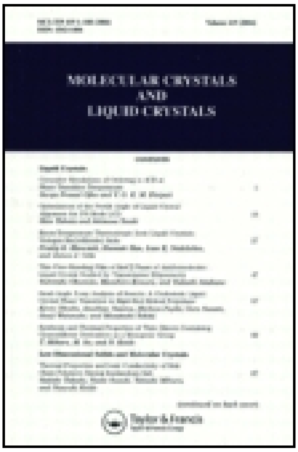

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Phase Transition Studies of 6.O12O.6 and 7.O6O.7 Using Density Measurements

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The symmetric liquid crystal dimer homologous series, α,ω-bis-(4-n-alkylaniline benzylidene-4′-oxy) alkanes, show a rich variety of smectic polymorphism. We report here the nature of different transitions exhibited by two of these dimers using density measurements as a function of temperature. The compound 6.O12O.6 exhibits only nematic phase; while 7.O6O.7 exhibits smectic A and smectic F phases. All the phase transitions studied viz., isotropic – nematic, isotropic – smectic A, and smectic A – smectic F are confirmed to be of first order nature. The calculated density jumps, thermal expansion coefficient data and pressure dependence of transition temperatures are analysed in the light of available literature data.

Keywords Isotropic – nematic transition; isotropic – smectic A transition; smectic A – smectic F transition; symmetric dimer

1. Introduction

Symmetric Schiff base liquid crystal dimers which are formed by linking two mesogenic units through a flexible spacer (alkyl or alkoxy chain) are an interesting class of liquid crystals in that they exhibit quite different and rich smectic mesomorphism compared to that of their precursors viz., monomers (nO.ms or nCBs) and are capable of acting as model compounds for semi flexible main chain liquid crystal polymers [1–8]. Some important aspects of these dimers, which attract special interest, are that the molecules with smaller spacer length promote smectogenic behaviour whereas the dimeric molecules with large spacer length promote nematic behaviour, in contrast to monomeric liquid crystals. Also, symmetric dimers exhibit a large odd – even effect with number of carbon atoms in the spacer in mesophase – isotropic

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transition temperature as well as transition entropy. However, the alteration in temperatures is attenuated as the spacer grows in length. In contrast, the alteration in the entropy is essentially unattenuated; at least for spacers containing up to twelve carbon atoms [9]. In addition, the entropy change at nematic – isotropic transition for dimers with odd spacers is comparable to that of monomers while for even spacer dimers the transitional entropy is typically three times larger. The behaviour of the transitional entropy suggest that the orientational order for even spacer dimers should be significantly greater than that for odd spacer dimers.

Measurement of variation of density as a function of temperature is an important experimental tool for studying the nature of phase transitions in liquid crystals. As a part of our systematic study of different phase transitions in symmetric Schiff base liquid crystal dimers, we report here the variation of density as a function of temperature in two compounds of the homologous series α,ω-bis(4-n-alkylaniline benzylidene-4′-oxy) alkane (hereafter referred to as m.OnO.m). The compounds studied are 6.O12O.6 and 7.O6O.7. The compound 6.O12O.6 exhibits a isotropic – nematic (I – N)phase transition, while the compound 7.O6O.7 exhibits isotropic – smectic A (I – SmA) and smectic A – smectic F (SmA – SmF) phase transitions.

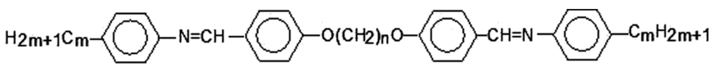
2. Experimental

The compounds were synthesized using a standard procedure reported in literature [1]. The crude products were repeatedly recrystallized from ethyl acetate until the transition temperatures were reproducible and constant. Differential Scanning Calorimetry studies were carried out using Shimadzu Differential Scanning Calorimeter (DSC-60). Various phases exhibited by the compounds were identified by observing their characteristic optical textures under a polarizing microscope attached with an indigenous hot stage. The temperature resolution of the microscopic studies was 0.1°C. The density measurements were carried out using a bicapillary pycnometer [10]. The capillary diameter of the pycnometer was about 3.5×10^{-4} m and accuracy in density measurements was $0.1\,\mathrm{kg\,m^{-3}}$. The permitted cooling rate was 2°C per hour and temperature accuracy was ±0.1°C.

3. Results and Discussion

A general molecular structure of the compounds is shown in Figure 1.

A DSC scan of 7.O6O.7 is shown in Figure 2. A sharp peak at the melting transition indicates the purity of the sample. The transition temperatures and transition enthalpy values are in very good agreement with the literature values [1].



6.O12O.6 : m = 6 and n = 12

7.O6O.7 : m = 7 and n = 6

Figure 1. General molecular structure of the compounds.

