Density Studies of Rare Phase Transitions in Liquid Crystals

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Abstract: *Phase transitions of two symmetrical liquid crystalline dimers of homologues series of α,ω-bis(4-n-alkylanilinebenzylidene-4′-oxy)alkanes were investigated using density measurement techniques as a function of temperature. The compound 7.O10O.7 exhibits Nematic, SmA and crystalG phases, whereas 8.O10O.8 exhibits SmA and crystalG phases. All the phase transitions studied viz., Isotropic – Nematic (I – N), Isotropic - SmA (I–SmA), Nematic – SmA (N – SmA) and the most rare transition SmA – crystalG (SmA – CrG), are confirmed to be of first order nature. The thermal expansion coefficient and the calculated pressure dependence of the transition temperatures using Clauasius- Clapeyron equation is also analyzed in the light of available literature data.*
Key Words: Phase transition, Isotropic – Nematic, Isotropic – Smectic A, Nematic - Smectic A and Smectic A – Crystal G transition.

I.   Introduction

The importance towards the study of liquid crystal dimers have grown steadily in recent years and this could be attributed to the vast use of dimers as model compounds to understand the meaning of polymeric structure containing both semi-flexible main chain and side group [1-6]. In addition, liquid crystal dimers are also of particular interest, because these materials exhibit quite unusual properties as compared to conventional low molar mass liquid crystals. For examples, the transition temperatures and transitional entropies, exhibits a strong dependence on the parity of the spacer length. Further, the stability of the SmA phase has been found very different with long and short terminal alkyl chains exhibiting smectic behaviour, This surprising observation was rationalized by proposing a novel intercalated structure for the SmA phase exhibited by short chain lengths and the conventional interdigitated structure for long chain lengths. Further studies by Date and his co-workers [2] on the other homologous series of the similar liquid crystal dimers established the identification of several new smectic modifications, namely, intercalated smectic C and I phase and the intercalated crystal B and J phases.
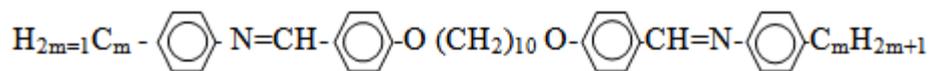
Due to the gaining importance of liquid crystal dimers, in this present study, we report here the phase transition studies of two liquid crystal dimers viz. 7.O10O.7 and 8.O10O.8 using the DSC and density measurements as a function of temperature across the I – N, I – SmA, N – SmA and the very rare SmA – Cr G phase transitions.
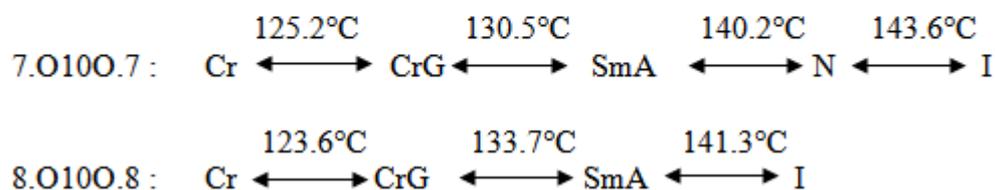
II.   Experimental

The compounds were synthesized following a standard procedure as discussed in literature [2]. The crude product was repeatedly recrystallized from ethyl acetate until the transition temperatures were found to be constant and reproducible. The differential scanning calorimetric studies (DSC) were carried out on DuPont 2000. Various phases exhibited by these compounds were characterized by observing their optical textures under a polarizing microscope attached with an indigenously built hot stage. The temperature resolution in these microscopic studies was 0.1°C. The transition temperatures and entropy change at different phase transitions are found to be in excellent agreement with literature values [2]. Density studies were carried out with a bicapillary pyknometer as describe elsewhere [7].

III.   Results and Discussion

The general molecular structure, phase sequences and transition temperatures of dimers studied viz. 7.O10O.7 and 8.O10O.8 are shown below.

$$H_{2m=1}C_m - \bigcirc - N{=}CH{-}\bigcirc{-}O\,(CH_2)_{10}\,O{-}\bigcirc CH{=}N{-}\bigcirc C_mH_{2m+1}$$

