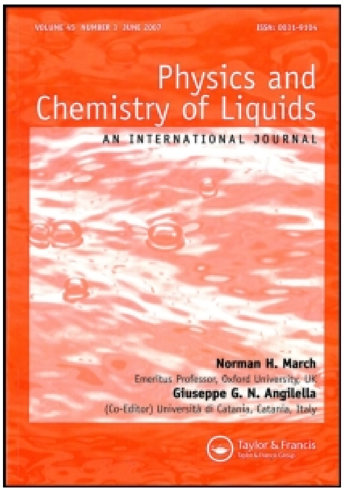

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Simultaneous characterisation and dilatometry studies on liquid crystalline N-(*p* - *n* -decyloxy and undecyloxybenzylidene)- *p* -toluidines

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Simultaneous characterisation and dilatometry studies on liquid crystalline N-(*p*-*n*-decyloxy and undecyloxybenzylidene)-*p*-toluidines

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An indigenous experimental setup has been designed and fabricated for the simultaneous observation of optical textures for the characterisation and the measurement of density of liquid crystal samples. The compounds studied are the well-known *n*O.*m*s, N-(*p*-*n*-decyloxy and undecyloxybenzylidene)-*p*-toluidines (10O.1 and 11O.1). The phase variants exhibited by these compounds are nematic, smectic-A and smectic-B and smectic-A (A), respectively. The density results reveal that the nature of transitions is of first-order. The results are discussed in the light of the data available on other *n*O.*m* and similar compounds. The advantages as well as further improvements contemplated in the design and development of such simultaneous measurements are presented.

Keywords: *n*O.*m* compounds; simultaneous measurements; dilatometry; pre-transitional effects

1. Introduction

Newly synthesised liquid crystal (LC) compound has to undergo characterisation before subjected to physical property measurements to understand the fundamental aspects and to test its viability for technological applications. The characterisation is done by polarising microscope with the hot stage attachment (for the variation of temperature of the sample) to observe the optical textures, the compound exhibits for the identification of the LC phases [1, 2]. The differential scanning calorimeter (DSC) is another technique (thermal) to obtain the phase transition temperatures and the associated heats of transition [3]. One more technique, X-ray, is not frequently used to obtain the molecular length and the layer spacing, etc. [4]. Of late, photo thermal [5], photo acoustic [6–8] and other methods such as rotating polarisation [9] and mirage effect [10] have been used to study the phase transitions involved in LC samples. The optical methods have an advantage over the thermal methods in detecting some of the second-order transitions where the heat of transition involved could not be detected by DSC (as it is negligible).

As a part of systematic studies on LC, the authors designed and fabricated an experimental setup for the simultaneous measurements, namely the characterisation and density of LC materials. The present manuscript describes such experimental

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Table 1. The phase variants, transition temperatures (°C) and the enthalpy values from different techniques.

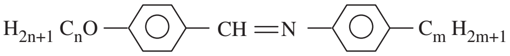
Compound	Phase variant	Method		I–N/A	N–A	A–B	A/B–K
10O.1	NAB	DSC	Heating	77.50[a]	76.65[a]	–	69.60
			ΔH (j gm^{-1})	16.29			106.25
			Cooling	73.94[a]	72.58[a]	60.33	43.75
			ΔH (j gm^{-1})	17.58		8.02	86.10
			Heating[b]	75.95	74.89		
			ΔH (j gm^{-1})	3.66	11.29		
			Cooling[b]	75.58	74.28		
			ΔH (j gm^{-1})	3.96	11.29		
		TM	Cooling	75.4	74.1		
			Density	73.9	73.1	65.3	
			Simultaneous measurements	73.8	73.0	65.2	
11O.1	A	DSC	Heating	–			80.93
			ΔH (j gm^{-1})				46.25
			Cooling	73.73			69.07
			ΔH (j gm^{-1})	5.27			36.82
		TM	Cooling	73.4			68.9
			Density	73.0			71.4
			Simultaneous measurements	73.2			71.2

Notes: [a]The peaks are not resolved in 10O.1 compound.
[b]The scan rate is 1°C min^{-1} (otherwise 10°C min^{-1}) to resolve the I–N and N–A transitions in 10O.1 compound.

technique briefly. The compounds studied using the present technique are the well-known *n*O.*m*s with $n=10$, 11 and $m=1$, namely N-(*p*-*n*-decyloxy and undecyloxy-benzylidene)-*p*-toluidines. The characterisations as well as the density results are discussed in the light of literature data available on similar compounds.

