Synthesis and Characterization of Homologues of *N*-(*p*-*n*-Alkylbenzylidene)-*p*-*n*-alkyl Anilines (*n.m’s*). A Comparative Study

N. Ajeetha and Venkata G. K. M. Pisipati

Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences, Acharya Nagarjuna University, Nagarjuna Nagar-522 510, A. P., India

Reprint requests to Prof. V. G. K. M. P.; E-mail: venkata_pisipati@hotmail.com

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Synthesis of a new family of various Schiff based mesogens, viz. *N*-(*p*-*n*-alkylbenzylidene)-*p*-*n*-alkyl anilines ($n.m's$) is carried out and for characterization thermal microscopy (TM) and differential scanning calorimetry (DSC) are used. The results of these systematic studies are presented in compounds with $n = 1, 2, 4, 5$ and $m = 10, 12, 14, 16$. These $n.m$ compounds are found to exhibit nematic or/and smectic phases. The results are compared with the available data on the well studied Schiff based compounds *N*-(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkyl anilines (nO.$m's$).

Key words: Nematic; Smectic; nO.m; $n.m$.

1. Introduction

The Schiff based benzylidene aniline compounds (nO.$m's$) exhibit various liquid crystalline phase variants [1 – 3]. Systematic studies on these compounds have revealed that the placement and/or removal of oxygen on either side of the rigid core plays a decisive role in the determination of the liquid crystalline phase variants they exhibit. Further, it was observed that in some cases the liquid crystalline nature is quenched altogether (or has been pushed below room temperature), depending on the position of the oxygen atom in the molecule. The system chosen for the present study includes *N*-(*p*-*n*-alkylbenzylidene)-*p*-*n*-alkyl anilines ($n.m's$), as they present a quite interesting case, interesting due to their low clearing temperatures and mesogenic abundance at room temperature. The results are discussed in the wake of available data [2, 4 – 7] on *N*-(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkyl anilines (nO.$m's$).

2. Experimental

2.1. Synthesis

The compounds of *N*-(*p*-*n*-alkylbenzylidene)-*p*-*n*-alkyl anilines are prepared by the condensation of the corresponding *p*-*n*-alkylbenzaldehyde (0.1 mol) and *p*-*n*-alkyl aniline (0.1 mol) and refluxing the ingredients with absolute ethanol in the presence of a few drops of glacial acetic acid. The crude compounds obtained after removing the ethanol are recrystallized repeatedly from absolute ethanol until the transition temperatures are found invariant. The general structure of the homologous series of the compounds is shown in Figure 1. The choice of interest of the compounds is: n.10, n.12, n.14 and n.16 where $n = 1, 2, 4$ and 5.

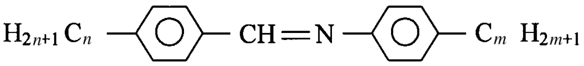

Fig. 1. Molecular structure of the homologous series of compounds, where $n = 1, 2, 4, 5$ and $m = 10, 12, 14, 16$.

2.2. Textural Identification (Thermal Microscopy, TM)

The changes in texture [8] that occur at a phase transition are an important factor in the phase identification. The phase variants and transition temperatures of $n.m's$ are determined from the characteristic textural observations under a polarizing thermal microscope OLYMPUS BX 50 supplemented by an optical display (DP-10) at a scan rate of 0.1 °C min^{-1}.

2.3. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is widely used for the study of phase transitions. The relevant thermodynamic parameters, such as transition tem-

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Table. 1 Transition temperatures (in °C) along with enthalpy values of liquid crystalline compounds.