7.O10O.7 (m=7) and 8.O10O.8 (m=8)

$$7.O10O.7: \quad Cr \xrightleftharpoons[\text{125.2°C}]{} CrG \xrightleftharpoons[\text{130.5°C}]{} SmA \xrightleftharpoons[\text{140.2°C}]{} N \xrightleftharpoons[\text{143.6°C}]{} I$$

$$8.O10O.8: \quad Cr \xrightleftharpoons[\text{123.6°C}]{} CrG \xrightleftharpoons[\text{133.7°C}]{} SmA \xrightleftharpoons[\text{141.3°C}]{} I$$

The sharp melting transitions in the DSC scans for both the compounds proved the purity of the compounds. The transition temperatures and entropies at the phase transition are also in good agreement with the literature values [2]. The variation of density as a function of temperature and the variation of thermal expansion coefficient ($\alpha = 1/M_V(\Delta M_V/\Delta T)$, where M_V is molar volume) with temperature for 7.O10O.7 and 8.O10O.8 are shown in Figure 1[(a) and (b)] and Figure 2[(a) and (b)] respectively. The density in both the compounds decreases with the increase of temperature, except in the vicinity of the phase transitions.
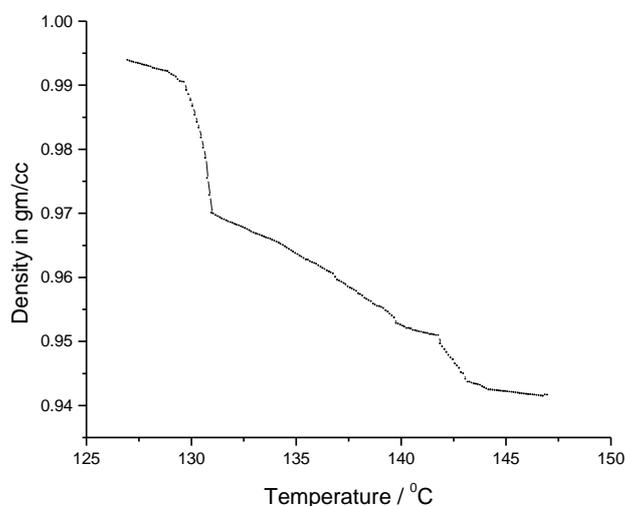

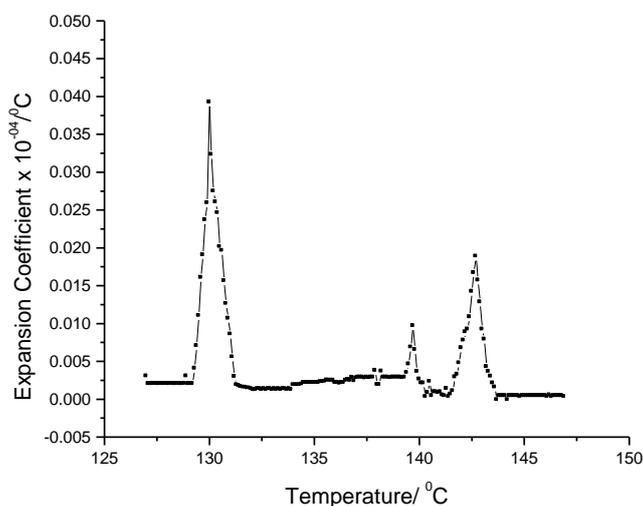**Figure 1** (a) Variation of density as a function of temperature in 7.O10O.7

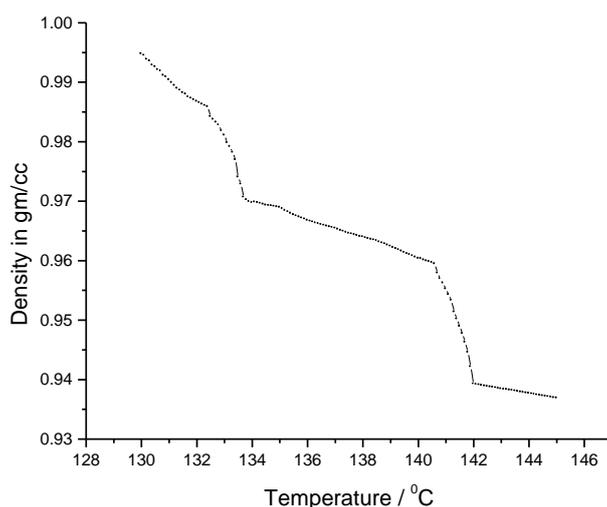**Figure 1**(b) Variation of thermal expansion coefficient 7.O10O.7

