# Phase Transitions and Pre-transitional Effects in *N*-(*p*-*n*-Pentylbenzylidene)-*p*-*n*-pentylaniline (5.5) and its Oxygen Derivatives – A Dilatometric Study

N. Ajeetha[a], M. Ramakrishna Nanchara Rao[b], P. V. Datta Prasad[c],
and Venkata G. K. M. Pisipati[a]

[a] Centre for Liquid Crystal Research and Education, Acharya Nagarjuna University,
Nagarjuna Nagar – 522 510, A.P., India
[b] Department of Physics, A.J. Kalasala, Machilipatnam, A.P., India
[c] Department of Physics, The Hindu College, Machilipatnam, A.P., India

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

Z. Naturforsch. **60a,** 749 – 752 (2005); received February 8, 2005

The density of *N*-(*p*-*n*-pentylbenzylidene)-*p*-*n*-pentylaniline (5.5) and its two oxygen derivatives, viz. *N*-(*p*-*n*-pentylbenzylidene)-*p*-*n*-pentyloxyaniline (5.O5) and *N*-(*p*-*n*-pentyloxybenzylidene)-*p*-*n*-pentyloxyaniline (5O.O5), is reported for the isotropic (I), nematic (N), smectic-G ($S_G$) and crystalline (K) phases. Dilatometric results reveal the first order nature of the I-N, N-$S_G$ and N-K transitions. A rare occurrence of the N-K transition is found for the compound 5O.O5 at a considerably higher temperature. From the observed density data pre-transitional effects are estimated for the isotropic to the first mesomorphic phase. The results are discussed in the light of data reported on other Schiff base benzylidene anilines.

*Key words:* Pre-transitional Effect; Dilatometry; Schiff Base.

## 1. Introduction

Schiff base benzylidine aniline compounds show rich but subtle polymesomorphisms [1 – 4]. Dilatometric studies of liquid crystals (LC) can provide complimentary information on phase transition temperatures obtained by thermal microscopy and calorimetry. The nature of phase transitions and pre-transitional effects can also be investigated by dilatometry [5 – 8]. The position of an oxygen atom on either side of the rigid core in benzylidene aniline molecules is found to influence the phase sequence, the thermal range and the clearing temperatures of such LC's [9, 10].

The present paper deals with the phase transitions and pre-transitional effects of three Schiff base benzylidine aniline compounds, viz. *N*-(*p*-*n*-pentylbenzylidene)-*p*-*n*-pentylaniline (5.5), *N*-(*p*-*n*-pentylbenzylidene)-*p*-*n*-pentyloxyaniline (5.O5), and N-(*p*-*n*-pentyloxybenzylidene)-*p*-*n*-pentyloxyaniline (5O.O5), across their isotropic-nematic (I-N), nematic-smectic-G (N-$S_G$) and nematic-crystalline (N-K) transitions. The phase variants and the density results are discussed in the light of the available data on another oxygen derivative of (5.5), viz. *N*-(*p*-*n*-pentyloxybenzylidene)-*p*-*n*-pentylaniline (5O.5) and other *N*-(*p*-*n*-alkyloxybenzylidene)-*p*-*n*-alkylanilines (*n*O.*m*) compounds [7, 11, 12].

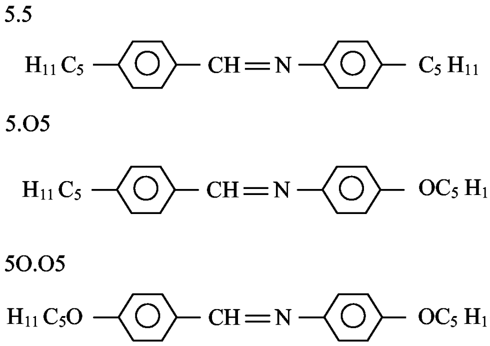

Fig. 1. Molecular structure of the compounds 5.5, 5.O5 and 5O.O5.

## 2. Experimental

The present LC's were synthesized following the standard procedure described in [9]. The molecular formulae of these compounds are given in Figure 1. A 'U'-shaped bicapillary pyknometer in conjunction with a cathetometer was used to study the temperature variation of the density [13].

