

# The Influence of the Position of Oxygen on the Phase Behaviour of Benzylidene Anilines

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Synthesis and Characterization of N (*p*-*n*-alkyl benzylidene)-*p*-*n*-alkoxy anilines (*n*.*Om*), N (*p*-*n*-alkoxy benzylidene)-*p*-*n*-alkoxy anilines (*nO*.*Om*) and N (*p*-*n*-alkyl benzylidene)-*p*-*n*-alkyl anilines (*n*.*m*), where  $n = m =$  either 4 or 5, has been carried out using thermal microscopy (TM) and differential scanning calorimetry (DSC). The results are discussed in the light of other experimental observations on N (*p*-*n*-alkoxy benzylidene)-*p*-*n* alkyl anilines (*nO*.*m*). It has been observed that the position of oxygen on either side of the rigid core of the benzylidene moiety plays an important role in the manifestation of different phase variants.

**Key words:** *nO*.*m*, *n*.*Om*, *nO*.*Om*, and *n*.*m*, Phase Variants.

## 1. Introduction

Phase transitions interest physicists, chemists and metallurgists. This interdisciplinary subject is also of technological relevance [1, 2]. The literature abounds in experimental and theoretical studies of phase transitions and many unifying concepts have emerged in the recent years [3, 4].

Liquid crystals are known for their anomalous physical properties near the phase transitions. They maintain orientational and/or positional order in a mesophase. The majority of mesogenic molecules are composed of an aromatic core with one or two flexible end alkyl chains [5]. Alkyl chains enhance the thermal range of the liquid crystal by lowering the melting point. The liquid crystal properties, mainly the clearing temperature and the entropy of transitions, are influenced by the end chains [6].

The N(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkylanilines, popularly known as *nO*.*m* of the schiff bases, constitute a series of compounds exhibiting rich polymeromorphism [7, 8]. The present preliminary communication presents investigations on schiff bases with the oxygen on either side (*nO*.*m* or *n*.*Om*), on both sides (*nO*.*Om*), or in the absence of oxygen (*n*.*m*). The phase behaviour observed in these compounds is discussed in the light of the available literature on well-studied *nO*.*m* compounds [9, 10].

## 2. 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 a few drops of glacial acetic acid. 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 molecular structure of the compounds is shown in Figure 1.

The compounds studied were: 4.O4, 4O.O4, 4.4, 5.O5, 5O.O5, and 5.5. The chain length on either side of the central rigid core has been taken equal, and only the position of the oxygen atom was changed. Further, oxygen was removed from either side. The mesomorphic behavior of the compounds with  $n = m =$  either 4 or 5 was studied through thermal microscopy (polarizing microscope) and differential scanning calorimetry (Perkin-Elmer DSC 7).

## 3. Results and Discussion

The phase variants exhibited by these compounds along with the phase transition temperatures and the corresponding enthalpy values are given in Table 1. The thermo grams (DSC) of the compounds 4O.4, 4.O4, and 4O.O4 are shown in Fig. 2, while

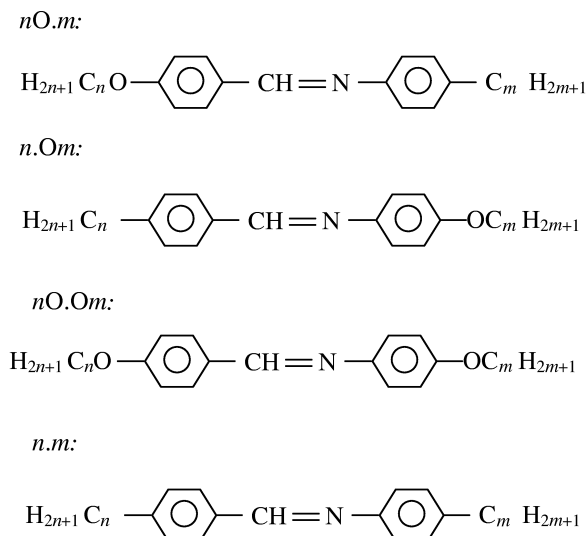


Fig. 1. Molecular Structures of the Homologous series of Compounds.