Compound	Phase variant	Method		I-N/A	N-A	A-B	I/N/A/B-K	Ref.
1O.10	N	TM	Cooling	58.9			—	[3]
1.10	N	DSC	Heating					
			ΔH/J/gm					
			Cooling					
			ΔH/J/gm					
		TM	Cooling	30.9			30	
1O.12	N	TM	Cooling	59.9			54.5	[3]
1.12	N	DSC	Heating	—			38.95	
			ΔH/J/gm	—			72.05	
			Cooling	29.76			—	
			ΔH/J/gm	1.61			—	
		TM	Cooling	35.2			30.2	
1O.14	N	TM	Cooling	61.3			55.2	[3]
1.14	Exhibiting non-liquid crystalline nature.							
1O.16	N	TM	Cooling	66.7			64.5	[3]
1.16	Exhibiting non-liquid crystalline nature.							
2O.10	N	TM	Cooling	77.2			—	[3]
2.10	N	DSC	Heating					
			ΔH/J/gm					
			Cooling					
			ΔH/J/gm					
		TM	Cooling	25.2			24.1	
2O.12	N	TM	Cooling	76.2			—	[3]
2.12	N	DSC	Heating	—			34.46	
			ΔH/J/gm				111.22	
			Cooling	24.41			—	
			ΔH/J/gm	1.31			—	
		TM	Cooling	31.9			25.2	
2O.14	NA	TM	Cooling	70.2	68.4		—	[3]
2.14	Exhibiting non-liquid crystalline nature.							
2O.16	A	TM	Cooling	67.4			53.2	[3]
2.16	Exhibiting non-liquid crystalline nature.							
4O.10	NAB	TM	Cooling	76.7	64.7	46.8	44.3	[9]
4.10	Exhibiting liquid crystallinity at a level below room temperature.							
4O.12	NAB	TM	Cooling	77.5	69.5	51.9	39	[10]
4.12	NA	DSC	Heating	34.06	—		32.54	
			ΔH/J/gm	2.03	—		8.51	
			Cooling	33.07	31.18		—	
			ΔH/J/gm	2.39	8.91		—	
		TM	Cooling	37.6	35.8		—	
4O.14	NA	TM	Cooling	74.4	70		62	[11]
4.14	A	DSC	Heating		—	—	40.64	
			ΔH/J/gm				72.71	
			Cooling	34.57			26.75	
			ΔH/J/gm	7.20			62.32	
		TM	Cooling	39.5			30.1	
4O.16	NA	TM	Cooling	69.8	69.1		51.3	[11]
4.16	A	DSC	Heating	—			48.56	
			ΔH/J/gm				134.63	
			Cooling	38.41			35.79	
			ΔH/J/gm	26.25			77.18	
		TM	Cooling	38.1			35	
5O.10	NAB	TM	Cooling	76.2	67	54	41	[12]
5.10	AB	DSC	Heating	—		—	43.35	
			ΔH/J/gm				22.02	
			Cooling	41.37*		40.72*	—	
			ΔH/J/gm				—	
		TM	Cooling	46.9		45.3	—	
5O.12	NAB	TM	Cooling	74.1	70.9	54.7	28.3	[13]
5.12	A	DSC	Heating	—			46.32	
			ΔH/J/gm	—			4.63	
			Cooling	45.48			—	
			ΔH/J/gm	4.47			—	
		TM	Cooling	49.9			—	
5O.14	NAB	TM	Cooling	71.2	68.9	51.6	40.8	[13]
5.14	A	DSC	Heating	49.0			38.36	
			ΔH/J/gm	20.03			73.77	
			Cooling	46.63			—	
			ΔH/J/gm	19.65			—	
		TM	Cooling	51.1			31.3	
5O.16	NA	TM	Cooling	68.8	67.4		55.1	[13]
5.16	A	DSC	Heating				50.80	
			ΔH/J/gm				28.69	
			Cooling	48.71			37.60	
			ΔH/J/gm	11.91			5.19	
		TM	Cooling	52.9			40.2	

* Peaks are not well resolved.

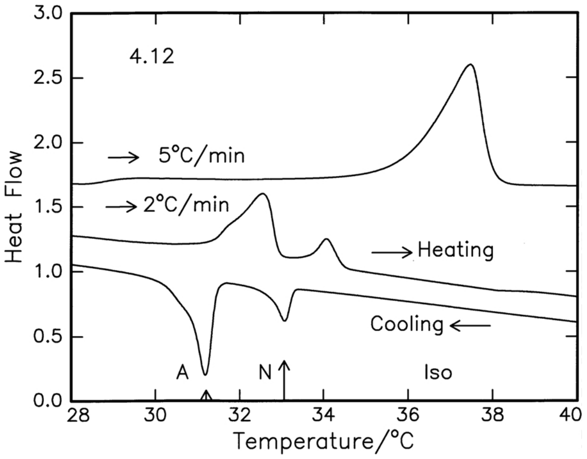

Fig. 2. DSC heating and cooling thermogram of compound 4.12; heating resolved at a scan rate of 2 °C min^{-1}.

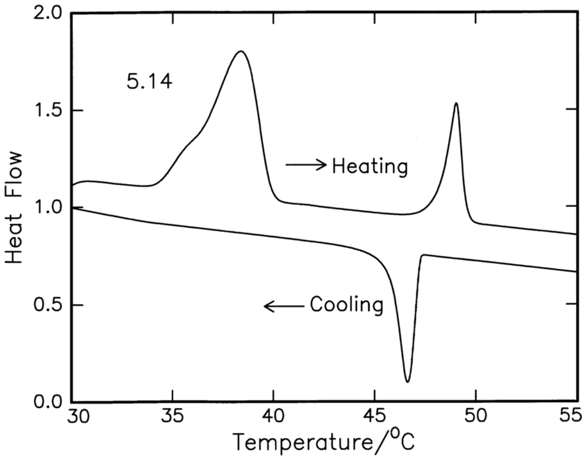

Fig. 3. DSC heating and cooling thermogram of compound 5.14.

peratures and the heats of transitions (the enthalpy changes, ΔH etc.), are obtained by this technique. The thermograms and enthalpy values are recorded by a Perkin-Elmer DSC 7. The results of TM and calorimetry are presented in Table 1 and Figs. 2 and 3.