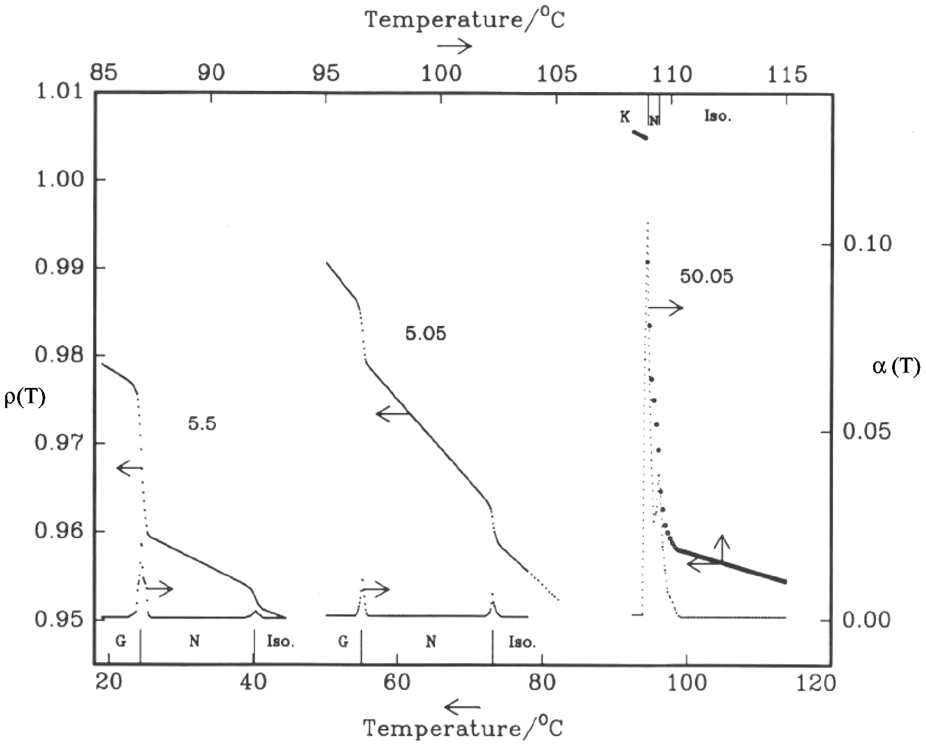

Fig. 2. Temperature variation of the density $\rho$ (g·cm$^{-3}$) and the thermal expansion coefficient $\alpha$ $(10^{-4}\,°\mathrm{C}^{-1})$ of 5.5, 5.O5 and 5O.O5. K, crystalline; G, smectic-G ($S_G$); N, nematic; Iso., isotropic.

## 3. Results and Discussion

The temperatures of the phase transitions obtained by thermal microscopy and differential scanning calorimetry (DSC) are reported in [9]. Those obtained by the density measurements are given in Table 1. They agree well with the reported results. Table 1 reveals the presence/absence of an oxygen atom whose position in the LC molecule influences the phase variants, the thermal range of the liquid crystalline phase and the LC clearing temperatures. Further, it is noted that in the compound 5O.O5, the thermal range of the nematic phase is reduced to about 0.5 °C.

The density is found to increase with decreasing temperature in the liquid crystalline phases except in the vicinity of phase transitions where it shows a steep decrease before it attains the equilibrium value of the next (lower temperature) phase. The temperature variation of the density $\rho(T)$ and the thermal expansion coefficient $\alpha(T)$ with temperature for these three compounds is presented in Figure 2. The density jump $(\Delta\rho/\rho)$ is calculated as the vertical distance between the density values ($\rho_1$ and $\rho_2$) obtained by linear extrapolation from either side of the transition, which are in fact the average value of the above two extrapolated density values, i. e., $[(\rho_1-\rho_2)/\{(\rho_1+\rho_2)/2\}]$. The observed density jump $(\Delta\rho/\rho)$ and the thermal expansion coefficient maxima ($\alpha_{\max}$) across I-N, N-G and N-K of the above compounds are presented in Table 2.

