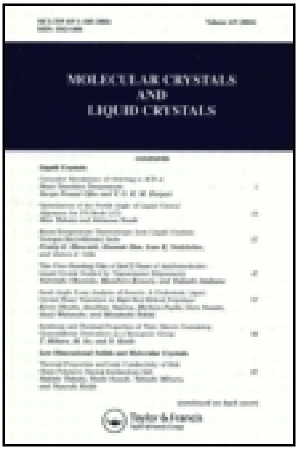

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Role of Position of Oxygen on Benzylidene Anilines: The Effect of End Chain

N. Ajeetha [a] & Durga P. Ojha [a]

[a] Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada, India

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Role of Position of Oxygen on Benzylidene Anilines: The Effect of End Chain

N. Ajeetha and Durga P. Ojha
Liquid Crystal Research Laboratory, Post-Graduate Department
of Physics, Andhra Loyola College, Vijayawada, India

A family of benzylidene aniline compounds with variable end chains (for n = 1, 2, 4, 8 and m = 16) are synthesized by placing the electro-negative oxygen atom on either side of the rigid core (nO.m, n.Om), on both sides of the rigid core (nO.Om) and with the absence of oxygen on rigid core moiety (n.m). The mesomorphic properties are studied by using Thermal Microscopy (TM) and Differential Scanning Calorimetry (DSC). The depression/elevation of melting/clearing temperature and the nature of liquid crystallinity are presented as a function of position of oxygen with end chains.

Keywords: benzylidene anilines; mesomorphic properties

INTRODUCTION

Liquid crystals (LCs) are versatile systems in the field of soft condensed matter physics. The special emphasis on their scientific research gives an insight into the potential applications [1]. The literature abounds in experimental and theoretical studies of phase transitions and many unifying concepts have emerged out in recent years, which provide a better understanding of the nature of phase transitions. The phase transitions in liquid crystals are often accompanied by interesting changes in their properties [2]. The investigation of physical parameter in homologous series of compounds is particularly useful in order to understand the relation between the molecular structure and polymorphic properties of liquid crystals [3,4].

The thermotropic LCs constituted by a variety of terminal, linking, and lateral chemical groups; especially have gained importance in the

Address correspondence to Durga P. Ojha, Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada 520-008, A.P., India. E-mail: durga_ojha@hotmail.com

development of commercial liquid crystalline materials for display applications [5]. The benzylidene aniline compounds are popularly known as *n*O.*m* compounds and are composed of two rigid aromatic nuclei attached with flexible end chains of *n* and *m*. The primary role of alkyl chain is to enhance the LC thermal range by lowering the melting point. The liquid crystalline properties such as the clearing temperature and the enthalpy of transitions are influenced by the end chains. It is well known that physical and chemical properties of the LC molecules change with the length of alkyl chains [6].

The alkoxy chain length that is in conjugation with the bridging group plays a major role in deciding the occurrence of an LC phase, transition, and melting/clearing temperature. The position of oxygen with respect to the bridging site and the influence of alkyl chain length in confirming the liquid crystalline nature at ambient temperature are the important aspects of work to be investigated. In the present investigation, the value of $n = 1, 2, 4, 8$ and $m = 16$, the position of oxygen is varied from aldehyde side to aniline side, the oxygen is introduced on both sides of the rigid core and in the absence of oxygen on rigid core moiety the phase transitions are studied. The results are compared with the data available on *n*O.*m* compounds [7].

EXPERIMENTAL

The compounds were 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, the solvent was removed by distillation under reduced pressure and the pure compound was recrystallized from absolute ethanol at low temperature. The optical textural observations [9] were 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 were carried out using a Perkin-Elmer DSC-7 instrument. The general molecular structure of benzylidene aniline compounds is shown in Fig. 1.

