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Influence of Oxygen on Phase Behavior of N (*p*-*n*-Octyloxy Benzylidene) *p*-*n*-Alkoxy Anilines: A Comparative Study

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The N (p-n-octyloxy benzylidene) p-n-alkoxy anilines (8O.Om) compounds were synthesized, and the mesomorphic properties were characterized by using thermal microscopy (TM) and differential scanning calorimetry (DSC) for $m = 3$ *to 7. The nematic (N), smectic-C* (S_C)*, and smectic-G* (S_G) *phases are the more commonly observed in these compounds. The smectic-A* (S_A) *and smectic-B* (S_B) *phases are observed only in the 8O.O5 compound. The influence of oxygen on phase behavior of the 8O.Om compounds is compared with the data available on nO.m compounds.*

Keywords: benzylidene aniline compounds; mesomorphic properties; phase behavior

INTRODUCTION

Liquid crystals (LC) have become synonymous with high technology. They provided for displays important to the current computer and communication revolutions. Liquid crystals are also at the center of enormous advances in our understanding of the fundamental science of condensed systems [1,2]. The phase transitions in liquid crystals are often accompanied by interesting changes in their properties. The experimental evidence shows that the influence of molecular structure on the incidence and temperature range of liquid crystal phases is an important, complex, and subtle topic [3].

The synthesis of liquid crystals containing terminal, linking, and lateral alkoxy groups play an important role in the realization of LC phases for display applications. Further, the terminal groups in a molecule have their own importance because of their polarity and

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direction. It has been found that terminally substituted compounds exhibit more stable mesophases than their unsubstituted mesogenic counterparts [4]. One of the most common types of recent investigation into structure–property relationships has been the synthesis of groups of molecules differing from one another by the number of methylene groups as a terminal substituent. There appears to be two principal motives for this type of study. The first involves the search for technologically useful liquid crystals, i.e., materials of specific nematic thermal ranges. The other reason for studying homologous series is more fundamental in nature. In proceeding along a homologous series, only very small changes are made at each step. It is thus hoped that more specific conclusions would be possible as to the mesophase behavior with molecular size and shape [5].

The benzylidene anilines are popularly known, as *n*O.*m* compounds, where *n* and *m* represent the number of carbon atoms in alkoxy and alkyl chains respectively, which not only exhibit rich and subtle liquid crystal polymorphism at ambient temperatures, but also useful as model systems in phase transition phenomena. In the present investigation, homologous series of benzylidene aniline compounds containing terminal alkoxy chain on both sides of the rigid core is taken as prime object. The values of $n = 8$ and m vary from 3 to 7. The results are compared with the data available on *n*O.*m* compounds [6,7].

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 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 Fig. 1.

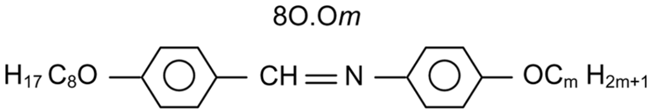

FIGURE 1 The general molecular structure of the 8O.O*m* compound.

RESULTS AND DISCUSSION

The transition temperatures from thermal microscopy and differential scanning calorimetry along with the heats of transition involved at the phase transformation are given in Table 1. For comparison, the data pertinent to the 8O.*m* compounds are also given in the same table. The DSC thermograms of 8O.O3 and 8O.O4 compounds are presented in Figs. 2 and 3.