Table 1. Phase transition temperatures (°C) obtained by density measurements.

| Compound | Phase variant | I-N | N-A | A-C | C-F | N/F-G | N/G-K | Ref. |
|---|---|---|---|---|---|---|---|---|
| 5.5 | NG | 40.4 | | | | 24.5 | | PW |
| 5.O5 | NG | 73.1 | | | | 55.1 | | PW |
| 5O.5 | NACFG | 77.8 | 54.4 | 53.1 | 49.0 | 47.0 | 28.0 | [12] |
| 5O.O5 | N | 109.5 | | | | | 109.0 | PW |

As the thermal range of the nematic phase is too small to stabilize the nematic before transforming to the solid state, the anomalous density jump across the I-N transition in 5O.O5 does not truly replicate the information regarding the phase transformation. The calculated combined jump is found to be 4.60%.

The I-N transition is accompanied by density jumps of 0.22%, 0.37% and 1.11% and thermal expansion coefficient maxima of $26.0\cdot10^{-4}\,°\mathrm{C}^{-1}$, $69.2\cdot10^{-4}\,°\mathrm{C}^{-1}$

Table 2. Thermal range of the nematic phase, density jump $(\Delta\rho/\rho)$ and thermal expansion coefficient $(\alpha_{\max})$ at the phase transitions of *N*-(*p*-*n*-pentylbenzylidene)-*p*-*n*-pentylaniline and its oxygen derivatives.

| Compound | Phase variant | Nematic range (°C) | % of $\Delta\rho/\rho$ I-N | % of $\Delta\rho/\rho$ N-G/K | $\alpha$ ($10^{-4}$ °C$^{-1}$) I-N | $\alpha$ ($10^{-4}$ °C$^{-1}$) N-G | Ref. |
|---|---|---|---|---|---|---|---|
| 5.5 | NG | 15.9 | 0.22 | 1.80 | 26.0 | 148.0 | PW |
| 5.O5 | NG | 18.0 | 0.37 | 0.62 | 69.2 | 105.9 | PW |
| 5O.5 | NACFG | 22.4 | 0.33 | — | 76.0 | — | [12] |
| 5O.O5 | N | 0.5 | 1.11* | 3.25* | 385.9 | 1055.0 | PW |

* The thermal range of the nematic phase in this compound is small, and hence the slope values are not reliable.

and $385.9 \cdot 10^{-4}$ °C$^{-1}$ for the 5.5, 5.O5 and 5O.O5 compounds, respectively. These values suggest the first order nature of the transition, as expected at an I-N interface. The density jump $(\Delta\rho/\rho)$ and the thermal expansion coefficient maxima $(\alpha_{\max})$ are found to be increasing with the introduction of oxygen atoms in the molecular moiety. However, these two values are of comparable magnitude for the compounds 5.O5 and 5O.5, suggesting that placement of an oxygen atom on either side of the central rigid core affects only the LC nature and has no effect on the clearing temperature. On the other hand, a pronounced effect is observed if either of the oxygen atoms is removed completely from the molecule, i. e. 5.5, or placing an oxygen atom on both sides of the central rigid core, i. e. 5O.O5. The density jump in 5.5 is on the lower side of the values reported for *n*O.*m* compounds, while a very high value is observed in case of the 5O.O5 compound [7]. However, the value obtained in 5O.O5 cannot be considered as a true value representing the jump at the I-N transition, since the thermal range is too small (for the nematic phase to stabilize before transforming into crystal). Further, the nematic range is drastically reduced (almost the LC nature is quenched) in the case of 5O.O5, while the clearing temperatures showed extremes, i. e. low as 40.4 °C and high as 110.0 °C for 5.5 and 5O.O5, respectively. The density variation at the equilibrium isotropic phase of 5.5, 5.O5 and 5O.O5, nematic and smectic-G phases for 5.5, 5.O5 along with the reported values for 5O.5 are given in Table 3.

The slope values are increasing with the onset of the low temperature phase, as expected, and exhibit an increase with the presence of oxygen (nematic and smectic-G phase). However, they are found to be low in the relevant LC phase reported [12].