RESULTS AND DISCUSSION

The transition temperatures from Thermal Microscopy (TM) and Differential Scanning Calorimeter (DSC) along with the heats of transition involved at the phase transformation are given in Table 1. The data pertinent to the *n*O.16 compounds are also given in the same table for comparison. The DSC thermograms of *n*.O16, *n*O.O16, and

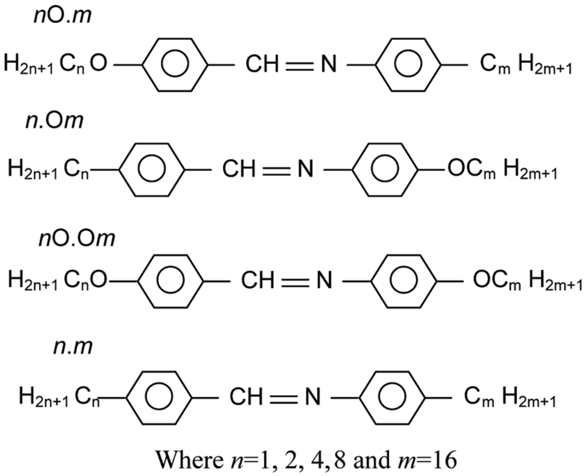

FIGURE 1 The general molecular structure of *n*O.16, *n*.O16, *n*O.O16, and *n*.16 compounds.

n.16 compounds along with *n*O.16 compounds for comparison are presented in Figs. 2 to 5. In case of compounds for alkoxy/alkyl chain number $n = 1, 2, 4$, and 8 and $m = 16$, the preliminary textural results on N-(*p*-*n*-alkoxy benzylidine)*p*-*n*-hexadecyloxy anilines (*n*O.O16's) infer that four compounds do not exhibit liquid crystalline nature and a direct transformation of isotropic liquid to solid crystal is observed on cooling.

The similar results are also observed in N-(*p*-*n*-alkyl benzylidine) *p*-*n*-hexadecyloxy anilines (*n*.O16's) compounds. However, in the case of N-(*p*-*n*-alkyl benzylidine)*p*-*n*-hexadecyl anilines, *viz*., *n*.16's also exhibit no liquid crystalline nature in the case for $n = 1, 2$, and 8, while the compounds with $n = 4$ exhibit monotropic smectic-A phase. The transition temperatures are observed in the vicinity of room temperature and the observed phase is monotropic. These results are found to be in contrast with the results those observed in the case of N-(*p*-*n*-alkoxy benzylidine)-*p*-*n*-hexadecyloxy anilines (*n*O.16's), where all the compounds show liquid crystalline phases [10].

Effect of Alkyl Chain Length with Change in Position of Oxygen

The change in position of oxygen from aldehyde to aniline side has no effect on melting/clearing temperature of the (*n*.O16) compounds, but the elimination of liquid crystallinity is observed. A glance at Table 2

TABLE 1 The Phase Variant, Transition Temperatures along with the Enthalpy Values are Shown

Compound name	Phase variant	Method		I-N/A	N-A	A-B	I/N/A/B-K	Ref.
1O.16	N	TM	Cooling	66.7			64.5	[10]
1.O16	Non LC	DSC	Heating				74.35	
			ΔH · J/gm				67.26	
			Cooling				63.12	
			ΔH · J/gm				55.17	
		TM	Cooling				65.16	
1O.O16	Non LC	DSC	Heating				109.74	
			ΔH · J/gm				123.43	
			Cooling				92.60	
			ΔH · J/gm				156.64	
		TM	Cooling				94.4	
1.16	Non LC	DSC	Heating				57.96	
			ΔH · J/gm				44.40	
			Cooling				37.03	
			ΔH · J/gm				106.87	
		TM	Cooling				38.2	
2O.16	A	TM	Cooling	70.1			52.2	[17]
2.O16	Non LC	DSC	Heating				76.75	
			ΔH · J/gm				54.56	
			Cooling				71.98	
			ΔH · J/gm				50.75	
		TM	Cooling				76.3	
2O.O16	Non LC	DSC	Heating				102.98	
			ΔH · J/gm				143.43	
			Cooling				89.60	
			ΔH · J/gm				136.64	
		TM	Cooling				91.4	
2.16	Non LC	DSC	Heating				51.96	
			ΔH · J/gm				34.40	
			Cooling				37.03	
			ΔH · J/gm				16.87	
		TM	Cooling				53.20	
4.O16	NA	TM	Cooling	69.2	68.5		51.3	[18]
4O.O16	Non LC	DSC	Heating				101.06	
			ΔH · J/gm				37.16	
			Cooling				88.46	
			ΔH · J/gm				37.17	
		TM	Cooling				90.5	
4.16	A	DSC	Heating				48.56	
			ΔH · J/gm				134.3	
			Cooling	38.41			35.79	
			ΔH · J/gm	26.25			77.18	
		TM	Cooling	38.1			35.0	

