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Synthesis, characterization and dilatometric studies on N-(p-n-tri and tetra decyloxybenzylidene)-p-toluidine

S Sreehari Sastry*, K Vijaya Lakshmi, M Ramakrishnancharya, Nanchara Rao, G Sahaya Baskaran
and C Ramachandra Prabhu[1]

Department of Physics, Acharya Nagarjuna University, Nagarjunanagar 522 510, Andhra Pradesh, India

[1] Faculty of Physics, Department of Applied Sciences, Higher College of Technology,
P.O Box -74, Al-Khuwair-133, Muscat, Oman

E-mail sreehari_ssastry@yahoo com

Abstract   Synthesis, characterization and phase transition studies are carried out on two Schiff base liquid crystal materials *viz.*, N-(p-n-tridecyloxybenzylidene)-p-toluidine, 13O 1 and N-(p-n-tetradecyloxybenzylidene)-p-toluidine, 14O.1. The characterization studies (phases and phase transition temperatures) are carried out using polarising microscope equipped with hot stage and differential scanning calorimeter. The phase transition studies are carried out using dilatometric technique The results infer that these two compounds possess only one monotropic liquid crystalline phase *viz.*, smectic-A. The order of phase transition across isotropic to smectic-A is found to be of first order The results are discussed in he light of the data available on other nO.m liquid crystal compounds

Keywords   Liquid crystal, synthesis. phase transition, dilatometry, density measurements

PACS Nos.   42.70 Df. 61 30 Eb 64.70.Md

1. Introduction

The homologous series, *viz.*, N-(p-n-alkoxybenzylidene)-p-n-alkylanilines, popularly known as nO.ms, exhibit rich but subtle polymorphism [1-3]. The compounds are model systems to study the different types of melting and attracted the interest of both theoreticians and experimentalists. Dilatometric technique is one of the powerful tools to study the order of phase transitions [4]. As a part of systematic studies on nO.m compounds, this communication presents the synthesis, characterization and dilatometric studies on two Schiff base compounds, N-(p-n-tridecyloxybenzylidene)-p-toluidine (13O.1) and N-(p-n-tetradecyloxybenzylidene)-p-toluidine, (14O.1). The density studies are carried out to infer the nature of isotropic–smectic-phase transition. The pressure dependence of transition temperatures across the transition, is estimated from the measured volume jumps and enthalpy data. The results are discussed in the light of the reported data on the nO.ms' liquid crystalline compounds, which exhibit isotropic to smectic-A transition.

2. Experimental

An Olympus polarising microscope (BX 50) along with Instec temperature controller with ± 0.1 °C temperature accuracy was used for the textural identification of liquid crystal phases and the determinations of phase transition temperatures. Perkin-Elmer DSC-7 was used to determine the transition temperatures and relevant enthalpy of transitions. A U-shaped bi-capillary pyknometer in conjunction with a cathetometer, was used to study the temperature variation of density. The absolute error in the determination of density is ±0.1 kg.m^{-3}. The cooling rate followed during the density measurements was 1°C/h in general, 0.5°C/h at the vicinity of isotropic to smectic–A transition.

The compounds in the present study are synthesized following the standard procedure [5]. The molecular structure for the compounds is given below.

$$C_nH_{2n+1}O - \bigcirc - CH=N - \bigcirc - CH_3$$

n=13 and 14

| Corresponding Author
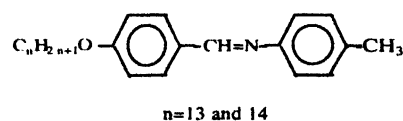
3. Results and discussion

3.1 Characterization and phase identification in 13O.1 and 14O.1 :

The compounds 13O.1 and 14O.1, exhibit a single-phase variant in between solid crystal and isotropic liquid. The observed phase is monotropic.

On cooling from isotropic liquid, a liquid crystalline phase S_1 separates out in the form of batonnets at 76.3°C and 76.5 °C in 13O.1 and 14O.1, respectively. These batonnets float in the isotropic liquid and finally, coalesce to form focal conic fan structure, a characteristic texture of smectic-A phase. This phase also exhibits homeotropic texture indicating it as an orthogonal phase. These observations indicate that the phase is smectic-A.