The $S_G$ phase is a three-dimensional ordered phase, and the inter-layer ordering is related by a simple translation along the long axes of the molecules. Hence an N-$S_G$ transition involves a transformation of orientational order into a long range three-dimensional hexagonal lattice (with orientational order), and is expected to be of first order. Further, this transition is almost analogous to the nematic to solid transition. The observed density jumps, $(\Delta\rho/\rho) = 1.80$ for 5.5 while 0.62 for 5.O5, indicate first order nature of the transition. The thermal expansion coefficient maxima $\alpha_{\max} = 148.0 \cdot 10^{-4}$ °C$^{-1}$ for 5.5 and $105.9 \cdot 10^{-4}$ °C$^{-1}$ for 5.O5 observed at the transition also suggest the first order nature. The large variation of the density jumps observed for these compounds may not be reckoned as uncommon, as similar trends of density variation are observed for the compounds 5O.2 (0.38) and 6O.2 (1.16) [14]. In the present case, this may be due to the difference in the observed transition temperatures (24.5 °C and 55.1 °C in the case of 5.5 and 5.O5). However, a systematic comparison could not be made owing to the scarcity of data available across this transition.

Table 3. Variation of the density of equilibrium isotropic phases of 5.5, 5.O5 and 5O.O5, nematic and smectic-G phases of 5.5, 5.O5 along with reported values of 5O.5.

| Compound | $(\mathrm{d}\rho/\mathrm{d}T)_{\mathrm{Iso}}$ ($10^{-4}$ °C$^{-1}$) | $(\mathrm{d}\rho/\mathrm{d}T)_{\mathrm{N}}$ ($10^{-4}$ °C$^{-1}$) | $(\mathrm{d}\rho/\mathrm{d}T)_{\mathrm{G}}$ ($10^{-4}$ °C$^{-1}$) | Ref. |
|---|---|---|---|---|
| 5.5 | 3.2 | 4.1 | 5.1 | PW |
| 5.O5 | 7.5 | 9.3 | 10.3 | PW |
| 5O.5 | 10.0 | 10.0 | — | [12] |
| 5O.O5 | 7.7 | — | — | PW |

The N-K transition, involving a change from a nematic phase (possessing orientational order) to a perfectly three-dimensional crystal, is expected to be of first order. In the case of 5O.O5 we are able to observe this transition, as the temperature involved with this transition is high (109.0 °C) compared to those compounds, which exhibit this transition in *n*O.*m* compounds. Further, the thermal range of the nematic phase is only 0.5 °C. The observed density jump, $(\Delta\rho/\rho) = 3.25\%$, and the thermal coefficient maxima, $\alpha_{\max} = 1055.0 \cdot 10^{-4}$ °C$^{-1}$, at this transition confirm the first order nature of the transition in the compound 5O.O5. Further, the density jump across the N-K transition may not be the true value, as it is not grown from the stabilized nematic phase (Table 2).

## 4. Pre-transitional Effects

Although the density is found to increase linearly with decreasing temperature, in the isotropic liquid phase its increment in density is found to be non-linear (normalized density variation for $T > T_{\mathrm{IN}}$) in the vicinity of the I-N phase transition. This type of non-linear variation of the density on both sides of the transition temperature reflects the growth of fluctuations, which converge to a finite value at $T_{\mathrm{IN}}$. However, these fluctuations cease for $T < T_{\mathrm{IN}}$ before a thermally stabilized nematic phase is established with further decrease of the temperature. The strength and longevity of these pre-transitional fluctuations, that grow at the I-N interface, are estimated following the relation

$$|\rho_1 - \rho_{\mathrm{C}}| \sim |T_{\mathrm{I}} - T_{\mathrm{C}}|^{(1-\alpha_{\mathrm{eff}})}, \quad (1)$$

where $\rho_{\mathrm{I}}$ is the observed density at the temperature of interest $T_{\mathrm{I}}$, and $\rho_{\mathrm{C}}$ is the observed density at $T_{\mathrm{IN}}$. As $\Delta T = |T_{\mathrm{I}} - T_{\mathrm{C}}|$, the fluctuation dominated non-linear region (FDNLR) reflects the persistence and longevity of the fluctuation growth, and $\alpha_{\mathrm{eff}}$ reflects the strength of the fluctuations.

