

Experimental investigation of phase transitions exhibited by symmetric liquid crystal dimers

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As a part of our systematic study of phase transitions in liquid crystal dimers we report here the variation of density across the phase transitions Isotropic – Smectic A and Smectic A – Smectic F exhibited by the Schiff base liquid crystal dimeric compounds of α,ω -bis(4-alkylanilinebenzylidene-4'-oxy)alkane (m.OnO.m) homologous series. The compounds studied are 6.O5O.6 and 6.O6O.6. The compound 6.O5O.6 exhibits only Smectic A phase, whereas the compound 6.O6O.6 exhibits Smectic A and Smectic F phases. The density jumps and peak in thermal expansion coefficient at the transitions confirm the first order nature of the transitions with a smaller density jumps compared to the monomeric liquid crystals. The calculated pressure dependance of the transition temperatures using Clauasius- Clapeyron equation is also reported.

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1 Introduction

The conventional structure of calamitic liquid crystals is a rigid core attached with flexible alkyl chains. The core provides the source of anisotropy for the formation of liquid crystal phases, while the disorder associated with the terminal flexible chains reduces the stability of the solid crystal phase, and allows the appearance of liquid crystal mesophases [1]. There are many variations on this basic liquid crystal structure, and one of the interesting class of liquid crystals with unconventional structure are known as liquid crystal dimers. The liquid crystal dimers are formed by linking two mesogenic groups by an alkyl chain (spacer). The liquid crystal dimers attracted a great deal of interest in recent years, both theoretically and experimentally, due to their unusual properties as compared to the low molar mass liquid crystals. They serve as model compounds for semi-flexible main-chain liquid crystal polymers [2-9]. The Nematic – Isotropic phase transition temperature in these dimeric compounds exhibit a marked alternation as the number of carbon atoms in the alkyl spacer changes from odd to even. However, these changes decrease as the spacer grows in length. In contrast, the variation of entropy of the Nematic – Isotropic phase transition is essentially unattenuated, at least for spacers containing upto twelve carbon atoms [9]. In addition, the entropy changes at the Nematic – Isotropic phase transition for dimers with odd chain length spacers is comparable to that of monomers while for compounds containing even chain length spacers, the translational entropy suggests that the orientational order for even spacers should be significantly greater than that for odd spacer dimers.

As these kinds of liquid crystal dimers are gaining importance, studies have been carried out using various experimental techniques with variable degree of sophistication. However, in the present study, we report the phase transition studies in two liquid crystal dimers viz. 6.O5O.6 and 6.O6O.6 using the DSC and density measurements as a function of temperature across the Isotropic – Smectic A, and Smectic A – Smectic F phase transitions.

2 Experimental

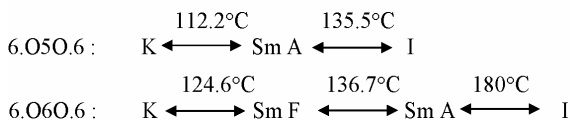
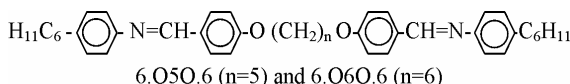
The compounds were synthesized following a standard procedure as discussed in literature [2]. The crude product was repeatedly recrystallized from ethyl acetate until the transition temperatures were found to be

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constant and reproducible. The differential scanning calorimetric studies (DSC) were carried out on Perkin – Elmer DSC – 7. Various phases exhibited by these compounds were characterized by observing their optical textures under a polarizing microscope attached with an indigenously fabricated hot stage. The temperature resolution in these microscopic studies was 0.1K. 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 pycnometer [10]. The diameter of the capillary was about 0.35 mm and the accuracy in the density measurements was $\pm 0.1 \text{ kg. m}^{-3}$. The permitted cooling rate during the experiment was 2K hr^{-1} and the temperature accuracy is $\pm 0.1\text{K}$.

3 Results and discussion

The general molecular structure and transition temperatures of dimers studied viz. 6.O5O.6 and 6.O6O.6 are shown below.