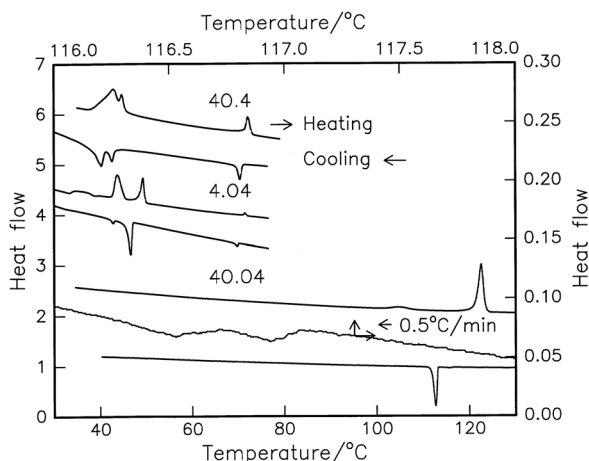


Fig. 2. DSC heating and cooling thermo grams of the compounds 4O.4, 4.O4 and 4O.O4.

those of 5O.5, 5.O5, 5O.O5, and 5.5 are shown in Figure 3.

For comparison, the DSC thermo grams of 4O.4 and 5O.5 are also recorded. They show both heating and cooling, first order transition peaks of all phase transitions. The transitions which have not shown any trace of a peak are NA in 4O.4, and NA and AC in 5O.5. They are reported [9, 11] to be of second order. The transition temperatures and the enthalpies of the transitions are given in the Table 1. They agree reasonably with the literature data.

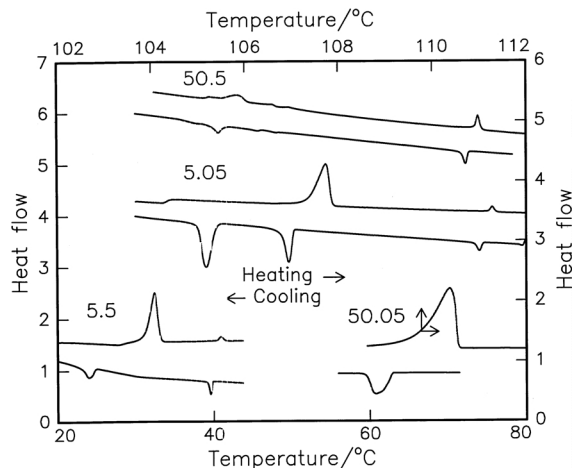


Fig. 3. DSC heating and cooling thermo grams of the compounds 5O.5, 5.O5, 5O.O5 and 5.5.

The thermal microscopic studies have revealed that all the compounds except 5O.O5 show a nematic phase by exhibiting characteristic threaded marble. The compound 5O.O5 exhibited only a monotropic smectic-G phase with mosaic texture that turned to a solid crystalline phase within a short span of about 0.2 °C (Fig. 3). This is in contrast to that observed in the compounds 4O.4 and 5O.5, which exhibited rich polymorphism with NABG and NACBG, respectively.

On shifting of an electronegative oxygen atom from the benzaldehyde side to the aniline side, or on completely removing the oxygen from the molecular moiety, intermediate smectic phases such as AB (with  $n = 4$ ) and ACB ( $n = 5$ ) are quenched in the former case, while in the latter there is a drastic lowering of the clearing temperature also. This is more pronounced in the case of 4.4, that showed below room temperature liquid crystallinity. Contrary to these observations, the presence of oxygen on both sides of the rigid core almost quenched the liquid crystal nature. This is evident from the small thermal ranges observed in the case of 4O.O4 and 5O.O5 (0.4 °C of the nematic range and 2.5 °C of the smectic-G phase, Fig. 2, and only a small range of the smectic-G phase, Fig. 3). The increase of the clearing temperatures and the reduction/quenching of the liquid crystal nature are attributed to the constraint on part of the chains to melt with the presence of oxygen. The absence of oxygen from the liquid crystal moiety caused a reduction of the clearing temperature, exhibiting a room temperature smectic-G phase in 5.5, while in 4.4 it exhibited the liquid crystal nature below room temperature.