(*Continued*)

TABLE 1 Continued

Compound name	Phase variant	Method		I-N/A	N-A	A-B	I/N/A/B-K	Ref.
8O.16	AB	TM	Cooling	75.5		71.4		[10]
8.O16	Non LC		Heating				60.67	
			ΔH · J/gm				112.10	
			Cooling				45.91	
			ΔH · J/gm				75.06	
		TM	Cooling				51.3	
8O.O16	Non LC	DSC	Heating				93.50	
			ΔH · J/gm				97.23	
			Cooling				78.46	
			ΔH · J/gm				94.13	
		TM	Cooling				90.1	
8.16	Non LC	DSC	Heating				47.42	
			ΔH · J/gm				30.23	
			Cooling				31.10	
			ΔH · J/gm				16.21	
		TM	Cooling				35.3	

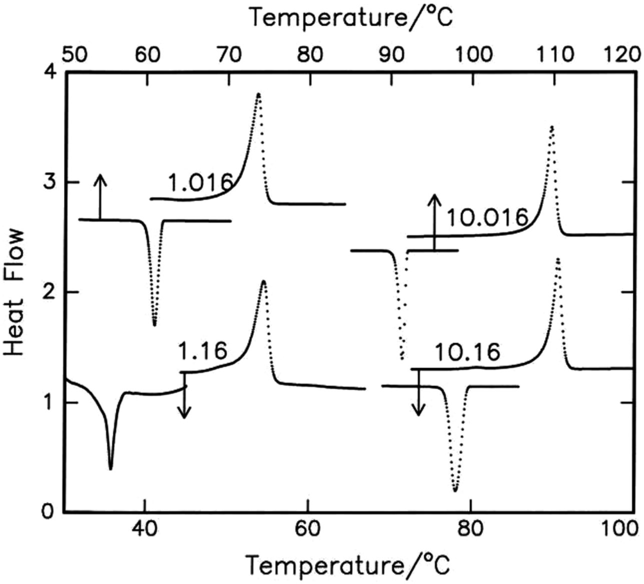

FIGURE 2 A comparative DSC thermograms of 1O.16, 1.O16, 1O.O16, and 1.16 compounds.

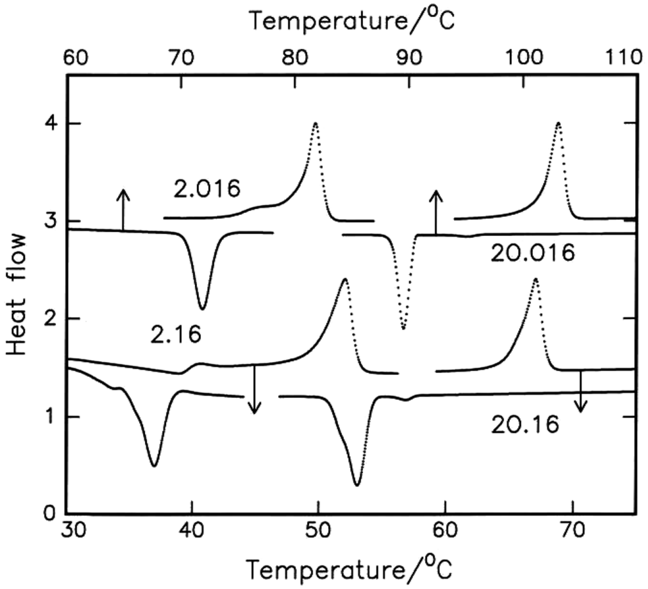

FIGURE 3 A comparative DSC thermograms of 2O.16, 2.O16, 2O.O16, and 2.16 compounds.