Figure 2 (a) Variation of density as a function of temperature in 8.O10O.8
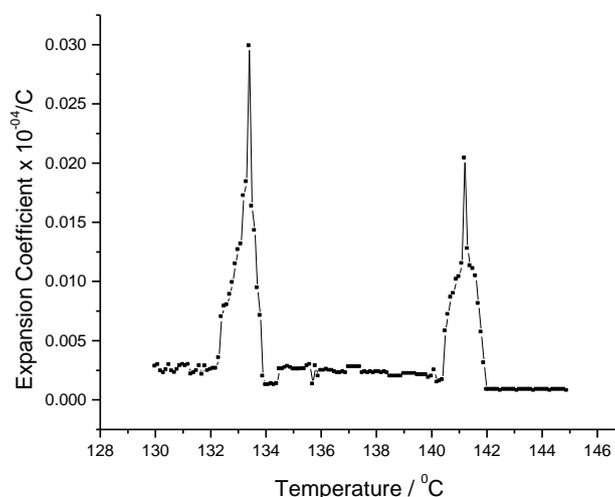

Figure 2(b) Variation of thermal expansion coefficient 8.O10O.8

Isotropic to Nematic Transition(7.O10O.7)

      The I –N phase transition was confirmed from the development of optical textures of nematic phase under the crossed polarizer. The schlieren texture which flashed when subjected to mechanical stress combined with the high mobility of the phase. As the rotational symmetry of the isotropic phase is broken at the I – N phase transition, this transition is expected to be a first order transition. The I - N transition of the compound, 7.O10O.7 is indicated by a significant density jump $\Delta\rho/\rho\% = 0.81\%$ and the thermal expansion coefficient peak 188.5 x $10^{-04\circ}C^{-1}$) at the transition. The discontinuous change in density and peak in the thermal expansion coefficient at the I – N transition confirmed this to be a first order nature of transition. Other remarkable change was the increase of slope from the isotropic to nematic phase indicating the closer packing of orientationally ordered molecules in the lower temperature nematic phase. Further, co-existence of isotropic to nematic phase is observed for 1.2°C, but the large part of the density jump is completed within 0.3°C.

      The pressure dependence of transition temperatures estimated from the Clausius – Clapeyron equation, $dT_t/dP = T_t(\Delta V/\Delta H)$; Where T_t, ΔV and ΔH are the transition temperature, change in molar volume and enthalpy values at the transition. The estimated pressure dependence of transition temperature of I – N transition is 28.72 K/k bar. A comparison of density jump and estimated pressure dependence of transition temperature of different compounds are presented in Table 1.

Table –1   Density jump ($\Delta\rho/\rho\%$) and pressure dependence of transitiontemperature (dT_t/dP) of some compounds at I – N transition

Compound	$\Delta\rho/\rho\%$	dT_t/dP (K/k bar)	Reference
7.O10O.7	0.81	28.72	Present study
4.O5O.4	0.28	31.22	8
6.O12O.6	2.09	98.70	9
7.O12O.7	1.49	49.80	10
CB.O10O.10	1.04	26.83	13
Terephthalylidene-bis-p-n-pentylaniline (TBPA)	0.356	56.05	14
Terephthalylidene-bis-p-n-hexylaniline (TBHA)	0.351	60.07	14
N(4-n-pentyloxybenzylidene)-4′-n-pentylaniline (5O.5)	0.34	36.5	15
N(4-n-pentyloxybenzylidene)-4′-n-hexylaniline (5O.6)	0.30	33.0	15
N(4-n-pentyloxybenzylidene)-4′-n-octylaniline (5O.8)	0.25	26.3	15
N(4-n-hexyloxybenzylidene)-4′-n-octylaniline (6O.8)	0.43	37.0	16

Isotropic to Smectic A Transition(8.O10O.8)

The I – SmA transition of 8.O10O.8 is inferred as a first order transition with a significant density jump as well as the peak in thermal expansion coefficient. The observed density jump ($\Delta\rho/\rho$ %) across the I – SmA transition is found to be 2.08% and is in comparable with the values of other similar dimers [11,12]. These density jumps and the thermal expansion coefficient peak value of 203×10^{-04} °C^{-1} confirm the Isotropic – SmA transition to be first order transition and the higher slope values for the density curve for the SmA phase compared to isotropic suggest the denser packing and higher structural ordering in SmA phase. Visual observation of density studies noted significant physical changes in the materials studied in the pyknometer bulb. The translucent SmA phase grew uniformly in the lower part of the bulb first and the less dense isotropic liquid appeared to float above the SmA phase with distinct boundary between them. In our observation, coexistence of isotropic and SmA phases is observed for 0.9°C in 8.O10O.8 but, significant jump in density at the transition is completed within 0.2°C. The estimated pressure dependence of transition temperature of I – SmA transition is 39.31 K/k bar and is in reasonable agreement with the reported values estimated for I – Sm A transition. The comparison of density jump and pressure dependence of transition temperature of different compounds is presented in Table 2.