Table 4. The values of $\alpha_{\mathrm{eff}}$ along with the thermal spans (°C) of fluctuation dominated non-linear region (FDNLR).

| Compound | $\alpha_{\mathrm{eff}}$ | FDNLR (°C) |
|---|---|---|
| 5.5 | 0.27 | 1.1 |
| 5.O5 | 0.47 | 1.6 |
| 5O.O5 | 0.69 | 1.0 |

The observed data of temperature variation and transition temperatures are fitted to the relation (1), and the resulting $\alpha_{\mathrm{eff}}$ values along with the data of the thermal span of the FDNLR are listed in Table 4. The goodness of the fit is demonstrated by the *p*-values ($> 0.996$) of the $\chi^2$-test in the present compounds.

The FDNLR, observed on the isotropic side of the I-N transition in these three compounds, are found to be large compared to those observed for the *n*O.*m* compounds [15, 16]. The calculated $\alpha_{\mathrm{eff}}$ values are found to be within the range of the values reported on the isotropic side of I-N transitions in *n*O.*m* compounds. However, the $\alpha_{\mathrm{eff}}$ values exhibit an increasing trend with the introduction of oxygen atoms in the molecular moiety. The variation of $\alpha_{\mathrm{eff}}$ is argued as due to the presence of the electronegative oxygen atom in the molecular moiety, and it may be noticed that the nature of the nematic fluctuations in the FDNLR of these three compounds are different from one another, suggesting a weak nature of the nematic fluctuations growth in 5.5 to a relatively strong growth in the case of 5O.O5. The large thermal ranges of FDNLR observed in these compounds indicate the large average life times of nematic-like fluctuations before they converge to bear a finite value at the I-N phase transition.

### *Acknowledgement*

The financial support by the Department of Science & Technology (Grant No. SP/S2/M-34/ 2000), New Delhi, India is gratefully acknowledged.

[1] H. Kelker, B. Scheurle, R. Hertz, and W. Bartsh, Angew. Chem. **9**, 962 (1970).

[2] G.W. Smith and Z.G. Garlund, J. Chem. Phys. **59**, 3214 (1973).

[3] A. Wiegeleben, L. Richter, J. Deresch, and D. Demus, Mol. Cryst. Liq. Cryst. **59**, 329 (1980).

[4] V. G. K. M. Pisipati, Z. Naturforsch. **58a**, 661 (2003).

[5] D. Demus, H. Konig, D. Marzotko, R. Rurainski, A. Hauser, L. Latif, C. Salbmann, and W. Weissflog, Cryst. Res. Technol. **29**, 443 (1994).

[6] M. Jitendra Nadh, C.G. Rama Rao, M. Srinivasulu, D.M. Potukuchi, and V. G. K. M. Pisipati, Mol. Cryst. Liq. Cryst. **366**, 457 (2001).

[7] C. Rama Chandra Prabhu, S. Lakshminarayana, and V. G. K. M. Pisipati, Z. Naturforsch. **59a**, 537 (2004).

[8] S. Padmaja, M. Ramakrishna Nanchara Rao, P. V. Datta Prasad, and V. G. .K. M. Pisipati, Z. Naturforsch. **60a**, 296 (2005).

[9] N. Ajeetha and V. G. K. M. Pisipati, Z. Naturforsch. **58a**, 735 (2003).

[10] N. Ajeetha, D. M. Potukuchi, and V. G. K. M. Pisipati, Phase Transitions **78**, 369 (2005).

[11] K. Hilltrop, Mol. Cryst. Liq. Cryst. **59**, 329 (1980).

[12] P. R. Alapati, D. M. Potukuchi, N. V. S. Rao, V. G. K. M. Pisipati, A. S. Paranjpe, and U. R. K. Rao, Liq. Cryst. **3**, 1461 (1988).

[13] N. V. S. Rao and V. G. K. M. Pisipati, J. Phys. Chem. **87**, 889 (1984).

[14] N. V. S. Rao and V. G. K. M. Pisipati, Phase Transitions **4**, 91 (1984).

[15] N. V. S. Rao, D. M. Potukuchi, and V. G. K. M. Pisipati, Mol. Cryst. Liq. Cryst. **196**, 71 (1991).

[16] P. Bhaskara Rao, D. M. Potukuchi, J. S. R. Murthy, N. V. S. Rao, and V. G. K. M. Pisipati, Cryst. Res. Technol. **27**, 839 (1992).