The preliminary polarizing microscopic studies on 8O.O*m* compounds (for $m = 3$ to 7) reveal that all compounds exhibit mesomorphic phases. These compounds show three different types of phase variants

TABLE 1 The Transition Temperatures in °C Along with the Enthalpy Values of N (*p*-*n*-Octyloxy Benzylidene) *p*-*n*-Alkoxy Aniline (8O.O*m*) are Shown

Compound name	Phase variant	Method		I-N/A	N/A-A/B	N/A-C/B	C-B	C/B-G	N/A/B/G-K	Ref.
8O.3	NABG	TM	Cooling	83.6	80.7	68.4		64.3		[17]
8O.O3	N	DSC	Heating	106.39					99.23	
			ΔH J/gm	1.47					62.58	
			Cooling	103.96					84.33	
			ΔH J/gm	1.80					51.41	
		TM	Cooling	105.2					85.3	
8O.4	ABG	TM	Cooling	81.2	68.0			64.8	39.5	[18]
8O.O4	NC	DSC	Heating	112.05					105.92	
			ΔH J/gm	2.35					74.43	
			Cooling	109.45		93.7			82.97	
			ΔH J/gm	2.25		1.55			57.36	
		TM	Cooling	110.0		95.0			84.2	
8O.5	ABG	TM	Cooling	85.7		70.8		52.7	42.2	[19]
8O.O5	ABG	DSC	Heating	108.87	99.65				89.79	
			ΔH J/gm	4.00	4.24				77.86	
			Cooling	105.85	96.44			83.26	74.74	
			ΔH J/gm	3.78	3.71			4.23	49.80	
		TM	Cooling	104.6	95.3			81.9	73.6	
8O.6	ACBG	TM	Cooling	86.2		75.8	75.0	65.0	54.7	[19]
8O.O6	NCG	DSC	Heating	111.8		104.23			93.85	
			Δ J/gm	4.93		4.09			73.12	
			Cooling	108.75		100.77		84.35	79.53	
			Δ J/gm	5.43		3.73		2.83	56.58	
		TM	Cooling	110.3		102.2		85.6	80.4	
8O.7	ACBG	TM	Cooling	87.0		75.6	74.4	58.2	29.6	[19]
8O.O7	NC	DSC	Heating	108.62		104.09			95.49	
			Δ J/gm	3.43		2.86			83.84	
			Cooling	105.54		100.63			87.13	
			Δ J/gm	2.56		2.45			60.68	
		TM	Cooling	105.6		100.8			87.6	

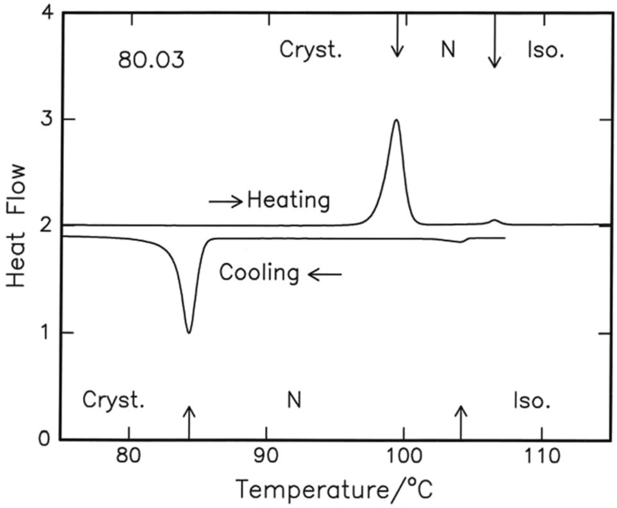

FIGURE 2 The DSC heating and cooling thermogram of the 8O.O3 compound at the scan rate of 10°C/min.

viz. monovariant, divariant, and trivariant phase sequences. On cooling the isotropic melt, the compounds for $m = 3$, 4, 6, and 7 (except 5) show a characteristic threaded marble texture of nematic phase at