2. Experimental

The LCs are synthesised by following the standard procedure [11]. Initially, the characterisation is carried out using polarising microscope with the hot stage attached (TM) and DSC. The general molecular formula of *n*O.*m* compounds is given below, where $n=10$, 11 and $m=1$. The results are given in Table 1. The DSC thermo grams of the two compounds are given in Figures 1 and 2.



3. Instrumentation

The block diagram of the fabricated setup is given in Figure 3. The polarising microscope for the observation of textures and the pyknometer for the measurement of density are housed in the same heating block. The different parts in the experimental setup are listed in the block diagram. The temperature gradient observed over the length of the heating block is less than 0.3°C and hence, the gradient that can be expected between the pyknometer and the sample in the polarising microscope is less than 0.1°C and the temperature

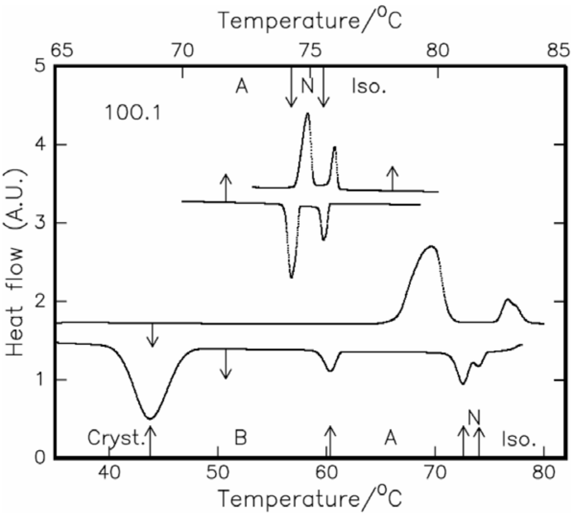


Figure 1. DSC thermogram of 10O.1 compound.

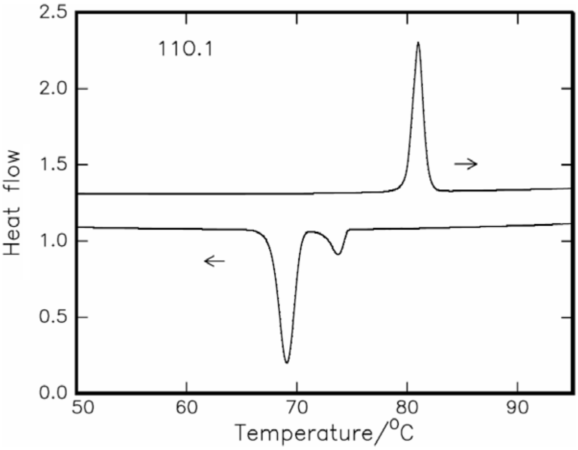


Figure 2. DSC thermogram of 11O.1 compound (heat flow in A.U.).

measurement is made by placing the thermocouple in between the pyknometer and the polarising microscope. The details of the density measurement are given below.

The density of the substances is measured with the help of specially designed pyknometer. The capillaries of the pyknometer having diameter about 300 microns and 15–20 cm length are arranged on the top of U-shaped glass tube, having bore about 6–8 mm diameter. The volume of pyknometer is about 0.88 cc. The bottom of the pyknometer contains about 96% of the total volume of the sample. The accuracy in density is about ±0.1 $\mathrm{Kg\,m^{-3}}$.

To determine the density of liquid crystal material at different temperatures, a hot oven with a provision for the observation of levels of liquid crystal materials in the capillaries is