For further confirmation of this phase, miscibility studies are carried out. The compounds, 13O.1 and 14O.1 are mixed with 2O.16 (independently), which also exhibit a single-phase smectic-A variant. As a representative case, the miscibility diagram of 13O.1 in 2O.16 is shown in Figure 1.
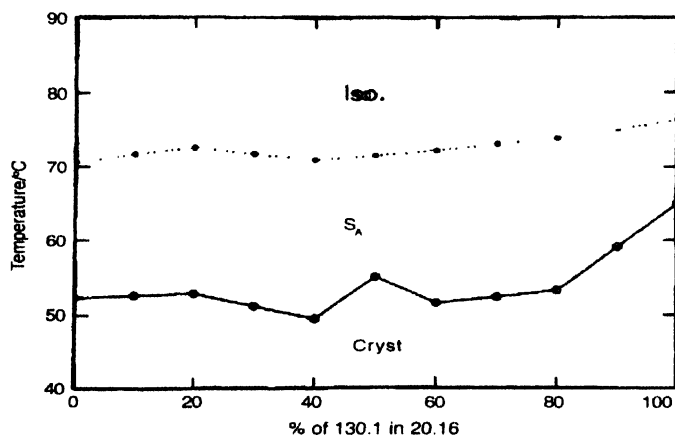

Figure 1. Miscibility diagram of 13O.1 in 2O.16.

This phase of 13O.1 is co-miscible with the phase of 2O.16. This confirms that the identified liquid crystalline phase of 13O.1 and 14O.1 is smectic-A.

The DSC thermo grams of 13O.1 and 14O.1 are shown in Figures 2 and 3. The transition temperatures along with enthalpy values from thermal microscopy and DSC, are presented in Table 1.

3.2 Dilatometric studies on 13O.1 and 14O.1 :

The density measurements are carried out on both these compounds using dilatometer technique, which is equipped with temperature variation accessory. The variations of density and

Table 1. Phase transition temperatures (in°C) in heating and cooling cycles due to thermal microscopy, DSC and density measurements

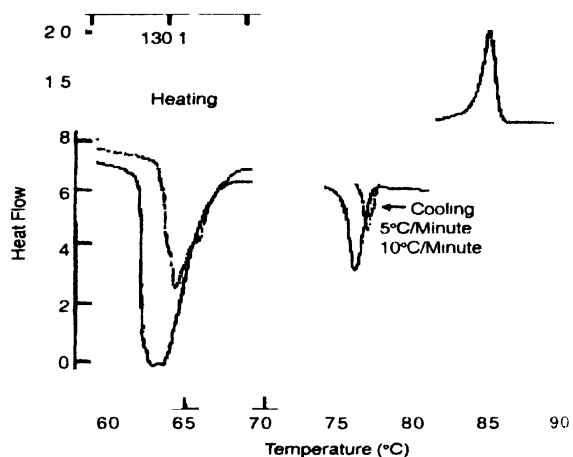| Compound Heating/Cooling	Crystal-Smectic-A	Smectic-A-isotropic	Melting
13O.1			
C TM	65.0	76.3	
H DSC			84 75
C DSC	64 2	76.5	
C Density		76.3	
14O.1			
C TM	68.6	76 5	
H DSC			82 96
C DSC	67 2	76 6	
C Density		76 5	

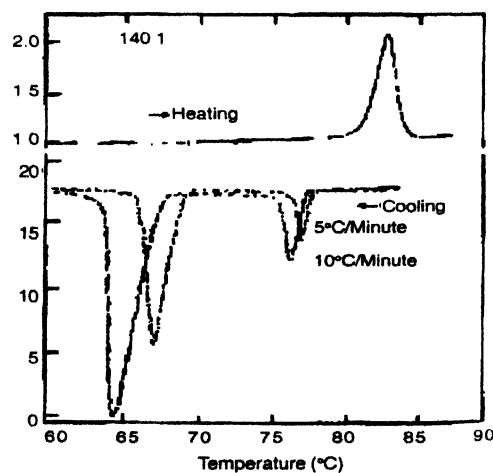**Figure 2.** DSC thermogram of 13O 1 heating and cooling for differ scan rates