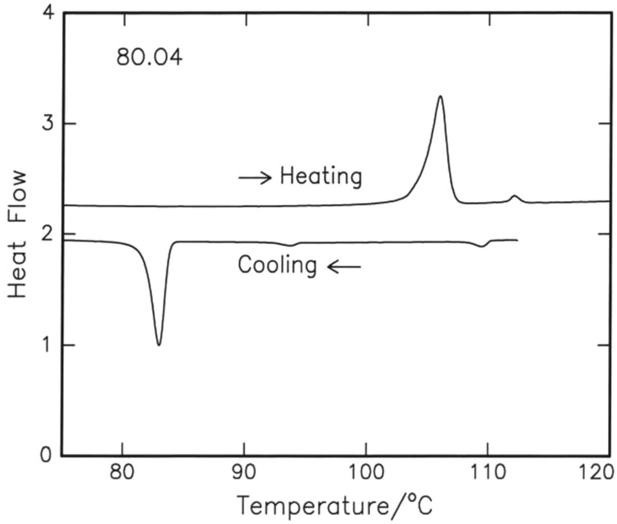

FIGURE 3 The DSC heating and cooling thermogram of the 8O.O4 compound at the scan rate of 10°C/min.

105.2, 110.3, 110.0, and 105.6°C, respectively. On further cooling, the nematic phase transformed to other liquid crystalline phase with the exhibition of schlieren texture characterizing the phase as smectic-C in all the compounds (except 8O.O3 and 8O.O5). The nematic phase in compound 8O.O3 transforms to solid crystalline phase at 85.3°C. Other compounds with $n=4$, 6, and 7 exhibit the nematic to smectic–C transition at 95.0, 102.2, and 100.8°C, respectively. Compounds 8O.O4 and 8O.O7 do not exhibit other liquid crystalline phases on further cooling. Instead, they transform to solid crystalline phase at 84.2 and 87.6°C. However, compound 8O.O6 is found to exhibit mosaic texture below smectic-C phase at 85.6°C characterizing the phase as smectic-G as shown in Plate 1. This compound is found to crystalize at 80.4°C. Compound 8O.O5 shows a smectic phase in the form of batonnets at 104.6°C by cooling from the isotropic melt. 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 pseudoisotropic texture in the homeotropic region, revealing the phase as an orthogonal phase indicating the phase in the present case as of smectic-A.

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

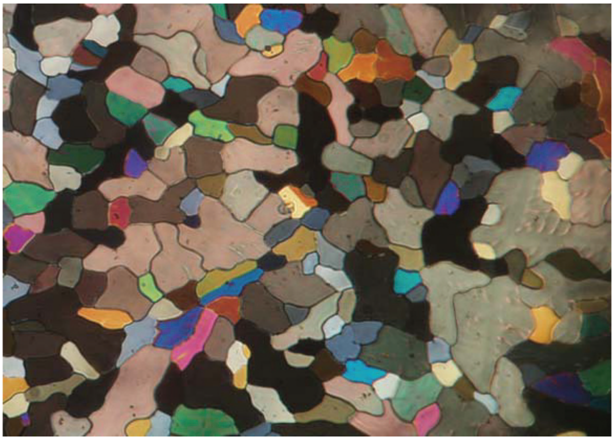

PLATE 1 The mosaic texture of smectic G (S_G) phase exhibited by the 8O.O6 compound at 85.6°C on cooling.

domain boundaries infer that this transformation is from smectic-A to smectic-B phase sequence. On further cooling of smectic-B phase exhibits striped broken focal conic fan texture from smooth focal conic texture at 81.9°C. These observations indicate that the phase is smectic-G phase. The smectic-G phase is found to transform to solid crystal phase on further cooling of the sample at 73.6°C.

Influence of Alkoxy Chain

The phase variants of 8O.O*m* compounds are presented in Table 2 along with the phase variants of 7O.*m* and 8O.*m* series for comparison. A glance at Table 2 reveals that the general trend is observed in case of 8O.*m* series, the increment of methylene group cause the compound to form pure smectogenic nature for $m \geq 4$. The 8O.O*m* series show an anomalous nature by exhibiting pure smectic character in 8O.O5 compound, where the former and latter compounds of this series exhibit both nematic and smectic mesomorphism. The similar trend is observed in the case of 7O.*m* series, for the value of $m = 6$ exhibit a pure smectogenic character unlike other compounds that show both nematic and smectic polymesomorphism [10].

