Role of Oxygen on Phase Behaviour of Benzylidene Aniline – A Comparative Study

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Four structurally related Schiff's base compounds are synthesized and their mesogenic properties are characterized by using 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*-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). The shift in the position of oxygen from the aldehyde to the aniline side and the removal of oxygen has a greater effect as they become room temperature liquids, whereas the oxygen on the aldehyde side and the oxygen on both sides of the rigid core moiety effect only the clearing temperatures. The results obtained are discussed in the light of the earlier data available on Schiff's base *n*O.*m* compounds.

Key words: Schiff's Base Compounds; Thermal Microscopy; Differential Scanning Calorimetry.

1. Introduction

In recent years, liquid crystal research has gained much prominence in multidirectional aspects with exciting practical applications [1]. The focus is laid on the investigation of new liquid crystalline materials with differing molecular chemistry in order to study their viability in technological applications [2]. The terminal groups present in a molecule find an increasing 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 the first type. The Schiff's base liquid crystals occupy a special place among many chemical systems that exhibit a liquid crystalline nature, as they present a scenario with a wide incidence of polymorphism [4]. N (*p-n*-alkoxy benzylidene) *p-n*-alkyl aniline, popularly known as *n*O.*m* compounds, represent an interesting case of liquid crystals because of the 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 encroach on the smectic state and eventually prevent the observation of the nematic state. 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 benzylidene 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 the oxygen atom in the terminal chain varied from either side of the core, the 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 *n*O.*m* compounds [7].
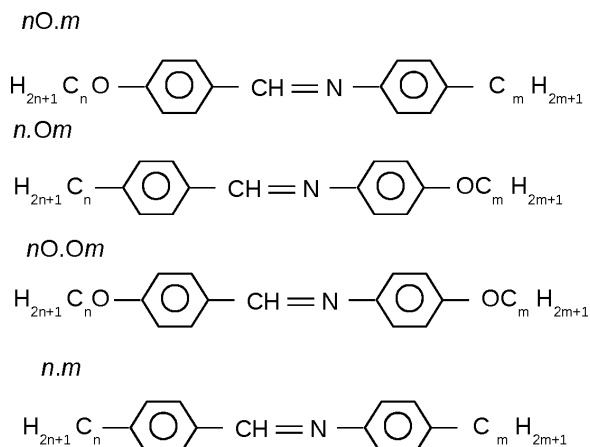
*n*O.*m*

$$H_{2n+1}C_nO \longrightarrow \langle O \rangle \longrightarrow CH = N \longrightarrow \langle O \rangle \longrightarrow C_mH_{2m+1}$$

n.O*m*

$$H_{2n+1}C_n \longrightarrow \langle O \rangle \longrightarrow CH = N \longrightarrow \langle O \rangle \longrightarrow OC_mH_{2m+1}$$

*n*O.O*m*

$$H_{2n+1}C_nO \longrightarrow \langle O \rangle \longrightarrow CH = N \longrightarrow \langle O \rangle \longrightarrow OC_mH_{2m+1}$$

n.*m*

$$H_{2n+1}C_n \longrightarrow \langle O \rangle \longrightarrow CH = N \longrightarrow \langle O \rangle \longrightarrow C_mH_{2m+1}$$

Fig. 1. General structure of *n*O.*m*, *n*.O*m*, *n*O.O*m*, and *n*.*m* compounds.

2. Experimental

The compounds are prepared by condensation of the corresponding benzaldehyde (0.1 mole) and aniline (0.1 mole) on refluxing with absolute ethanol in the presence of a 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 recrystalized 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 ± 0.1 °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 Figure 1.

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 in reasonable agreement with the corresponding DSC values. The DSC thermograms of 8O.O5 and 8O.5 compounds are shown in Figure 2 and 3.