Figure 3. DSC thermogram of 14O.1 heating and cooling for differ scan rates

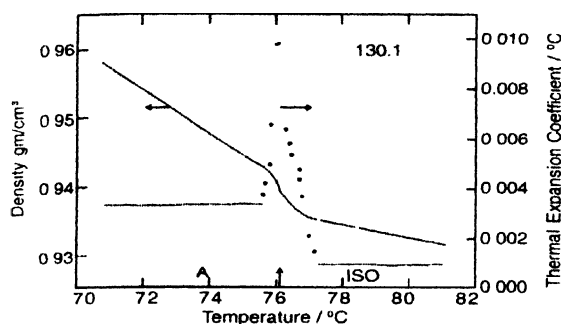ermal expansion coefficient (α) with temperature of these impounds are shown in Figures 4 and 5.

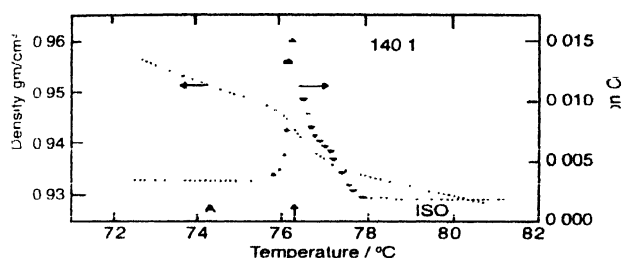**gure 4.** Variation of density and thermal expansion coefficient with nperature in 130 1

gure 5. Variation of density and thermal expansion coefficient with aperature in 140.1

The estimated contribution of molar volume per methylene up increment of nO.1 series in the isotropic liquid at T_{IA} +5K found to be 16.4 x 10⁻⁶ m³ mol⁻¹ in 130.1 and 15.5 x 10⁻⁶ m³)l⁻¹ in 140.1. These are found to be in good agreement with ² reported values of other nO.m compounds 4O.m [6], 5O.m], 6O.m [8,9], 7O.m [10,11], 8O.m [9,12, 13,14,11], 9O.m 5,16,17,11], 10O.m [18] and 12O.m [19] series of nO.m mpounds. It is further noticed that these results are in ement with the reported values of 16.42 x 10⁻⁶ to 17.2 x10⁻⁶ ¹mol⁻¹ for methylene group contribution for isotropic liquids.

The density jumps ($\Delta\rho/\rho$×100) and the computed ermal expansion coefficient maxima at isotropic-smectic-A insition α_{max} = 1/ $Mv(dMv/dT)$ for these compounds along ith other compounds [20] which exhibit isotropic-smectic-A ase transition, are given in Table 2.

le 2. Smectic-A thermal range, density jump, thermal expansion fficient maxima and pressure dependence of transition temperatures ss I-A transition in nO.m compounds.

npound	S_A–Thermal range °C	$\Delta\rho/\rho$×100	α_{max} 10⁻⁴ °C⁻¹	dT_C/dP K.k.bar⁻¹
I I	11.3	0.57	98.7	14.86
	4.5	0.93	133.7	15.85

The isotropic-smectic-A transition is accompanied by a change from a disordered molecular arrangement of isotropic liquid to a long-range orientation of the molecules with simultaneous growth of periodic layer arrangement in smectic-A phase. Generally, this transition is regarded as of first order. The density jumps ($\Delta\rho/\rho$×100) estimated from the vertical distance between density values of extrapolated curve from isotropic and smectic-A regions at the observed transition temperatures across the transitions are 0.57% for 130.1 and 0.93% for 14.O1 (Table 1). The larger density jump observed across $I - S_A$ transition than at I-nematic or I-cholesteric transition is due to the transformation of random orientation of molecules in isotropic phase into ordered molecular phase (which possess both long range orientational order with one dimensional periodic ordering) compared to only long range orientational order in nematic phase. .