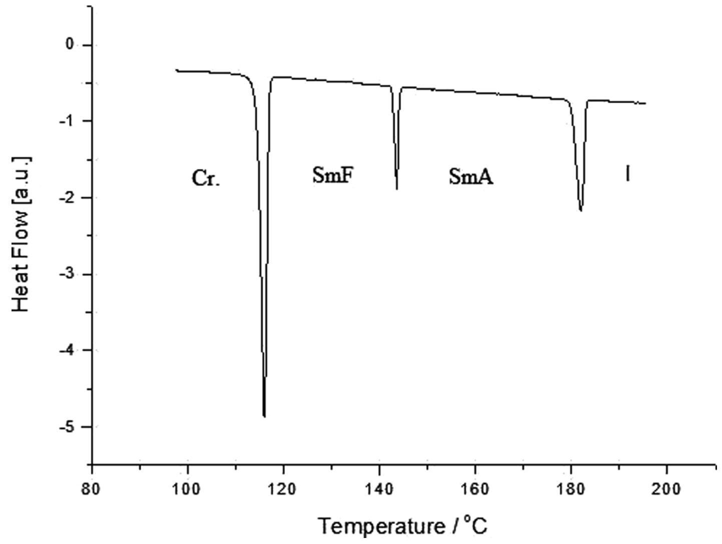


Figure 2. DSC scan of 7.O6O.7.

The transition temperatures of the compounds 6.O12O.6 and 7.O6O.7 are given below.

$$6.0120.6: \ \mathrm{Cr.} \xrightarrow{129.1^{\circ}\mathrm{C}} \mathrm{N} \xrightarrow{132.2^{\circ}\mathrm{C}} \mathrm{I}$$

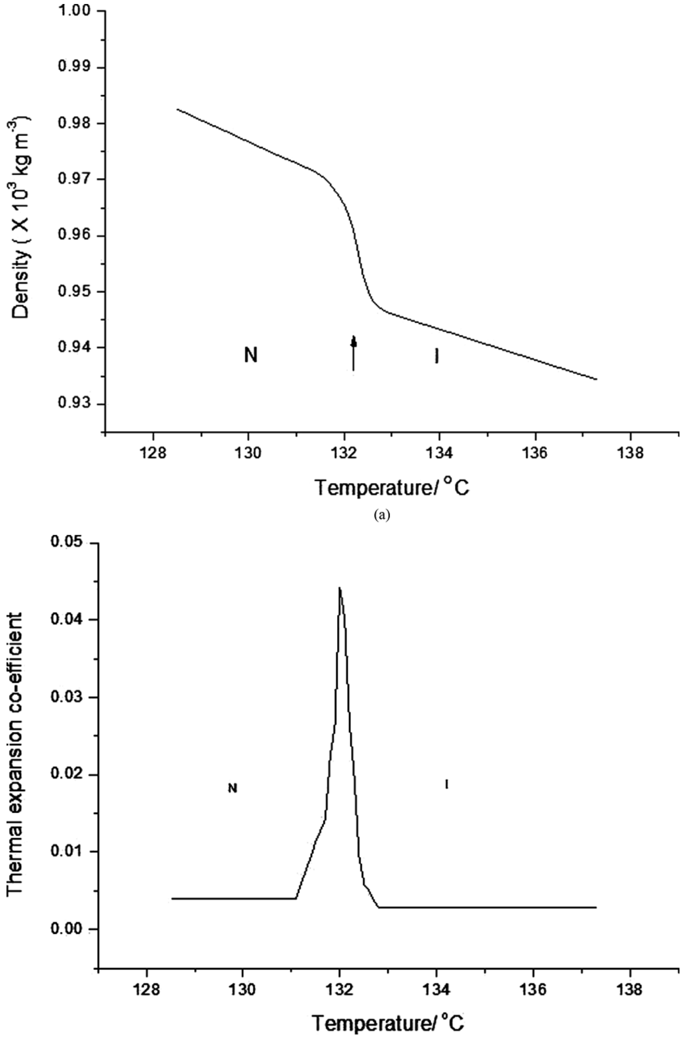
$$7.060.6: \ \mathrm{Cr.} \xrightarrow{115.8^{\circ}\mathrm{C}} \mathrm{SmF} \xrightarrow{144.1^{\circ}\mathrm{C}} \mathrm{SmA} \xrightarrow{182.5^{\circ}\,\mathrm{C}} \mathrm{I}$$

The variation of density as a function of temperature and the variation of estimated thermal expansion coefficient ($\alpha = \mathrm{dlnV/dT}$, where V is the molar volume and T is temperature) with temperature for the compounds 6.O12O.6 and 7.O6O.7 are shown in Figures 3 and 4, respectively.