Figure 3 shows that the compound 8O.5 exhibits an enantiotropic smectic-A and smectic-B phase and a monotropic smectic-G phase. The solidification peak has not observed up to room temperature. The compound 8O.O5 exhibits a pure smectogenic character
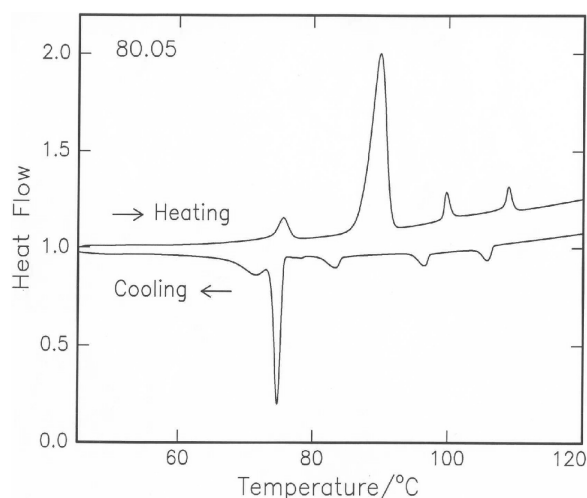

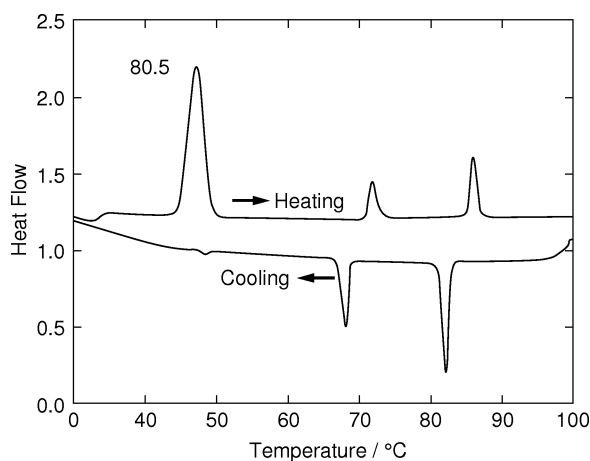Fig. 2. DSC heating and cooling thermogram of 8O.O5 compound at scan rate of 10 °C/min.

Fig. 3. DSC heating and cooling thermogram of 8O.5 compound at scan rate of 10 °C/min.

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 a white crystalline solid, stable at room temperature. Moreover, it exhibits a high degree of thermal stability when subjected to repeated thermal scans during 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 floats 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

Table 1. Transition temperatures in °C along with the enthalpy (J/gm) values.

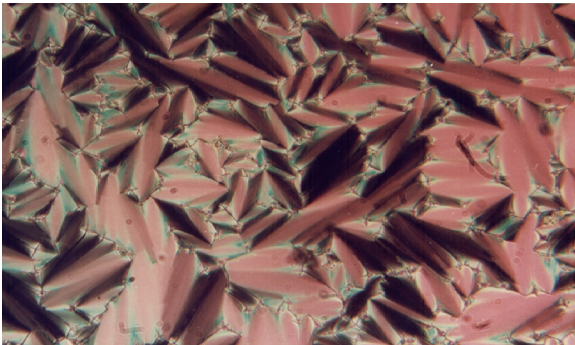| Compound Name	Phase	Method	Cycle	I-A	A-B	B-G	G-K
8O.5	ABG	DSC	Heating	87.78	73.35	—	47.51
			ΔH (J/gm)	16.73	9.84		99.26
			Cooling	86.07	71.53	50.86	—
			ΔH (J/gm)	16.49	9.44	0.24	—
		TM	Cooling	85.7	70.8	52.7	42.2
8.O5	Room temperature liquid						
8O.O5	ABG	DSC	Heating	108.8	99.6		89.7
			ΔH (J/gm)	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 temperature liquid						

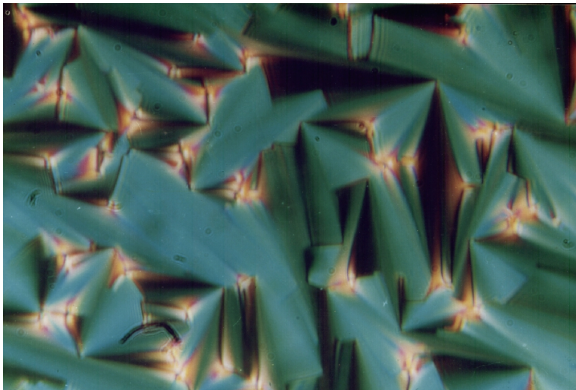Plate 1. Smectic-A focal conic fan texture observed in 8O.O5 compound at 104.6 °C.