DSC scans of 6.O5O.6 and 6.O6O.6 show sharp melting transition, which is an indication of the purity of the compound. It is observed that the entropy values at different phase transitions for the dimeric compounds are larger than that of the monomeric compounds. It may be noted that the entropy change at Isotropic – Sm A phase transition for the even spacer dimer is twice that of monomeric compounds. Further, the entropy value ($\Delta S/R = 2.21$) of odd spacer dimer (6.O5O.6) at the Isotropic – Sm A transition is nearly half ($\Delta S/R = 3.81$) compared to the even spacer dimer (6.O6O.6). These very large entropy values suggest that, both the orientational and translational ordering in the smectic A phase are high for even spacers and also reflect the alternation of entropies in varying the flexible spacer for any given length of terminal chain.

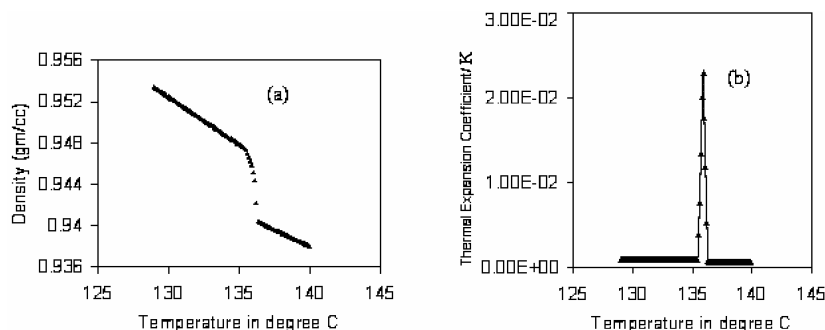


Fig. 1 a) Variation of density with temperature in Isotropic, Smectic A phases in 6.O5O.6, b) Variation of thermal expansion coefficient with temperature for 6.O5O.6.

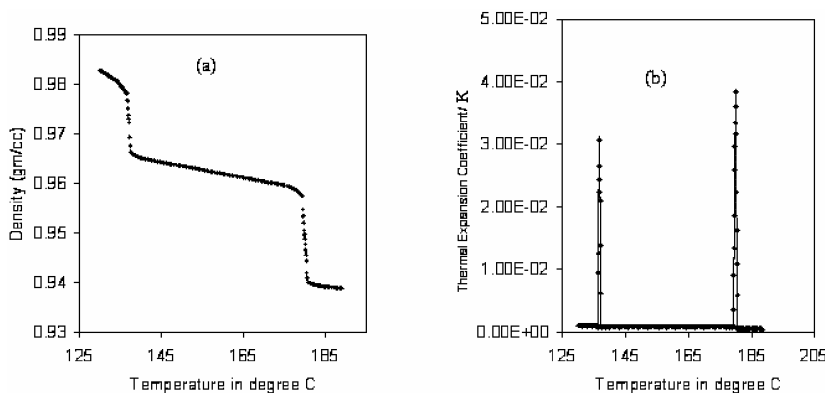


Fig. 2 a) Variation of density with temperature in Isotropic, Smectic A and Smectic F phases in 6.O6O.6, b) Variation of thermal expansion coefficient with temperature for 6.O6O.6.

The variation of density as a function of temperature and the variation of estimated thermal expansion coefficient ($\alpha = d\ln V/dT$ where V is molar volume) with temperature for 6.O5O.6 and 6.O6O.6 are shown in Figure 1 [(a) and (b)] and Figure 2 [(a) and (b)] respectively. In both compounds, the density increases as the temperature decreases, except in the vicinity of the phase transitions. The molar volume of 6.O5O.6 at $T_{AI}+5K$ was found to be $673.05 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ whereas the molar volume of 6.O6O.6 at $T_{AI}+5K$ was found to be $686.80 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. Therefore, the increment in molar volume per methylene unit is $13.75 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, which is in agreement with the literature data [11].