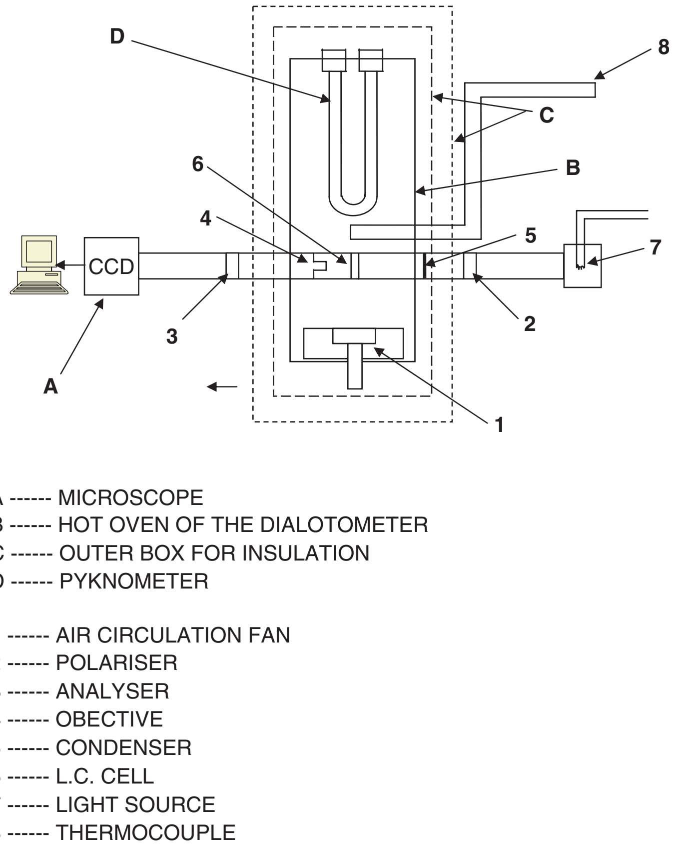


Figure 3. Block diagram of the setup.

essential. The hot oven consists of three brass blocks of 1.5 cm thickness, 40 cm length and 10 cm width were fixed in rectangular shape with fourth side opening and this side is fixed with a glass door for observation. Each brass block is fixed with electrical heater of 250 watts at 220 volt AC, having dimensions 40 cm long and 6 cm width and thickness of 3 mm. To maintain a uniform temperature throughout the volume of the oven, air circulation is maintained by fixing a fan at the bottom of the oven. The entire hot oven is placed in two diathermous jackets to prevent thermal shocks. The glass doors are fixed to the front side of the jackets to observe the LC levels in the capillaries.

A conventional cathetometer is used to measure the liquid crystal levels in the capillaries. It has a telescope with around 6–8X magnification. The main scale of the cathetometer is graduated in mm and each division corresponds to 0.5 mm. The vernier with 50 divisions is attached to the main scale corresponding to the least count of 0.01 mm. Taking a number of readings using conventional cathetometer is tedious task. For experimental ease and accurate measurement the main scale and vernier is replaced with a digital scale which gives an accuracy of ±0.01 mm. Instead of viewing through the telescope eyepiece a CCD camera is attached to the telescope and the levels of capillary were observed on a 14″ television with very high magnification.

4. Results and discussion

4.1. *Characterisation and dilatometry*

The *n*O.*m* compounds have the unique nature of exhibiting a variety of polymorphism. The systematic studies and the literature data [12] reveal that these compounds exhibit 21 different types of phase variants, starting from mono variant (nematic, N or smectic-A, A or smectic-F, F) to hexa variant (NACBFG). The compounds with a smaller number of alkyl chains exhibit nematic and smectic-A phases, with few exceptions [12]. The compounds in the present study belong to the smallest alkyl chain, namely $n = 1$. In the present homologous series (*n*O.1), the liquid crystalline nature manifests in the compound with $n = 4$ with the exhibition of nematic and smectic-A phases and the increase of one more alkoxy chain, and the compound ($n = 5$) exhibits nematic and smectic-G phases. The smectic-G phase is quenched with the increase of one more chain length with manifestation of two more orthogonal smectic-A and smectic-B phases, and this phase variant persists until $n = 10$. Later, when $n = 11$, the nematic and smectic-B phases quench, leaving only the smectic-A phase, and this mono variant persists until $n = 14$. Further increase of chain length and the liquid crystalline nature is quenched [12] in *n*O.1 series. It is interesting to note that the *n*O.*m* compounds with $n = 5$ show a variety of polymorphism when compared to any other series of compounds [12]. The phase variants of all the compounds in this series (*n*O.1) are presented in Table 2.

The density increases linearly with the decrease of temperature in the thermal equilibrium state of different LC phases, except across the phase transformations, where it shows a sudden increase in its value. In the simultaneous measurement, it has been observed that while the compound approaches the first liquid crystalline phase, the density measurement shows the non-linear increase in its value and the optical black region under the crossed polars (isotropic state) slowly transforms first into nematic droplets which slowly coalesce to form the threaded marble texture characteristic of the nematic phase [13] in 10O.1. The non-linear region observed in the density measurement is nearly identical with the thermal range from the isotropic black region to the complete formation of the nematic texture. The thermal gradient observed between the two measurements is less than 0.2°C. In the case of 11O.1, the pre-transitional region between the isotropic phase and first LC phase is dominated by the formation of batonents (which float in the isotropic regions) which slowly coalesce to form the focal conic fan texture characteristic of the smectic-A phase [2].

