



Influence of Oxygen and Flexible Chain Length on Schiff's Base Compounds –
Experimental Approach

D. P. Ojha

School of Physics, Sambalpur University, Jyoti Vihar-768 019, Sambalpur, Odisha, India

The present article deals with the synthesis of four Schiff's base compounds and characterized by using the Thermal Microscopy (TM) and Differential Scanning Calorimetry (DSC). The position of oxygen is varied from either sides of the bridging site, oxygen introduced on both sides and the oxygen is removed from the bridging site for the values of $n=8$ and $m=5$. The influence of oxygen atom to the extent of increase in thermal range, depression in melting temperature, elevation of clearing temperature is observed for all four compounds viz., N (*p-n*-Octyloxybenzylidene) *p-n*-Pentylaniline (80.5), N (*p-n*-Octyl benzylidene) *p-n*-Pentyloxyaniline (8.05), N (*p-n*-Octyloxybenzylidene) *p-n*-Pentyloxy aniline (80.05) and N (*p-n*-Octyl benzylidene) *p-n*-Pentylaniline (8.5). The shifting of position of oxygen from aldehyde to aniline side and the removal of oxygen has greater effect as they become room temperature liquids whereas the oxygen on aldehyde side and the oxygen on both the sides of rigid core moiety have effect only on clearing temperatures. The results are discussed in the light of the earlier data available on Schiff's base (*nO.m*) compounds.

Key words: Schiff's Base Compounds, 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]. They have different phases like nematic, smectic and cholestric are innovative class of functional materials and have attracted great deal of attention due to their various applications in electro-optics. For many applications of liquid crystal characteristics need to be satisfied such as stability of mesophase range and existence of phases at a desired temperature [2]. 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 [3].

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 [4]. N (*p-n*-alkoxy benzylidene) *p-n*-alkyl aniline are popularly known as *nO.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 [5]. 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 [6].

The compounds chosen for the present investigation are the bezlylidene anilines with $n=8$ and $m=5$, viz., 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). 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, oxygen atom is introduced on both sides and the oxygen is removed from the terminal chain. The observed values are discussed in the light of earlier data available on Schiff's base *nO.m* compounds [7].

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 [8]. 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 [9] are made with an OLYMPUS DX 50 polarizing microscope equipped with DP 10 CCD display, in conjunction with an INSTEC temperature controller of accuracy $\pm 0.1^{\circ}\text{C}$. The calorimetric investigations are carried out using a Perkin-Elmer DSC-7 instrument. The general molecular structure of benzylidene aniline compounds is shown in Figure1.

3. Results and Discussion

The phase variants exhibited by these compounds along with the phase transition temperatures and the corresponding enthalpy values are listed in Table 1. The phase transition temperature observed by thermal microscopy is found to be reasonable agreement with the DSC thermogram as shown in Figure 2.

The compound 8O.O5 is exhibiting a pure smectogenic character among the four compounds, as observed in case of 8O.5 compound [10]. 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 [11] indicating the phase in the present case as of smectic-A (see Plate 1).

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 *nO.m* compounds with smectic-A and smectic-B phase sequence [12]. 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 $nO.m$ 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 versus compounds is shown in Figure 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 as well as oxygen on both side/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 8.05 and 8.5.

3.1 Influence of Oxygen's Position on Compounds

The Position of oxygen in the aldehyde side, N (*p-n*-Octyloxybenzylidene) *p-n*-Pentyl aniline (80.5) compound exhibiting its smectogenic character as smectic-A, smectic-B and smectic-G at above room temperature [10]. However, the change in position of oxygen from aldehyde side to the aniline side N (*p-n*-Octylbenzylidene) *p-n*-Pentyloxy aniline (8.05) causes the compound to become room temperature liquid. But the effect is less prominence in the case of middle homologue (50.5 and 5.05) because both are exhibiting liquid crystalline nature at above room temperature level.[13]. Furthermore, in lower homologous series like 10.5, 1.05 and 20.5, 2.05, there is no pronounced effect is observed on melting/clearing temperature, but major effect, quenching of liquid crystallinity is observed in case of 1.05 and 2.05 [14]. The change in position of oxygen has a pronounced effect on higher homologous series compared to lower homologous. The thermal stability of the compound 8.05 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 Pronounced Effect of Oxygen

The melting/clearing temperatures of N (*p-n*-alkoxybenzylidene) *p-n*-alkoxyaniline (*nO.Om*) 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 [15]. 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 [13]. 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. Conclusion

The salient features of the present work are as follows:

1. The placement of oxygen atom plays an influential role in forecasting the polymorphism, and the alkyl chain length further tunes the occurrence of phase variant in benzylidene aniline compounds.
2. 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.
3. The alkyl chains can be regarded as source of entropy to realize a given condensed state.

