accuracy ±0.1°C. The calorimetric investigations are carried out using a Perkin-Elmer DSC-7 instrument.

3. Results and Discussion

The chemical structures of NAPHE1 and NAPHE2 have been shown in Figure 1. The density functional theory (DFT) optimized electronic structures have been shown in Figure 2. The general molecular structure of benzylidene aniline compounds is shown in Figure 3.

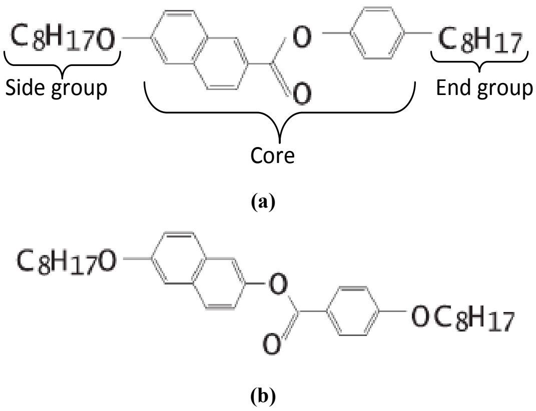

Figure 1. The chemical structure of NAPHE1 ($C_{33}H_{44}O_3$), and NAPHE2 ($C_{33}H_{44}O_4$) molecules

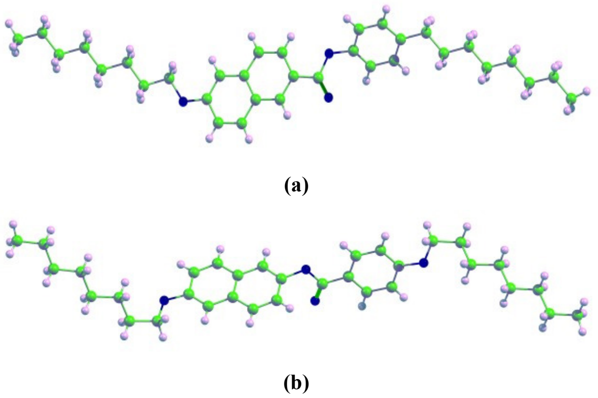

Figure 2. The density functional theory (DFT) optimized electronic structures of (a) NAPHE1 and (b) NAPHE2 molecules (Green: Carbon, Blue: Oxygen, and Pink: Hydrogen atoms)

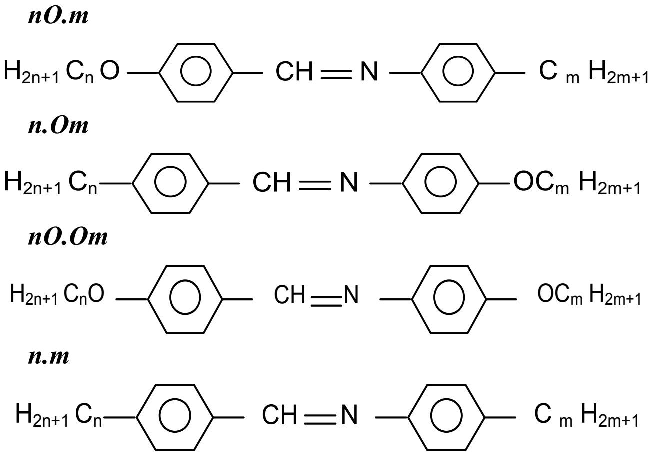

Figure 3. The general structure of *n*O.*m*, *n*.O*m*, *n*O.O*m* and *n*.*m* compounds

3.1. Part First: Theoretical

3.1.1. Substituent Induced Shifts

The density functional theory (DFT) data shows that NAPHE1 molecule exhibits absorption maxima (λ_{max}) at 201.76nm, and NAPHE2 at 239.84nm. Thus, the substitution of oxygen atom (with inversion of direction of ester linkage) in NAPHE1 molecule (forming NAPHE2) leads to a red-shift (the shift of absorption maxima to a longer wavelength), and also causes the hypochromic effect (decrement in absorbance). The HOMO (H), LUMO (L) energies, and energy band gap (E_g) values have reported in Table 1. Evidently, the HOMO (H), LUMO (L) energies, and energy gap (E_g) values have been found to be increased due to the substitution.

It has been observed that the substitution of electro negative atom (oxygen) has a dominant effect on the spectral parameters. The substituent induced red-shift of absorption wavelength causes a decrement in excited energies. This ultimately, affects the other spectral parameters.