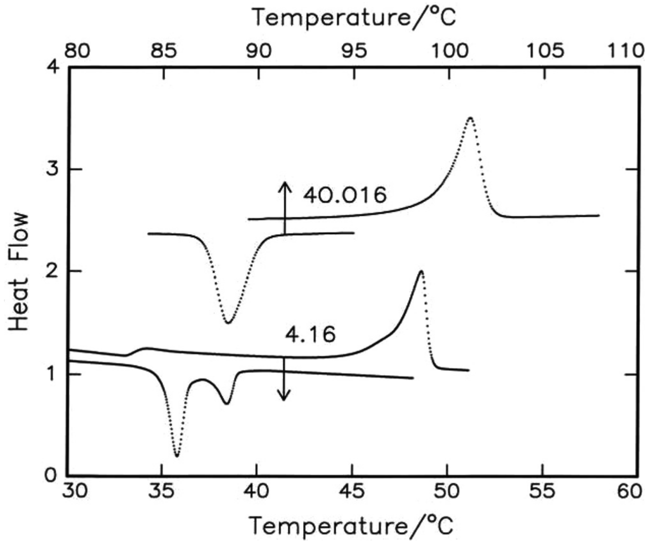

FIGURE 4 A comparative DSC thermograms of 4O.O16 and 4.16 compounds.

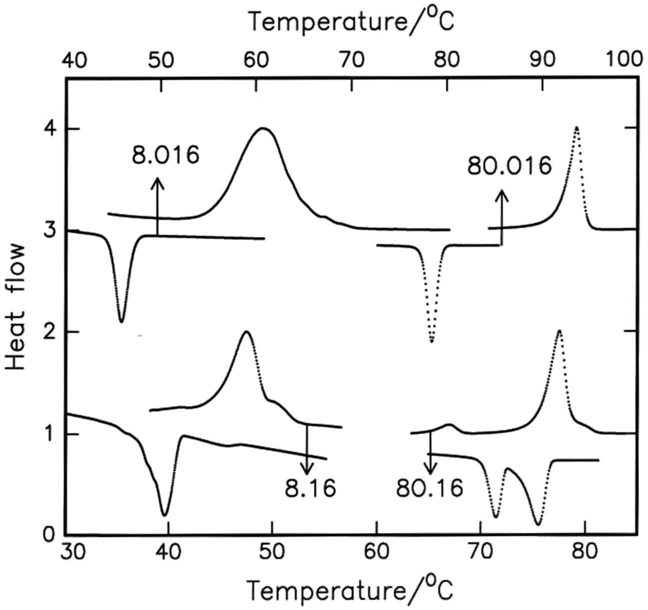

FIGURE 5 A comparative DSC thermograms of 8O.16, 8.O16, 8O.O16, and 8.16 compounds.

reveals a pronounced effect in case of lower ($n = 1$, 2) and higher homologous series ($n = 8$) of compounds with $m = 16$. However, no prominent effect is observed in case of middle ($n = m = 4$, 5) homologous series with identical alkyl chain lengths [11]. Further, the reduction of liquid crystallinity and the change in phase length are observed. This indicates that the position of oxygen in aldehyde side is more favourable for liquid crystallinity and polymesomorphism of

TABLE 2 The Phase Variants Observed in n.Om Compounds

n/m	4	5	16
1		No LC phase (N)	No LC phase (N)
2		No LC phase (N)	No LC phase (A)
4	NG (NABG)		
5		NG (NACFG)	
8		RT liquid (ABG)	No LC phase (AB)

Blank space refers the phases are to be identified.
The phases given in parentheses are the phases observed in nO.m compounds.

compounds. It may be due to the linking group that disturbs the conjugation of rigid core [12].