Compound	Phase variant	Method		I-N/G	N-A	A-C/B	C/F	N/B/F-G	I/N/G-K	Ref.
4O.4	NABG	TM	Cooling	74.60	46.1	44.30		42.10	12.00	[11]
4.O4	NG	DSC	Heating	71.38				49.26	43.68	
			$\Delta H$ /j/mol.	0.83				15.19	22.52	
			Cooling	69.74				46.59	42.80	
			$\Delta H$ /j/mol.	0.92				14.30	0.95	
4O.O4	NG	TM	Cooling	72.10				47.20	42.20	
		DSC	Heating	—				—	122.46	
			$\Delta H$ /j/mol.	—				—	53.63	
			Cooling	116.52*				116.94*	113.39	
			$\Delta H$ /j/mol.	0.2				0.11	50.16	
		TM	Cooling	117.80				117.50	114.10	
4.4	Exhibits liquid crystalline nature below room temperature									
5O.5	NACFG	TM	Cooling	77.80	54.40	53.10	49.00	47.00	28.00	[9]
5.O5	NG	DSC	Heating	75.64				—	54.39	
			$\Delta H$ /j/mol.	2.40				—	63.14	
			Cooling	74.03				49.66	39.06	
			$\Delta H$ /j/mol.	2.88				18.89	34.30	
5O.O5	G	TM	Cooling	76.80				51.60	40.70	
		DSC	Heating	—				—	113.25	
			$\Delta H$ /j/mol.	—				—	86.09	
			Cooling	108.97*				—	108.80*	
			$\Delta H$ /j/mol.	—				—	75.98	
		TM	Cooling	109.70				—	109.10	
5.5	NG	DSC	Heating	40.33				—	32.88	
			$\Delta H$ /j/mol.	2.13				—	47.10	
			Cooling	39.58				23.97	—	
			$\Delta H$ /j/mol.	2.00				5.05	—	
		TM	Cooling	40.80				24.5	—	

Table 1. The transition temperatures ( $^{\circ}\text{C}$ ) from thermal microscopy, and differential scanning calorimetry along with enthalpy values.

\* The peaks are not resolved.

#### 4. Salient Features of the Work

- A change in the position of the oxygen on either side of the rigid core (benzylidene aniline group) affects the phase transitions.

- If the oxygen is on the benzaldehyde side the compound exhibits rich polymorphism (4O.4 and 5O.5). This is the trend that has been observed in systematic studies that have been carried out on nO.m compounds.

- If the oxygen is on the aniline side, the intermediate smectic phases are quenched with no considerable change in the clearing temperatures.

- When the oxygen is on both sides of the rigid core (benzylidene aniline group) the clearing temperature is higher and the compounds almost lose their liquid crystalline nature.

- On absence of oxygen in the liquid crystal moiety the clearing temperature decreases and shows the liquid crystal nature at ambient temperature.

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- [1] S. Chandrasekhar, *Liquid Crystals*, University Press, Cambridge 1992.
- [2] P. G. de Gennes and J. Prost, "The Physics of Liquid Crystals", Clarendon Press, Oxford 1993.
- [3] D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, and V. Vill, *Handbook of Liquid Crystals*, Vol. 1. Wiley – VCH, 1998.
- [4] D. P. Ojha, D. Kumar, and V. G. K. M. Pisipati, *Z. Naturforsch.* **56a**, 873 (2001).
- [5] P. A. Kumar, M. L. N. Madhu Mohan, and V. G. K. M. Pisipati, *Liq. Cryst.* **27**, 727 (2000).
- [6] P. J. Collings, and M. Hird, "Introduction to Liquid Crystals", Taylor and Francis, U.K. 1997.
- [7] N. V. S. Rao, D. M. Pothokuchi, and V. G. K. M. Pisipati, *Mol. Cryst. Liq. Cryst.* **196**, 71 (1991).
- [8] P. A. Kumar, Swathi Pisupati, V. G. K. M. Pisipati, Ch. Srinivasu, and P. Narayana Murthy, *Liq. Cryst.* **29**, 967 (2002).
- [9] P. R. Alapati, D. M. Pothukuchi, N. V. S. Rao, V. G. K. M. Pisipati, A. S. Paranjpe, and U. R. K. Rao, *Liq. Cryst.* **3**, 1461 (1988).
- [10] D. M. Potukuchi, G. Padmaja Rani, M. Srinivasulu, and V. G. K. M. Pisipati, *Mol. Cryst. Liq. Cryst.* **319**, 19 (1998).
- [11] J. V. Rao, N. V. S. Rao, V. G. K. M. Pisipati, and C. R. K. Murty, *Ber.Bun.Ges.Phy.Chem.*, **84**, 1157 (1980).