Table –2   Density jump, Heat of Transition and Pressure Dependence of Transition Temperature of some compounds at I – SmA transition

Compound	$\Delta\rho/\rho\%$	ΔH /J mol^{-1}	dT_t/dP(K/k bar)	Reference
8.O10O.8	2.08	18061.78	39.31	Present study
4.O4O.4	0.88	11670.00	21.70	8
6.O5O.6	0.78	7511.33	26.89	17
6.O6O.6	1.80	14342.48	39.60	17
7.O4O.7	1.57	17665.73	29.08	11
7.O5O.7	0.95	9046.68	30.07	11
7.O6O.7	2.63	17605.00	47.80	10
10.O10O.10	2.26	20515.34	39.71	12

Nematic to Smectic A transition (7.O10O.7)

On cooling the nematic phases of many members of the m.OnO.m family, the schlieren texture changed to give regions of focal-conic fan and homeotropic textures. The presence of focal-conic fans implied a layer structure, while a homeotropic alignment indicated an orthogonal arrangement of the director with respect to the layer planes. In consequence, this lower temperature phase is assigned as a SmA phase. On cooling the isotropic liquid, batonnets developed which coalesced to form a focal-conic fan texture co-existing with regions of homeotropic texture and thus concluded as an I – SmA transition.

At the N – SmA transition, a small but measurable density jumps at the transition temperature indicate this to be first order transition. The observed density jump ($\Delta\rho/\rho$ %) across the N – SmA transition is found to be 0.13% and is in good agreement but lower than the values of other similar dimers [6]. This is found to be in good agreement with the prediction of the Mc Millan's theory as according to this theory if the Mc Milan parameter approaches to unity, it would be the first order transition. The Mc Millan's parameter T_{NA}/T_{IA} is found to be 0.977 and far higher than the value of 0.87 to predict the first order nature of Nematic to SmA phase transition. The thermal expansion coefficient peak value 96.60×10^{-04} °C^{-1} and the estimated value of pressure dependence of transition temperature is found to be 47.42 K/k bar and comparable with similar dimeric compounds. The small density jump and thermal expansion coefficient peak inferred the first order nature of transition. Further, the observed higher slope of density plot in the SmA phase are argued due to the growth of layer order in addition to orientational order [2].

SmA to CrystalG transition (7.O10O.7 and 8.O10O.8)

On cooling the SmA phase, a mosaic texture composed of large poorly coloured areas develops from the homeotropic region while the focal conic fans become broken giving rise to a patch work texture. This is the typical SmA to CrG transition [2]. The SmA – CrG transition is a very rare kind of phase transition and is an example of a transition between layered structured liquid phases to a well-defined three- dimensional structure in smectic phase. The I – CrG transition in 7.O10O.7 and 8.O10O.8 are inferred by their density jumps at the transition 1.95% and 1.48% respectively. In addition to this, the peak in thermal expansion coefficient 322×10^{-04} $^{o}C^{-1}$ and 298×10^{-04} $^{o}C^{-1}$ respectively indicated the transition to be first order in nature. In our study, it is observed that the density jump is much less, than what would have been expected for a transition for a large entropy change [9-11]. This density jump is lesser than the I – CrG transition of 8.O12O.8 (2.7%) but comparable with 10.O12O.10 (1.57.%) [11]. It may be due to the dimensionality and crystal structure order change is different at the SmA to CrG transition. Also it could be due to the spacer and terminal chain length. The calculated pressure dependence of transition temperature is found to be 36.70 K/k bar for 7.O10O.7 and 39.31 K/k bar for 8.O10O.8 and which are comparable with that at any transition in these dimers reported so far.

IV.   Conclusion

In conclusion, we have studied the I – N, I – SmA, N - SmA and SmA – CrG phase transitions exhibited by two liquid crystal dimers using density measurement technique and all the transitions are found to be first order in nature but density jumps are smaller than the precursor monomers though the changes in enthalpy across the phase transitions are high.

Acknowledgements:

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