The reported [6-19] minimum and maximum jumps across I-smectic-A transition are 0.35% and 2%. This shows that the values of density jumps observed for these two compounds fall in the middle range. The large density jump and the calculated thermal expansion coefficient maximum (α_{max}) 98.7 ×10⁻⁴ °C⁻¹ and 133.7 × 10⁻⁴ °C⁻¹ in 130.1 and 140.1, respectively, confirm the order of the transition as first order.

The higher slope value of density for the smectic-A phase (33.4 x 10⁴ for both the compounds) suggests the denser packing of molecules and higher structural ordering in smectic-A phase compared to isotropic phase. It is interesting to note that the density slope in the isotropic phase of 9.34 × 10⁻⁴ for 130.1 is found to be in agreement with value reported for other compounds of nO.m series while the value of 18.9 × 10⁻⁴ for 140.1 is found to be higher.

The $I- S_A$ transition can also be visually observed in the pyknometer bulb. The translucent smectic-A phase grew uniformly in the lower part of the bulb and the less dense isotropic liquid appeared to float above smectic-A phase with a clear boundary between them. This type of co-existence and the S_A embryos appearing simultaneously at the bottom of the bulb suggest nucleation growth analogy of the isotropic to smectic-A transition. Further, the embryos, which are developed at the bottom of the bulb appeared with a characteristic translucent appearance rather than with a uniform, opaque, milky nematic appearance throughout the bulb. This suggests the simultaneous development of orientational and translational order.

The pressure dependence of transition temperatures estimated from the Clausius-Clapeyron equation $[(dT_C/dP) = T_C (dM_v/\Delta H)]$ (where T_C, dM_v, ΔH are transition temperature, change in volume and enthalpy, respectively) is 14.86 K.k bar⁻¹ and 5.85 K.k bar⁻¹ in the compounds 130.1 and 140.1,

respectively. The observed poor agreement in the pressure dependence of $I-S_A$ transition temperature (Table 1) among different compounds, which accounts the mesophase thermal stability in the domain of chemical environment, may be due to the parameters being obtained in different experimental conditions.

3.3 DSC characterization of the order of phase transition:

The differential scanning calorimetry is an extensive technique not only for the detection of phase transitions, quantitative determination of the associated enthalpy changes at the transition and for the qualitative analysis of materials (purity, isothermal crystallization etc.), but also for the determination of the order of transition whether first or second order. Navard and Haudin [21] proposed an elegant and simple method to determine the order of phase transition from the DSC peak heights or material quantities. The order of phase transition can be determined from the magnitude of the ratio (N) of different enthalpy peak heights h_2/h_1, performed with two different scan rates (T_2 and T_1), which is a function of the ratio of the scanning rates, T_2/T_1 $(= R)$, keeping the weight of compound constant. It follows that for a first order transition, N varies as the square root of R, while for second order transition, N should be directly proportional to R. Here, we have used $R=2$ (i.e., keeping the mass of the sample constant, the DSC thermograms are obtained for scan rates 10 °C/min and 5 °C/min).

The DSC thermograms scanned at 10 °C/min and 5 °C/min are shown in Figures 2 and 3 for the two compounds, respectively. The heights calculated for 10 °C/min (h_2) and 5 °C/min (h_1) are 4.5 and 3.1 in 130.1 and 4.1 and 3.1 in 140.1, respectively. The Navard and Haudin parameters, $(h_2/h_1 = R)$ are 1.45 and 1.37 for both the compounds, respectively. The values suggest that the order of $I-S_A$ transition in these compounds is of the first order.

4. Conclusions

(i)   The thermal microscopic textural observations show that the compound exhibits a monotropic smectic-A phase.

(ii)   The data available on a number of nO.m compounds which exhibit isotropic to smectic-A transition, reveal that the density jumps across this transition varies between 0.36% to 1.99%. The density jump in the present compound (0.93 %) falls in the middle range of the observed values (0.36% to 1.99%).

(iii)   It is interesting to note that the Isotropic-smectic-A phase transition can be visually observed in the pyknometer with the smectic-A phase settling to the bottom and the isotropic phase floating over it.

(iv)   The observed density jump and the calculated thermal expansion coefficient (α) confirm the order of I transition as first order, which is further confirm from the value of Navard and Haudin parameter $(h_2/h_1 = 1.37)$ obtained form DSC.

Acknowledgments

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