Table 1. The HOMO (H), LUMO (L) energies, and the band gap (E_g=E_L-E_H) values of pure NAPHE1, and NAPHE2 molecules using density functional theory (DFT) method

Molecule	Method	H/ eV	L/ eV	E_g/ eV
NAPHE1	DFT	-8.16	-0.76	7.40
NAPHE2	DFT	-7.83	-0.61	7.42

3.1.2. Intensity Profiles of NAPHE1 and NAPHE2

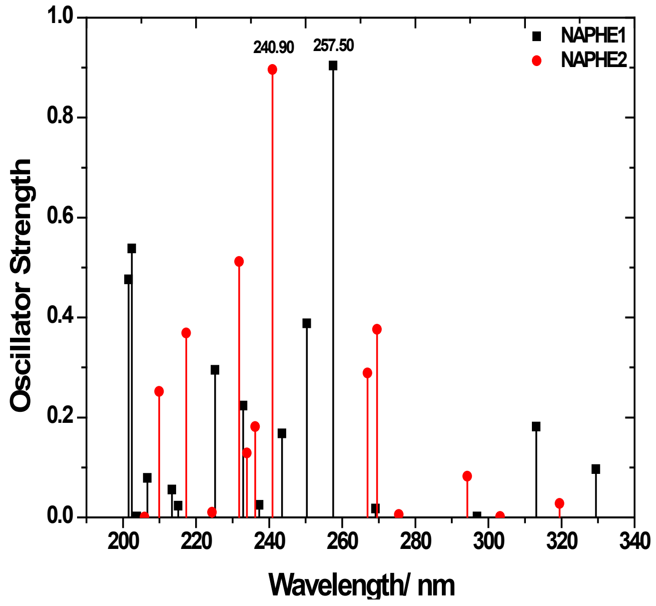

Figure 4. Intensity profiles of NAPHE1 and NAPHE2 molecules using density functional theory (DFT) data

The oscillator strength (*f*) is a dimensionless quantity that expresses the probability of absorption of electromagnetic radiation in transitions between energy levels of an atom or molecule. It indicates the allowedness of electronic transitions in a molecule, and it is particularly valuable as a method of comparing ‘transition strengths’ between different types of quantum mechanical systems. A graph has been plotted between wavelength, and oscillator strength (*f*) (Figure 4) to understand the intensity profiles of the compounds. It may be observed from the figure that NAPHE1 molecule exhibits the highest oscillator strength (*f*) at 257.50nm, while NAPHE2 molecule at 240.90nm. Further, NAPHE1, and NAPHE2 molecules exhibits the last intensity peak around 330nm, and 320nm respectively. This indicates the much flexibility of NAPHE1 molecule for electronic transitions over a long wavelength region. Further, this causes high photo sensitivity for NAPHE1 molecule, which may be exploited for electro-optic applications. The continuous decrease in oscillator strength (*f*) (Figure 4) clearly indicates the breakage of aromatic rings with respect to the higher wavelengths, and subsequently loosing the photo sensitivity.

3.2. Part Second: Experimental

The phase variants exhibited by synthesized compounds along with the phase transition temperatures and the corresponding enthalpy values are listed in Table 2. The phase transition temperature observed by thermal microscopy is found to be reasonable agreement with the DSC thermogram as shown in Figure 5.

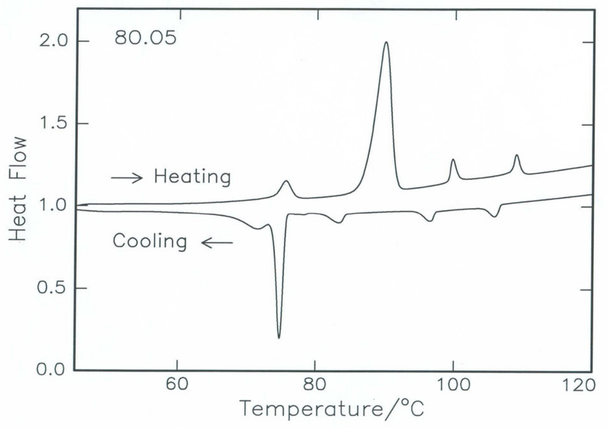

Figure 5. The DSC heating and cooling thermogram of 8O.O5 compound at scan rate 10°C/min

The compound 8O.O5 is exhibiting a pure smectogenic character among the four compounds, as observed in case of 8O.5 compound [18]. At room temperature, the compounds 8.O5 and 8.5 are liquid. The obtained 8O.O5 compound is white crystalline solid, stable at room temperature. Moreover, it exhibits a high degree of thermal stability when subjected to repeated thermal scans during the thermal microscopy and DSC studies. On cooling from the isotropic melt, the compound 8O.O5 shows a smectic phase in the form of batonnets at 104.6°C. These batonnets float in the isotropic phase are observed to coalesce and form focal conic fan texture with the decrease of temperature. This phase also exhibits pseudo isotropic texture in the homeotropic region, revealing the phase as an orthogonal phase. These observations are similar to those observed in the case of lower homologues of 13O.*m*, 14O.*m* and 16O.*m* series of compounds [19] indicating the phase in the present case as of smectic-A (*see* Plate 1).