In the case of the 10O.1 compound, the decrease of temperature exhibits two more phase transitions. The nematic phase transforms to smectic-A by exhibiting the formation of focal conic fan texture from the nematic treaded marble and the value of density shows an abrupt increase from its linear path in the nematic region. However, the nematic phase has not shown any thermal equilibrium region as the thermal range of nematic phase is too narrow. Further, lowering the sample temperature, a clear transformation is observed from smectic-A to smectic-B. The transient transition bars across the fans appear before

Table 2. The phase variants in *n*O.1 compounds.[a]

n	4	5	6	7	8	9	10	11	12	13	14
Phase variant	NA	NG	NAB	NAB	NAB	NAB	NAB	A	A	A	A

Note: [a]For $n = 1$, 2, 3, 15, 16 and 18, there is no liquid crystalline nature.

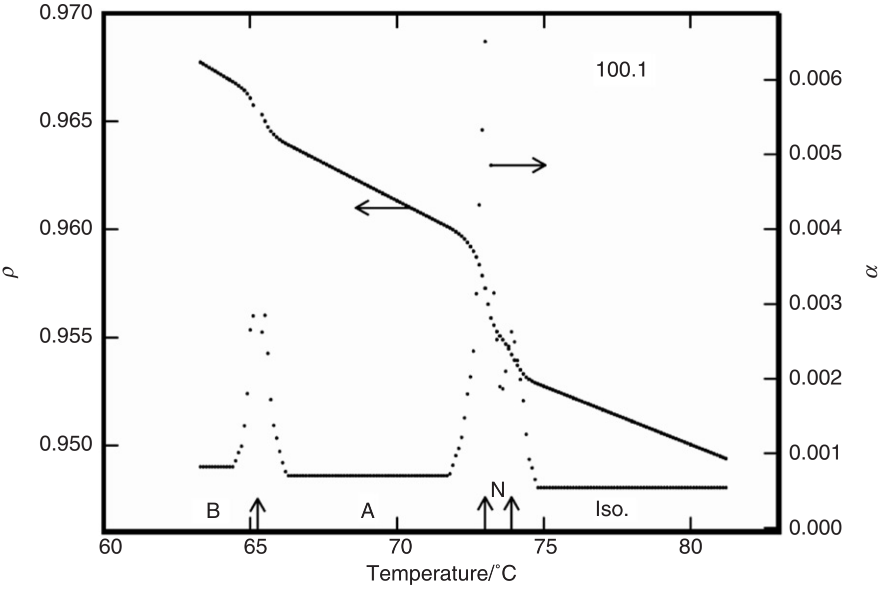


Figure 4. Temperature variation of density and thermal expansion coefficient in the 10O.1 compound.

smooth focal conic fans are formed in smectic-B phase, which is nearly equal to the non-linear region observed on the higher side of the smectic-A to smectic-B transition. The measurements are carried out until the compound attains sticky nature and the fall could not be observed in the pyknometer. However, the smectic-B texture transforms to crystal at about 45°C. In the case of 10O.1, the nematic to smectic-A (NA) is resolved from the slow scan rate of 1°C/minute in DSC measurements (Figure 1).

The variation of density and the thermal expansion coefficient, $1/M_V\ (\mathrm{d}M_V/\mathrm{d}T)$ (M_V, the molar volume = molecular weight/the density) with temperature for the two compounds are presented in Figures 4 and 5. The vertical distance between the density values (ρ_1 and ρ_2) obtained from extrapolating the observed equilibrium linear dependence from either sides of the transition normalised over the average value obtained from them i.e. $\{[(\rho_1-\rho_2)]/[(\rho_1+\rho_2)/2]\}$ is taken as the density jump ($\Delta\rho/\rho$) across a transition.

The molar volumes (M_V) in the isotropic phase of 10O.1 and 11O.1 at $(T_{\mathrm{IN\ or\ IA}}+3)$°C are 368.8 and $384.9\times10^{-6}\,\mathrm{m^3\,mol^{-1}}$, respectively. Figure 6 exhibits the variation of molar volume at $(T_{\mathrm{IN\ or\ IA}}+3)$°C with the alkoxy chain number of *n*O.1 homologues. The slope of the graph shows the increment of molar volume per methylene unit is $16.04\times10^{-6}\,\mathrm{m^3\,mol^{-1}}$. If the additive of molar volume is assumed in the isotropic liquid, the increment per methylene group estimated from the difference in the molar volumes of these compounds is slightly less than for those reported (16.4–$17.2\times10^{-6}\,\mathrm{m^3\,mol^{-1}}$) for CH_2 unit contribution in normal isotropic liquids [14], 4O.*m* [15], and other *n*O.*m* [16] and PBnA [9] compounds.