The molar volume of 6.O12O.6 at $(T_{NI} + 5)$°C is found to be $778.61 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$ and that for 7.O6O.7 at $(T_{AI} + 5)$°C is found to be $719.37 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$. This was reported to be $686.80 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$ for 6.O6O.6 [11] and a comparison of this value with those obtained for 6.O12O.6 and 7.O6O.7 infers an increment of $15.03 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$ per methylene unit in 6.O12O.6 and $16.29 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$ in 7.O6O.7. The compound 6.O12O.6 exhibits a I – N phase transition and the thermal range of nematic phase is 3.1°C. While the compound 7.O6O.7 exhibits I – SmA and SmA – SmF phase transitions.

3.1. *Isotropic – Nematic Transition in 6.O12O.6*

A density jump ($\Delta\rho/\rho\%$) of 2.09% and peak in thermal expansion coefficient of $441 \times 10^{-4}\,{}^{\circ}\mathrm{C}^{-1}$ confirms the strong first order nature of I – N transition in 6.O12O.6. The density jump at the transition is very large compared with those of I – N transition in nO.m compounds (monomers) which is of the order of only 0.30 to 0.40 (see Table 1 presented later). This may be due to the fact that the large number of methylene units present in the alkyl chains of spacer as well as in the



(a)

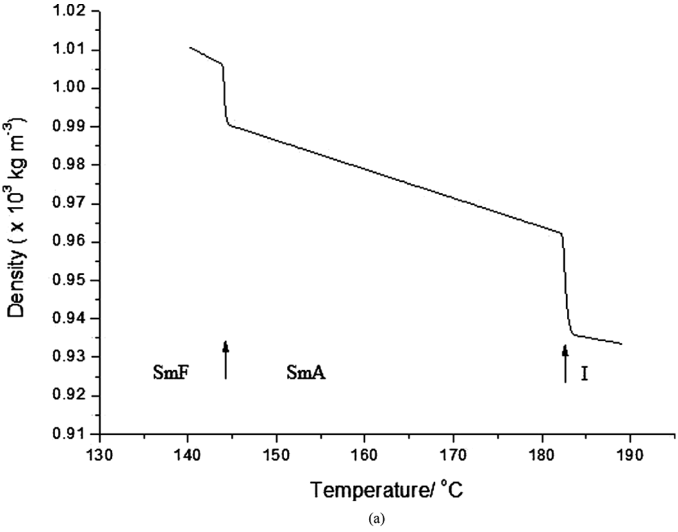
(b)

Figure 3. (a) Variation of density as a function of temperature in isotropic and nematic phases of 6.O12O.6; (b) variation of thermal expansion coefficient at for transition from isotropic to nematic phase of 6.O12O.6.

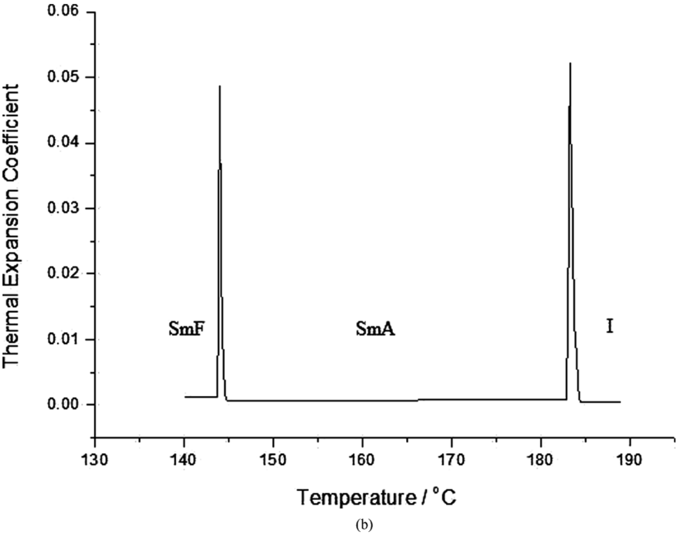
terminal alkyl chains of the dimer molecule which are expected to contribute to the large entropy change at the transition. As such at the I – N transition the infinite rotational symmetry of the molecules in isotropic phase is broken down leading to the formation of nematic phase.