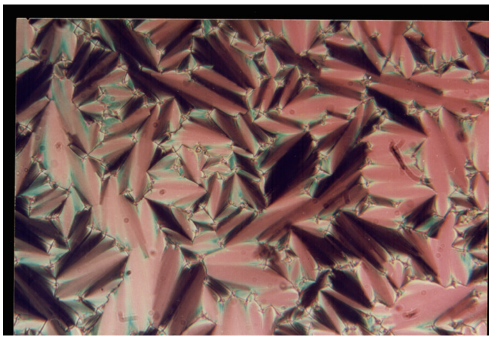

Plate 1. Smectic-A focal conic fan texture observed in 8O.O5 compound at 104.6°C

Further, lowering of temperature results in the appearance of transient transition bars across the fans and these bars slowly disappear and transform to smooth focal conic fans at 95.3°C. The appearance of transient transition bars and the formation of smooth focal conic fan texture with reduced discontinuities at the focal conic domain boundaries infer that transformation (Plates 2 and 3) is from smectic-A to smectic-B as observed in *n*O.*m* compounds with smectic-A and smectic-B phase sequence [20]. On further cooling, the smectic-B phase exhibits striped broken focal conic fan texture from smooth focal conic texture at 81.9°C. These observations are similar to those observed in the case of other *n*O.*m* compounds, to indicate that the phase is smectic-G (Plate 4). The smectic-G phase transforms into solid crystal phase on further cooling of the sample at 73.6°C.

A comparative picture of liquid crystallinity is listed in Table 3 for better understanding the influence of oxygen in benzylidene aniline compounds. A glance at lower homologous series, reveals, *n* =1 and 2, *m* = 5, the shifting of position of oxygen cause the liquid crystallinity to quench while removal of the same cause the compounds to become a room temperature liquid. In middle homologue, *n* = *m* =5, the change in position of oxygen on both sides/removal has effect only on liquid crystalline ranges but not on the stability whereas in higher homologous, *n* = 8 and *m* = 5, the compounds become room temperature liquid as observed in case of 8.O5 and 8.5.

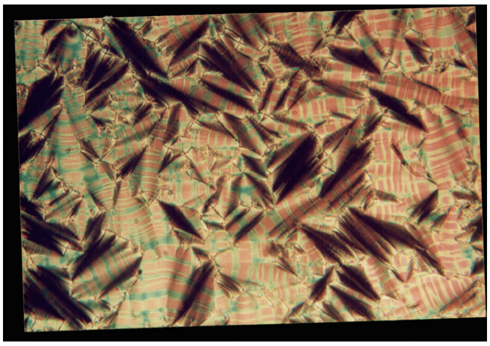

Plate 2. Smectic-A to Smectic-B transient transition bars observed in 8O.O5 compound at 95.3°C

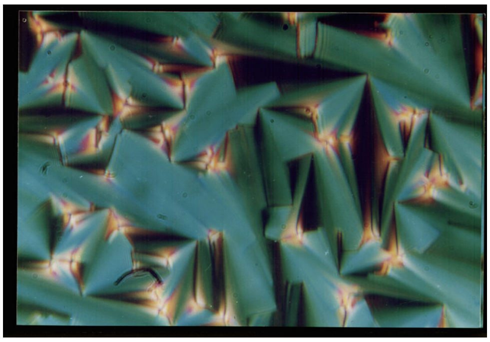

Plate 3. Smectic-B texture observed in 8O. O5 compound

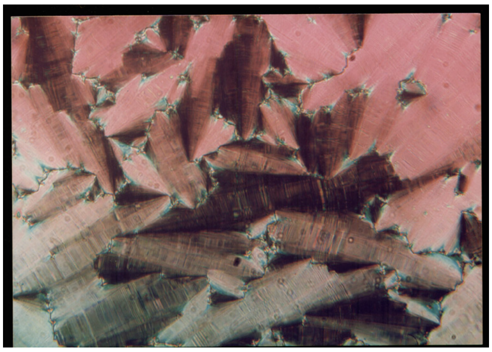

Plate 4. Paramorphic Smectic-G textures observed in 8O. O5 compound at 81.9°C

Table 2. The transition temperatures in °C along with the enthalpy (J/gm) values are shown