Acknowledgement

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Table- 1

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

Compound Name	Phase	Method	Cycle	I-A	A-B	B-G	G-K	Ref.
80. 5	ABG	TM	Cooling	85.7	70.8	52.7	42.2	[10]
8.05	Room Temperature Liquid.							
80. 05	ABG	DSC	Heating	108.8	99.6		89.7	
			$\Delta H/J/gm$	4.0	4.2		77.8	
			Cooling	105.8	96.4	83.2	74.7	
			$\Delta H/J/gm$	3.7	3.7	4.2	49.8	Phase
ABG = A, B &		TM	Cooling	104.6	95.3	81.9	73.6	Smectic-
			8.5	Room Temperature Liquid.				

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Figures caption

Fig. 1 The general structure of $nO.m$, $n.Om$, $nO.Om$ and $n.m$ compounds.

Fig. 2 The DSC heating and cooling thermogram of 80.O5 compound at scan rate $10^{\circ}\text{C}/\text{min}$.

Fig. 3 A comparative picture of liquid crystallinity versus compounds.

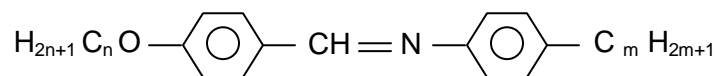
Plate 1 Smectic-A focal conic fan texture observed in 80.O5 compound at 104.6°C .

Plate 2 Smectic-A to Smectic-B transient transition bars observed in 80.O5 compound at 95.3°C .

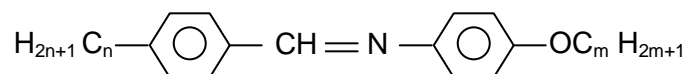
Plate 3 Smectic-B texture observed in 80. O5 compound.

Plate 4 Paramorphic Smectic-G textures observed in 80. O5 compound at 81.9°C .