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

$$\frac{dT}{dP} = T_t\left(\frac{\Delta V}{\Delta H}\right) \tag{1}$$



(a)



(b)

Figure 4. (a) Variation of thermal expansion coefficient for transition from isotropic to smectic A and smectic A to smectic F transition of 7.O6O.7; (b) variation of thermal expansion coefficient at for transition from isotropic to smetic A and smetic A to smectic F transitions of 7.O6O.7.

where T_t is the transition temperature; ΔV is the molar volume change associated with the transition and ΔH is the heat of transition. The estimated pressure dependence of I – N transition temperature is found to be 98.7 K/kbar for 6.O12O.6. A comparison of the density jump at the I – N transition and dT/dP values for different compounds including 6.O12O.6 and monomers is presented in Table 1. From this comparison it is clear that both the density jump at the I – N transition and estimated value of the pressure dependence of the I – N transition temperature are higher compared with the monomers. This work is the first ever study of the I – N transition in symmetric dimers using density measurements, to the best of our knowledge.

Table 1. Density jumps and the estimated values of pressure dependence of transition temperature at I – N transition for different compounds

Name of the compound	Density jump at I – N transition ($\Delta\rho/\rho\%$)	Estimated value of dT/dP (K/kbar)	Reference
6.O12O.6	2.09	98.70	Present work
CB.O10O.10	1.04	26.83	[12]
TB5A	0.356	56.05	[13]
TB7A	0.351	60.07	[13]
5O.5	0.34	36.50	[10]
5O.6	0.30	33.00	[10]
5O.8	0.25	26.30	[14]
6O.8	0.43	37.0	[15]

3.2. *Isotropic – Smectic A Transition in 7.O6O.7*

The I – SmA transition is a manifestation of the simultaneous growth of orientational as well as translational ordering which is accompanied by the breakdown of infinite rotational symmetry of the isotropic phase. I - SmA phase transition in 7.O6O.7 is accompanied by a large density jump of 2.63% and a peak in thermal expansion coefficient of $523 \times 10^{-4}\,°C^{-1}$ which confirm this transition to be a first order transition. It may be noted that the density jump at the I – SmA transition is much larger than that observed for the transition in monomers such as nO.m and TBnA compounds. The estimated pressure dependence of transition temperature, using Clausius – Clapeyron equation, was found to be 47.8 K/kbar. A comparison of the density jumps, heat of transition and dT/dP values observed for this transition in some other compounds of the dimers as well as a monomer is made in Table 2.

3.3. *Smectic A – Smectic F Transition in 7.O6O.7*

The SmA – SmF transition is inferred by a large jump in density and a peak in thermal expansion coefficient at the transition. The observed density jump of 1.40% and a large peak in thermal expansion coefficient of $488 \times 10^{-4}\,°C^{-1}$ confirms

Table 2. Density jump, heat of transition and pressure dependence of transition temperature at I – SmA transition of few mesogenic dimers and monomers

Name of the compound	$\Delta\rho/\rho\%$	$\Delta H/J\,mol^{-1}$	dT_t/dP K/kbar	Reference
7.O6O.7	2.63	17605	47.80	Present work
7.O4O.7	1.57	17666	29.08	[16]
7.O5O.7	0.95	9047	30.07	[16]
6.O5O.6	0.78	7511	26.89	[11]
6.O6O.6	1.80	14342	39.60	[11]
10.O10O.10	2.26	20515	39.71	[17]
TB10A	1.82	7080	55.50	[18]

the SmA – SmF transition to be a first order transition. SmA phase is a disordered phase which is characterized by a one-dimensional density wave along layer normal and the molecules are orthogonal to the layer planes with no correlations among the centre of mass positions of the molecules. Whereas the SmF phase is an ordered phase in which the molecules are packed in layers with a pseudo hexagonal arrangement with a 2-dimensional order of the positional order and long axis is tilted with respect to the layer planes (i.e., with uncorrelated layers but long range bond orientational order). As a result SmA – SmF transition is expected to be a first order transition. However, this transition is observed rarely and hence attracts much attention for phase transition studies. The other compounds on which density studies were reported so far across SmA – SmF transition are 6.O5O.6, 6.O6O.7, 7.O4O.7, 7.O5O.7, 10.O10O.10 which are listed in Table 2 with references and 9O.4 [19]. The estimated pressure dependence of transition temperature is found to be 57.4 K/kbar for 7.O6O.6 which is found to be highest reported so far, to the best of our knowledge [11].

4. Conclusions

All the three transitions viz., I – N transition in 6.O12O.6, I – SmA and SmA – SmF transitions in 7.O6O.7 are found to be of the first order nature. A comparison of the density jumps with other dimers at the I – SmA transition revealed that the density jumps is smaller in case of odd spacer dimers and large in case of even spacer dimers at this transition. The estimated values of dT/dP at this transition in 7.O6O.7 is in very good agreement with those of other dimers. However, the dT/dP value at I – N transition in 6.O12O.6 is relatively large compared with those for monomers and that for SmA – SmF is found to highest reported so far, to the best of our knowledge.

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