3.1 Isotropic to smectic A transition

The Isotropic – Smectic A transition in both 6.O5O.6 and 6.O6O.6 is inferred as a first order transition with a significant jump in density as well as indicated by a peak in thermal expansion coefficient. Further, coexistence of isotropic and smectic A phases is observed for 0.9°C in 6.O5O.6 and for 1.4°C in 6.O6O.6. However, significant jump in density at the transition is completed within 0.2°C in 6.O5O.6 and 0.4°C in 6.O6O.6. The observed density jump ($\Delta\rho/\rho$ %) across the Isotropic – Sm A transition is 0.78% in 6.O5O.6 and 1.80% in 6.O6O.6 and is in agreement with the values of other similar dimers [11,12]. These density jumps and a thermal expansion coefficient peak value of $230.10 \times 10^{-4} \text{ K}^{-1}$ for 6.O5O.6 and $383.90 \times 10^{-4} \text{ K}^{-1}$ for 6.O6O.6 confirms the Isotropic – Sm A transition to be first order transition. The minimum and maximum values of density change reported so far across Isotropic – Sm A transition are 0.35% and 2.26% respectively. However, the density jumps across the Isotropic – Sm A transition in both of these compounds is significantly smaller than that for the transition exhibited by monomers. A comparison of density jumps and transition enthalpy at Isotropic – Sm A transition in different mesogenic dimers is presented in Table 1.

Table 1 Density jump, heat of transition and pressure dependence of transition temperature at Isotropic – Sm A transition of few mesogenic dimers.

Compound	$\Delta\rho/\rho\%$	$\Delta H/J \text{ mol}^{-1}$	dT_i/dP (K/kbar)	References
6.O5O.6	0.78	7511.33	26.89	Present work
6.O6O.6	1.80	14342.48	39.60	Present work
7.O4O.7	1.57	17665.73	29.08	11
7.O5O.7	0.95	9046.68	30.07	11
10.O10O.10	2.26	20515.34	39.71	12

An estimate of the pressure dependence of transition temperatures can be obtained using Clausius-Clapeyron equation

$$\frac{dT_i}{dP} = T_i \left(\frac{\Delta V}{\Delta H} \right)$$

where T_i - Transition temperature, ΔV - Molar volume change associated with the transition, ΔH - Heat of transition.

The estimated value of pressure dependence of transition temperature from the molar change and heat of transition, (dT_i/dP) is 26.89 K/kbar for 6.O5O.6 and 39.60 K/kbar for 6.O6O.6. These values are in reasonable agreement with the reported values estimated for Isotropic – Sm A transition as compared in table 1.

3.2 Smectic A to smectic F transition

The smectic A – smectic F transition is inferred by a large jump in density in 6.O6O.6. The observed density jump is 0.61%. This density jump along with a large thermal expansion coefficient peak value of $307 \times 10^{-4} \text{ K}^{-1}$ for 6.O6O.6 at the transition confirm Smectic A – Smectic F transition as first order transition. Smectic A – Smectic F transition is an example of a transition from disordered orthogonal structure in smectic A to the ordered smectic F phase in which the molecules are packed in layers with a pseudo-hexagonal arrangement with a two-dimensional structure of the positional order and long axis tilted (direction of tilt is towards an edge of hexagon) with respect to the layer planes (i.e., with uncorrelated layers but long range bond orientational order) is expected to be a first order transition. This transition is observed very rarely. The other compounds on

which density studies were reported so far across smectic A – smectic F transition are 7.040.7, 7.050.7, 10.0100.10 and 90.4 in which observed density jumps were 0.55%, 0.62%, 1.83% and 1.42% respectively [11,13]. The estimated pressure dependence of transition temperature is found to be 53.59 K/kbar. The maximum value reported so far is 48.25 K/kbar for 90.4 which is lower than our observed value on 6.060.6. This may be due to the molecular topology of the dimeric compounds [14].

In conclusion, we have studied the I – Sm A and Sm A – Sm F phase transitions exhibited by two liquid crystal dimers using density measurement technique and both the transitions are found to be first order in nature but density jumps are smaller than the monomers [13] though the changes in enthalpy across the phase transitions are high.

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