Compound	Phase	Method	Cycle	I-A	A-B	B-G	G-K
8O.5*	ABG	TM	Cooling	85.7	70.8	52.7	42.2
8.O5	Room	Temp.	Liqud				
8O.O5	ABG	DSC	Heating	108.8	99.6		89.7
			ΔH/J/gm	4.0	4.2		77.8
			Cooling	105.8	96.4	83.2	74.7
			ΔH/J/gm	3.7	3.7	4.2	49.8
		TM	Cooling	104.6	95.3	81.9	73.6
8.5	Room	Temp.	Liquid				

*Reference [18]
Phase ABG = Smectic-A, Smectic-B & Smectic-G

Table 3. A comparative picture of liquid crystallinity is listed in the table below

Compounds \ n	1	2	5	8
nO.5	23.1	67.4	49.8	43.5
n.O5	0	0	36.1	0
nO.O5	11.7	30.8	0.6	31
n.5	0	0	25.8	0

3.2.1. Influence of Oxygen's Position on Compounds

The position of oxygen in the aldehyde side, N (*p*-*n*-Octyloxybenzylidene) *p*-*n*-Pentyl aniline (8O.5) compound exhibiting its smectogenic character as smectic-A, smectic-B and smectic-G at above room temperature [18]. However, the change in position of oxygen from aldehyde side to the aniline side N (*p*-*n*-Octylbenzylidene) *p*-*n*-Pentyloxy aniline (8.O5) causes the compound to become room temperature liquid. But the effect is less prominence in the case of middle homologue (5O.5 and 5.O5) because both are exhibiting liquid crystalline nature at above room temperature level [21]. Furthermore, in lower homologous series like 1O.5, 1.O5 and 2O.5, 2.O5, there is no pronounced effect is observed on melting/clearing temperature, but major effect, quenching of liquid crystallinity is observed in case of 1.O5 and 2.O5 [22]. The change in position of oxygen has a pronounced effect on higher homologous series compared to lower homologous. The thermal stability of the compound 8.O5 is greatly affected and it leads to below room temperature level. This is due to the change in position of oxygen as well as contribution of alkyl chain length. It may be concluded from the above fact that the alkyl chain length is also actively participating in polymesomorphic property, melting and clearing temperature of the liquid crystalline compound.

3.2.2. Pronounced Effect of Oxygen

The melting/clearing temperatures of N (*p*-*n*-alkoxybenzylidene) *p*-*n*-alkoxyaniline (*n*O.O*m*) compounds are very high, above 100°C in all cases of lower, middle and higher homologous series. An alkoxy group present in both sides of the rigid core is expected to enhance the stability by its oxygen unshared–pair overlap with the associated benzene ring [23]. In the case of N (*p*-*n*-alkylbenzylidene) *p*-*n*-alkylaniline (*n*. *m*), the absence of oxygen in rigid core causes the melting/clearing temperature to room temperature/below room temperature level. In both the cases, lower and higher homologous series (1.5, 2.5 and 8.5), the effect is merely same; the thermal stability of compound went to below room temperature. However, in middle homologue $n = m = 5$, 5.5 compound, the existence of liquid crystallinity is at and above the room temperature [21]. It is well known that physical and chemical properties of the liquid crystal molecules change with the length of alkyl chains. Subsequently, an identical alkyl chain length (5.5) present in both sides of the rigid core may responsible for the existence of liquid crystallinity, thermal stability and the change in length without oxygen has a pronounced effect.

4. Conclusions

The salient features of the present work are as follows:

1. NAPHE1 exhibits the last intensity peak at longer wavelength compared to NAPHE2. This shows that NAPHE1 is much flexible for electronic transitions over a long wavelength region. Further, this causes the intensity peaks over a large wavelength region, and high photo sensitivity for NAPHE1, which may be useful for electronic applications.
2. The HOMO (H), LUMO (L) energies, and energy gap (E_g) have been found to be increased due to the substitution of oxygen. Further, it also causes the lower band gap in NAPHE1 compared to NAPHE2 molecule. Hence the conductivity is expected to be high for NAPHE1.
3. The placement of oxygen atom plays an influential role in forecasting the polymesomorphism, and the alkyl chain length further tunes the occurrence of phase variant in benzylidene aniline compounds.
4. Although the major effects may be due to the presence/absence of oxygen in the terminal chain, a possible contribution from alkyl chain length could not be ruled out.
5. The alkyl chains can be regarded as source of entropy to realize a given condensed state.

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