The observed density jump ($\Delta\rho/\rho$) and the thermal expansion coefficient maxima ($\alpha_{\mathrm{max.}}$) across IN, NA and AB and IA in the two compounds are presented in Table 3 along with the data on other compounds in this homologous series. These values suggest the order of these transitions is of first-order as expected. The individual density jumps of

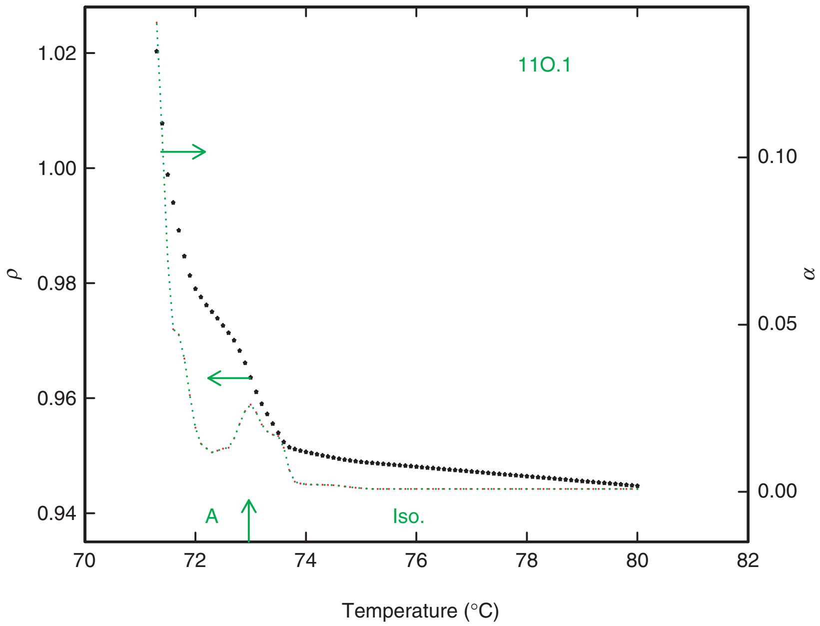


Figure 5. Temperature variation of density and thermal expansion coefficient in 11O.1 compound.

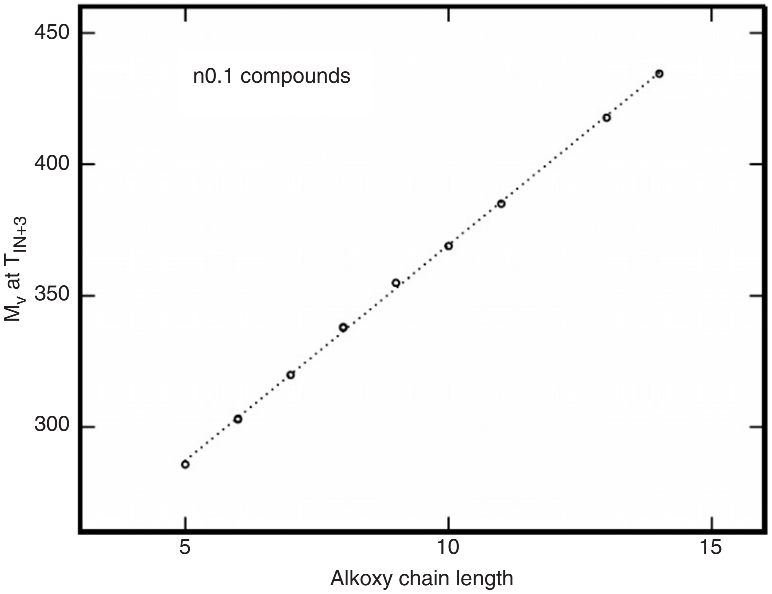


Figure 6. Variation of molar volume at $(T_{\mathrm{IN\ or\ IA}}+3)$°C of *n*O.1 series with alkoxy cahin.