A comparison between the 8O.*m* series and the 8O.O*m* series reveals that the alkoxy derivatives, which have higher values of polarizability than those of the corresponding alkyl compounds should always exhibit higher clearing temperature [11]. Both nematic and smectic-C phases are more favored and the nematic phase is existing up to $m = 7$ (except 5) that is not observed in case of the 8O.*m* series [12]. In general, the intermolecular attractive forces such as van der Waals forces, hydrogen bonds, electron donor interactions, and intermolecular repulsion forces influence the situation of molecules in a mesophase. These forces, separately or together, may be responsible for increasing or decreasing the stability of liquid crystalline phases or for creating new phases. However, the increase of attractive forces involves the creation of phases [13].

TABLE 2 The Phase Variants Exhibited by 8O.O*m* along with the Phase Variants of 7O.*m* and 8O.*m* Compounds

M	3	4	5	6	7
7O.*m*	NAB	NACG	NACBG	ACFG	NACG
8O.O*m*	N	NC	ABG	NCG	NC
8O.*m*	NAB	ABG	ABG	ACBG	ACBG

Role of Oxygen

The terminal group that increases the molecular polarizability (without significantly increasing the molecular breadth) increases the thermal stability of the resulting mesophase. It has been argued that increasing the anisotropy of polarizability should enhance the nematic thermostability [14]. The two terminal alkoxy groups of benzylidene anilines may confer a stronger lateral dipole that aids the formation of tilted phases. The alkoxy group is expected to enhance the mesophase stability by its oxygen unshared-pair overlap with the associated benzene ring [15,16]. The nematic and smectic C phases are more favored, and the increase in alkoxy chain length is directly proportional to the phase length of S_C, and it shows inverse proportion to N. The close observation on Table 1 reveals that the phase length of S_C is increasing with the decrease of N, and it reaches to maximum at $m = 6$ and decrease in phase length of both S_C, N phases is observed for $m = 7$.

Figure 4 shows the comparative chart of alkoxy carbon number versus liquid crystallinity of the compounds. The gradual increasing trend is observed from $m = 3$ to 5, at $m = 6$ the liquid crystallinity reaches the maximum, and a sudden decrease is started from $m = 7$. A comparison between Table 2 and Fig. 4, we may drive a general conclusion that as the alkoxy chain goes on increasing the polymesomorphism is also increasing up to $m = 3$ to 6, further increment of

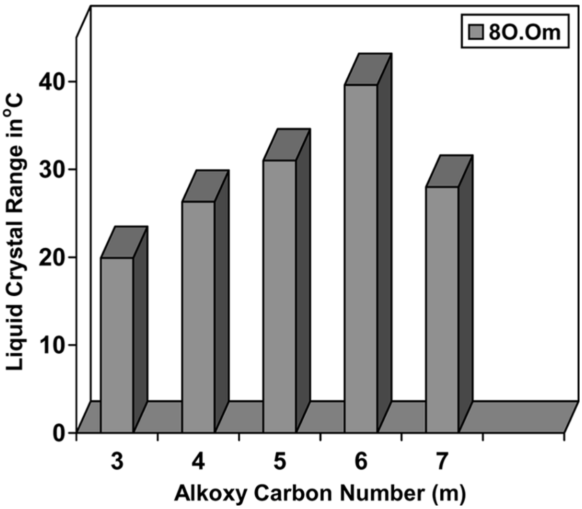

FIGURE 4 A comparative chart of alkoxy carbon number versus liquid crystalline range.

alkoxy chain cause the reduction of ploymesomorphic behavior that observed from $m = 7$. Further more, increment of alkoxy chain may eliminate the mesomorphism slowly, and it is indicating a limit to which the end alkoxy group can be extended in a mesogen.

CONCLUSION

The data presented for homologous series of Schiff base 8O.O*m* compounds with alkoxy group on both sides indicate that the kind of interaction between the end group, and the core portion of the molecule plays an important role in determining the polymesomorphism and the liquid crystalline nature.

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