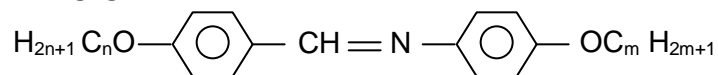
nO.m



n.Om



nO.Om



n.m

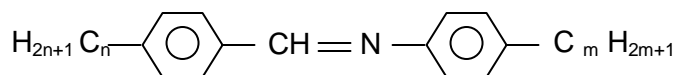


Figure 1

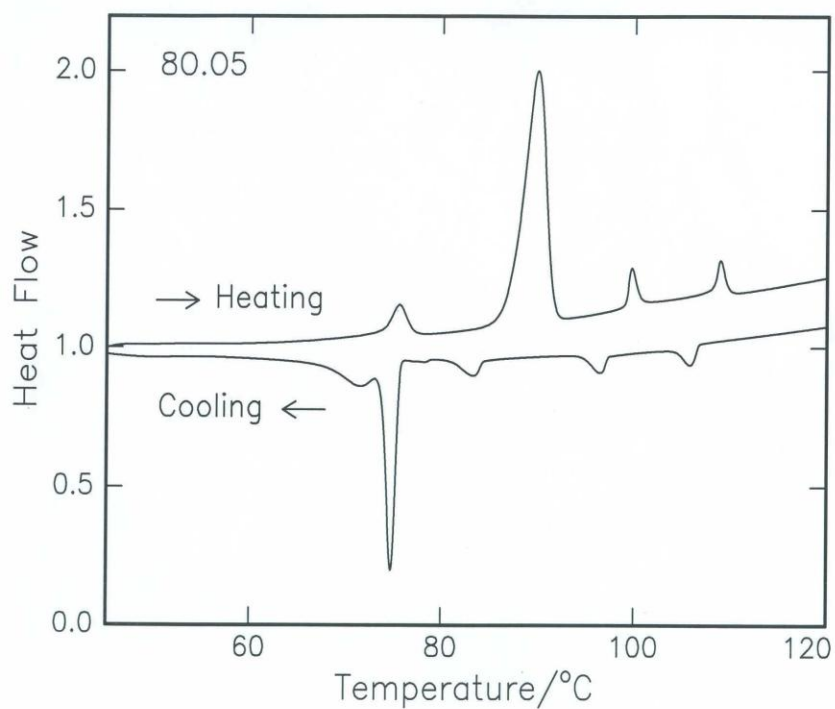
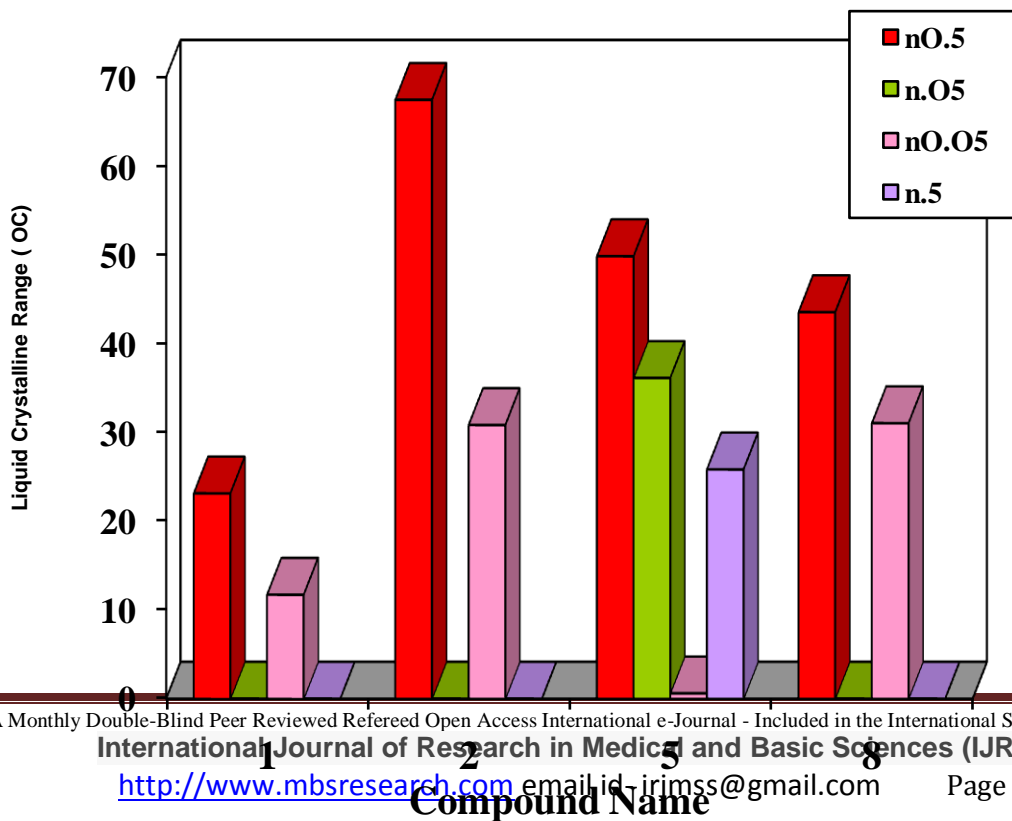


Figure 2





$n = 1, 2, 5$ and 8

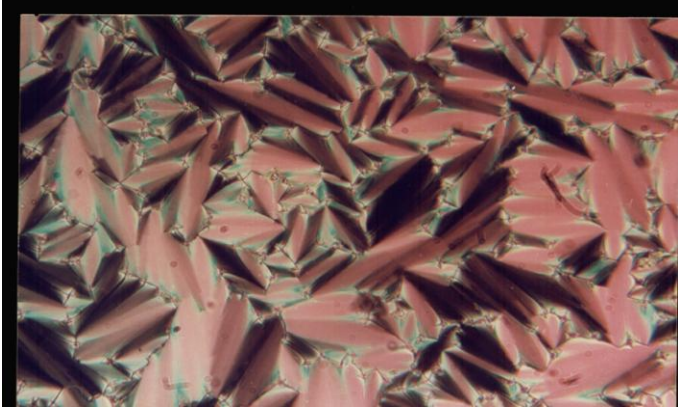
Figure 3

Plate 1

Plate 2

Plate 3

Plate 4



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