3. Results and Discussion

3.1. Characterization of N-(p-n-Alkylbenzylidene)-p-n-decyl Aniline, n.10 Compounds

It is interesting to note that the compounds of this series show different types of phase behaviour on changing the alkyl chain length. The compounds studied in this series generally exhibit clearing temperatures below 50 °C (with an exception in some cases which show mesomorphic behaviour below room temperature). The compounds 1.10 and 2.10 exhibit a mesophase to isotropic transition nearer to ambient temperatures. However, they are found to exhibit a monotropic (cooling) nematic phase at 30.9 °C and 25.2 °C, respectively, with a characteristic threaded marble texture. Although the compound 4.10 is liquid crystalline nature below room temperature, the higher homologues of this series of compounds, viz. 5.10 shows smectic-A and smectic-B phases, while the LC phase exists almost down to room temperature.

3.2. Characterization of n.12 Compounds

With the increase of the chain length compared to the previous *n*.10 compounds by two methylene groups in the *n.m* series, viz. 1.12, 2.12, 4.14 and 5.12 by increasing *m*, a slight increase in clearing temperatures is found to result. The compounds 1.12 and 2.12 show the monotropic nematic phase only. Even though compound 4.12 exhibits nematic and smectic-A phases very close to room temperature (Fig. 2), the higher homologue 5.12 of this compound only exhibits the smectic-A phase.

3.3. Characterization of n.14 and n.16 Compounds

The TM and DSC investigations of these higher homologues are accompanied by an increase in the clearing temperatures as expected [7] in Schiff base compounds. The compounds 4.14 and 5.14 show only the smectic-A phase on cooling the corresponding isotropic melt with the onset of focal conic fan texture. The transition temperatures along with the enthalpy values are given in Table 1. It may be noticed that [3] long terminal alkyl chain benzylidene mesogenic compounds favour to form smectic phases rather than the nematic phase. However, it remains conspicuous that the liquid crystalline nature is quenched when the chain length on the bezaldehyde side is ≤ 2 (1.14 and 2.14). A similar trend of quenching is observed in the 4.16 and 5.16 compounds. The lower homologues, viz. 1.16 and 2.16, exhibit no liquid crystallinity.

From our previous systematic studies on these Schiff based benzylidene aniline compounds (with or without an oxygen atom in the alkyl chains) and the present studies on *n.m* compounds, the following is noticed:

1. When the chain length on the benzylidene side is minimal (one), the higher homologous compounds (with the alkyl chain lengths 10 and 12) show nematic phases irrespective of the presence of oxygen on the other side of the rigid core. However, if the alkyl chain length is $\geq$ 14 with conspicuous absence of oxygen at the rigid core, the liquid crystalline nature is found to be quenched. Further, it is observed that on absence of oxygen the clearing temperatures are depressed.

2. The increment of the methyline unit on the left side of the core remaines least effective towards the quenching of liquid crystallinity and depressing the clearing temperature when the alkyl chain length is $\geq$ 14. However, the appearance of a layered smectic-A phase resulted in the compounds 2O.14 and 2O.16.

3. It is observed [14] that, when the chain length is increased (to four and five on the left side of the rigid core) with the presence of an oxygen atom, the variety of polymorphisms is increased, *i. e.*, 4O.10 (NAB), 4O.12 (NAB), 4O.14 (NA), 4O.16 (NA), 5O.10 (NAB), 5O.12 (NAB), 5O.14 (NAB), and 5O.16 (NA). However, the absence of the oxygen atom is found to result in quenching some of the phases, [except 4.12 with (NA) variant]. Further, it is observed that the absence of oxygen reduces the clearing temperature in all compounds. The depressing trend of the clearing temperatures due to the absence of oxygen becomes quite predominant with the 4.10 exhibiting liquid crystallinity below ambient temperature.

In conclusion it is argued that, while the placement of an electro-negative atom like oxygen plays an important role in forecasting polymorphism [15], the alkyl chain length further furthers the occurrence of the phase variant in benzylidene aniline compounds [16].

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