Influence of Oxygen with Long Alkyl Chain Length

In nO.O16 compounds, the quenching of liquid crystallinity is observed in the lower, middle, and higher homologous series of compounds. The clearing temperature of these are raised to above 100°C compared to nO.m and n.Om compounds. The Table 3 shows the reduction of polymorphism in all stages of nO.Om compounds, however, the drastic change is observed in nO.O16. Further, it is evident from Table 3 that in nO.Om compounds the alkyl chain length is playing a major role in nO.O16 and some nO.O5 compounds with $n = 4$, 5, 16, and 18 [13]. It is observed that the identical alkyl chain length and long alkyl chain length with oxygen on both sides of the rigid core may eliminate the liquid crystalline nature. Although, the oxygen is playing the major role, the effect of alkyl chain cannot be ruled out.

In case of n. m compounds, except 4.16 compounds, are exhibiting nonliquid crystalline nature [14]. Table 4 shows the polymesomorphic properties of compounds with various n and m values. The compounds 1.5, 2.5, 4.4 are exhibiting their liquid crystalline nature at below room

TABLE 3 The Phase Variants Observed in nO.Om Compounds

n/m	3	4	5	6	7	16
1			N (N)			No LC (N)
2			N (N)			No LC (A)
3			N (NA)			
4		NG (NABG)	N (NACG)			No LC (NAB)
5			N (NACFG)			
6			N (NABG)			
7			NCBG (NACBG)			
8	N (NAB)	NC (ABG)	ABG (ABG)	NCG (ACBG)	NC (ACBG)	No LC (AB)
9			ABG (ABG)			
10			ABG (ABG)			
11			AB (ABG)			
13			AB (ABG)			
14			AB (ABG)			
15			AB (ABG)			
16			A (F)			
18			No LC (F)			

Blank space refers the phases are to be identified.
The phases reported in parentheses are the phases observed in nO.m compounds.

TABLE 4 The Phase Variants Observed in $n.\ m$ Compounds

n/m	4	5	10	12	14	16
1		Below RT LC (N)	N (N)	N (N)	No LC (N)	No LC (N)
2		Below RT LC (N)	N (N)	N (N)	No LC (N)	No LC (A)
4	Below RT LC (NABG)		Below RT LC (NAB)	NA (NAB)	A (NAB)	A (NA)
5		NG (NACFG)	AB (NAB)	A (NAB)	A (NAB)	
8		RT liquid (ABG)	RT liquid (ABG)	RT liquid (ABG)	No LC (ABG)	No LC (AB)

Blank space refers the phases to be identified.

The phases reported in parentheses are the phases observed in nO.m compounds.

temperature level [15]. However, in higher homologous series for $n = 8$ and $m = 5$, 10, 12 the effect is more pronounced, and they exhibit room temperature liquid nature. Furthermore, the quenching of liquid crystallinity is observed in both lower and higher homologous series of compounds for the values of $m = 14$ and 16, and the middle homologous the effect is less, only the reduction of polymesomorphism is observed. It is argued that the alkyl chains actually take an active part in anisotropic interaction and alkyl chain carbon atoms plays an important role in the anisotropy of the molecule and helps the ordering process and hinders it also [16]. It is indicating that the limit which the end chain can be extended in a mesogen.

CONCLUSIONS

- The phase ranges of all compounds are affected, in particular short and long chain homologous. However, the effect is more pronounced compared to middle homologous compounds.
- The total number of enantiotropic phases is less and most of the compounds become monotropic in nature.
- The effect of chain length in presence of oxygen on both sides of the benzylidene aniline (nO.O16) compounds seems to be greater, the elimination of liquid crystallinity.
- The change in position of oxygen with long terminal alkyl chain has no effect on clearing temperature. The inclusion of oxygen on both sides of the rigid core cause the rise in clearing temperature where as the absence of oxygen cause a fall in it.

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