IN and NA phase transitions (in 10O.1) could not be determined as the nematic thermal range is too small for the nematic phase to attain equilibrium conditions. However, the thermal expansion coefficient maxima suggest both the transitions are of first-order. The combined density jump for both the transitions is given in Table 3. Even though the

Table 3. The phase variant, the density jumps, the thermal expansion coefficient maxima and the pressure dependence of the transition temperatures in 10O.1 and 11O.1 compounds

		$\Delta\rho/\rho \times 100$			$\alpha \times 10^{-4\circ}\mathrm{C}^{-1}$		
Compound	Phase variant	I–N/A	N–A/G	A–B	I–N/A	N–A/G	A–B
70.1[a]	NAB	0.20	0.46	0.05	133.0	151.0	30.0
10O.1	NAB	0.56		0.16	26.4	67.3	28.5
11O.1	A	1.63			260.5		
130.1[b]	A	0.57			98.4		
140.1[b]	A	0.93			133.7		

Notes: [a]From [24].
[b]From [25].

density measurements could not resolve the NA transition, it can be argued that order of the transition will be of first-order as the McMillan parameter for this compound is 0.998 which is higher compared to the value predicted (0.88) [17] for a first-order transition. Further, the systematic studies on NA transition in *n*O.*m* compounds [18] envisage the decisive role played by the alkoxy chain in governing the order of NA transition rather than the nematic or smectic-A thermal range or the alkyl chain length. Further, it is reported [18] that in *n*O.*m* series the minimum alkoxy carbon chain number should be six for a possible first-order NA transition irrespective of the alkyl chain number, the nematic thermal range and the McMillan value. To test and to confirm this, the authors have carried out the synthesis, characterisation and dilatometric studies on other Schiff base compounds with alkoxy number 5, namely N-(*p*-*n*-pentylbenzylidene)-*p*-*n*-pentylaniline (5.5) [19], and N-(*p*-*n*-pentylbenzylidene)-*p*-*n*-hexadecylaniline (5.16) [20] and their oxygen derivatives. However, except 5O.5 and 5O.16 (which are *n*O.*m* compounds), the rest of the compounds 5.O5, 5O.O5, 5.5, 5.O16, 5O.O16 and 5.16 [20] show no NA transition.

Crystalline smectic-B has a long-range three-dimensional order with positional correlations of hexagonal in plane packing of molecules as well as layers stacking. The smectic-A to smectic-B (AB) transition is accompanied by a density jump of 0.16 and thermal expansion coefficient maxima of $28.5 \times 10^{-4\circ}\mathrm{C}^{-1}$ (Table 3). This suggests the first-order nature of the transition. However, it is observed that the density jump value is small compared to those observed for other compounds [21], but it is not uncommon in this series, as in 7O.1, as the AB transition showed a jump of 0.05 [22] (Table 3).

The isotropic to smectic-A (IA) transition (11O.1) is accompanied by the simultaneous onset of long-range orientational order and periodic translational order due to the onset of a layered arrangement of molecules from the completely disordered isotropic liquid, and is expected to be a first-order. The IA transition is accompanied by a large density jump of 1.63 in 11O.1 compound and this value is high compared to the values observed in the higher homologues, namely 13O.1 and 14O.1 [23]. The density jump across IA transition in this compound along with the thermal expansion coefficient maxima ($\alpha_{\max}$) are presented in Table 3 and is found in agreement with the reported values in the other *n*O.*m* [24] and terephthalylidene-*bis*-*p*-*n*-alkylanilines (TBnA) [25] compounds. The magnitude of density jump and thermal expansion coefficient maxima suggest the first-order nature of the IA phase transition.

The dilatometric studies and the TM textural across IA transition are accompanied by fluctuation dominated non-linear regions with a value ≈1.1°C in this compound. It is observed that the translucent smectic-A phase grows and floats in the isotropic liquid. The smectic-A phase with a clear separation boundary is found to permeate from the isotropic liquid all through the pyknometer with the decrease of the temperature when smectic-A phase is thermally stabilised. The formation of smectic-A embryos at the bottom and their consequential growth clearly indicate the nucleation type of growth at IA phase transition. The density jump and $\alpha_{\max}$ values are presented in Table 3.

The salient features observed from the simultaneous measurement of density and characterisations through textural observations are:

(1) The temperature deviations observed through different experiments for the same sample can be avoided.
(2) The time taken for the characterisation can be eliminated through the measurement of physical property (density).
(3) The pre-transitional regions can be visually observed while the physical property measurement is being performed.

Further work is in progress to rope in the birefringence measurement along with these two, and the results will be published shortly.

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