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

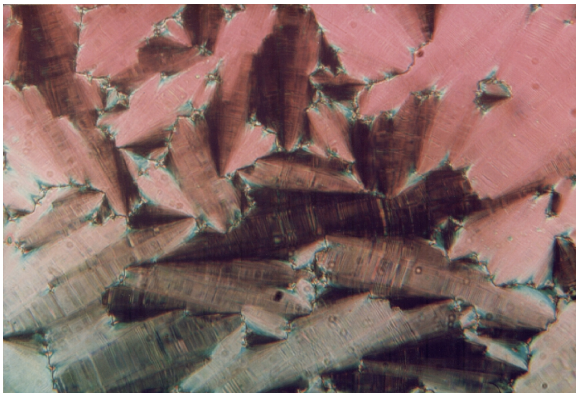Plate 2. Smectic-A to smectic-B transient transition bars observed in 8O.O5 compound at 95.3 °C.

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

homeotropic region, revealing the phase as an orthogonal one. 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 the 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 tran-

sient transition bars and the formation of smooth focal conic fan texture with reduced discontinuities at the focal conic domain boundaries infer that this 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 sequences [12]. On further cooling, the smectic-B phase exhibits striped broken fo-
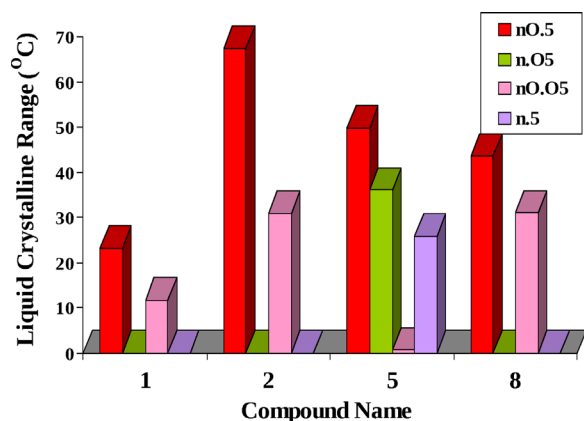
Fig. 4. Comparative picture of liquid crystallinity versus compound.

cal conic fan texture from smooth focal conic texture at 81.9 ℃. These observations are similar to those observed in the case of other $nO.m$ compounds, indicating 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 ℃.

A comparative picture of liquid crystallinity versus compounds is shown in Figure 4 for better understanding of the role of oxygen in benzylidene aniline compounds. A glance at lower homologous series, $n = 1$ and 2, $m = 5$, reveals the shift of the 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 liquids as observed in the case of 8.O5 and 8.5.

3.1. Influence of Oxygen Position

The Position of the oxygen atom in the aldehyde side N (*p-n*-Octyloxy benzylidene) *p-n*-Pentyl aniline (8O.5) compound exhibits 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*-Octyl benzylidene) *p-n*−Pentyloxy aniline (8.O5) causes the compound to become a room temperature liquid. But the effect is less prominent in the case of middle homology (5O.5 and 5.O5) because both are exhibiting liquid crystalline nature at

above room temperature level [13]. Furthermore, in lower homologous series like 1O.5, 1.O5, 2O.5, and 2.O5, there is no pronounced effect observed on melting/clearing temperature, but quenching of liquid crystallinity is observed in case of 1.O5 and 2.O5 [14]. The change in the position of the oxygen atom has a pronounced effect on higher homologous series compared to lower homologous one. The thermal stability of the compound 8.O5 is greatly affected and it went below room temperature level. This is due to the change in the position of oxygen and also the 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. Role of Oxygen

The melting/clearing temperatures of N (*p-n*-Alkoxy benzylidene) *p-n*-Alkoxy aniline (*nO.Om*) compounds are very high, above 100 ℃ in all cases of lower, middle and higher homologous series. An alkoxy group 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*-Alkyl benzylidene) *p-n*-Alkyl aniline (*n.m*), the absence of oxygen in rigid core causes the melting/clearing temperature to room temperature/below room temperature level. In both cases of lower and higher homologous series (1.5, 2.5 and 8.5), the effect is merely the same; the thermal stability of the compound went below room temperature. However, in middle homologue $n = m = 5$, 5.5, compound, the existence of liquid crystallinity is at and above 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) presented in both sides of the rigid core may be responsible for the existence of liquid crystallinity and thermal stability and the change in length without oxygen has a pronounced effect.

4. Conclusion

Therefore, it may be concluded from the above discussion that the placement of the 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. 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.

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