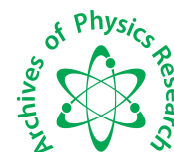




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Density studies of two dimeric liquid crystals of the α,ω -bis-(4-n-alkylaniline benzylidene-4'-oxy) alkanes series

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ABSTRACT

As a part of our systematic study of symmetric liquid crystal dimer homologous series, α,ω -bis-(4-n-alkylaniline benzylidene-4'-oxy) alkanes, we report here the nature of different phase transitions exhibited by two of these dimers using density measurements as a function of temperature. The compound 7.O12O.7 exhibits only nematic phase; whereas 8.O12O.8 exhibits smectic G phase. The phase transitions studied viz., isotropic – nematic (I–N) and the rare transition i.e., isotropic – smectic G (I–SmG), are confirmed to be of first order nature. We also report here the calculated density jumps, thermal expansion coefficients and pressure dependence of transition temperatures which are analyzed in the light of available literature data.

Key words: Symmetric dimer, isotropic-nematic transition, isotropic-smectic G transition.

INTRODUCTION

Dimeric liquid crystals which differ from conventional low molar mass mesogens as they are composed of molecules consisting of two mesogenic groups joined by flexible spacer. The interest in this class of mesogen stems not only from their ability to act as model compounds for semi flexible main chain liquid crystalline polymers but also from their quite different properties to conventional low molar mass liquid crystals [1]. It has been reported that the biaxiality in the Sauepe ordering matrix of a solute dissolved in liquid-crystal dimers is greater when the flexible spacer contains an even number of atoms than when there is an odd number. A new model was suggested for the molecular organisation in liquid-crystal dimers with odd and even spacers [2]. Several series of a family of non-symmetric dimers [3, 4] and symmetric dimers [5] have been investigated. The phase behaviour and transitional properties of a family of non-symmetric dimers have been investigated using optical microscopy and differential scanning calorimetry, while the structures of the mesophases have been studied using X-ray diffraction [3]. The nature and structure of the monotropic nematic phase is discussed by Fletcher and Luckhurst [4]. Binary mixtures of non symmetric liquid crystal dimers were discussed [6] to understand the origin of the different phase structures at the molecular level. Three sets of non-symmetric liquid crystal dimers consisting of a cholesteryl-based unit and either 4-methoxybiphenyl, 4-cyanobiphenyl or (S)-2-methylbutyl 4'-oxybiphenyl-4-carboxylate were investigated by Donaldson et al [7]. The transitional properties of these non-symmetric dimers are compared to those of the corresponding parent symmetric dimers. The molecular origins of the intercalated smectic phases have been studied on symmetric and non-symmetric dimers containing azobenzene groups [8]. By varying the spacer length it was found to exert a profound influence on the clearing temperatures of these materials and a large odd-even effect was observed for the series. The enhanced odd-even effect was also observed for the methylene linked dimers relative to those with ether linked dimers [9].

Dimeric liquid crystal molecules with smaller spacer length promote smectogenic behaviour whereas the dimeric liquid crystal molecules with large spacer length promote nematic behaviour which is in contrast to monomeric liquid crystal molecules. Also, symmetric dimers exhibit a large odd – even effect with number of carbon atoms in the spacer of the molecule. However, the alteration in temperatures is attenuated as the spacer grows in length. In contrast, the alteration in the entropy of nematic – isotropic transition is essentially unattenuated; at least for spacers containing upto twelve carbon atoms [10]. 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 suggests that the orientational order for even spacer dimers should be significantly greater than that for odd spacer dimers.

MATERIALS AND METHODS

The compounds were synthesized using a standard procedure as discussed in literature [1]. The crude products were repeatedly recrystallized from ethyl acetate until the transition temperatures were found to be reproducible and constant. The Differential Scanning Calorimetry (DSC) studies were carried out using Shimadzu Differential Scanning Calorimeter (DSC-60). Various phases exhibited by the compounds were characterized by observing their 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 [11]. The capillary diameter of the pycnometer was about 3.5×10^{-4} m and accuracy in density measurements was 0.1 kg m⁻³. The permitted cooling rate was 2°C per hour and temperature accuracy was $\pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

In DSC scan, two sharp peaks were observed for both the compounds. A DSC scan of 7.O12O.7 is shown in Figure 1. 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]. Schlieren texture was observed for the compound 7.O12O.7 and characteristic mosaic texture was observed for the compound 8.O12O.8 under polarizing microscope which indicates the nematic and smecticG phase in the compounds respectively.

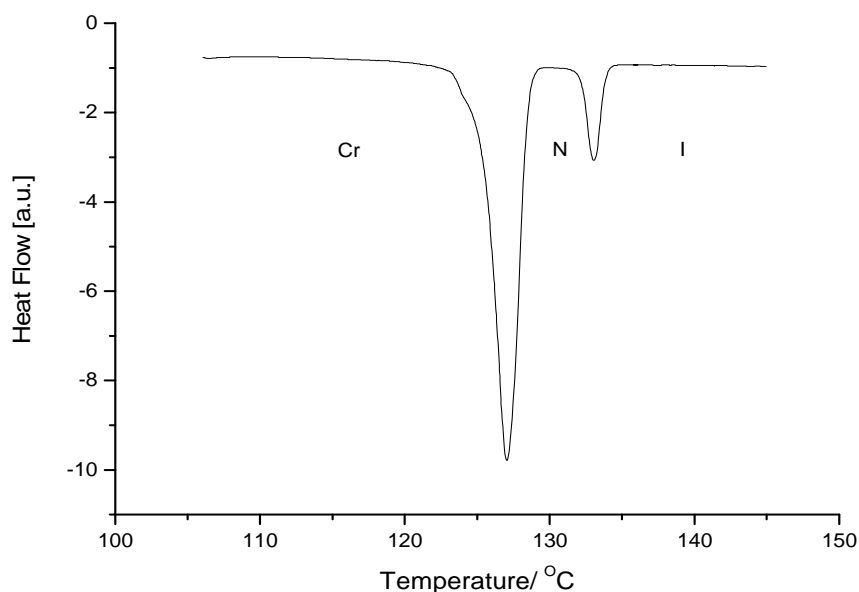


Fig.1: DSC scan of 7.O12O.7

The general molecular structure of the compounds and the phase transition temperatures are given below.



7.O12O.7 : m=7 and n=12
8.O12O.8 : m=8 and n=12

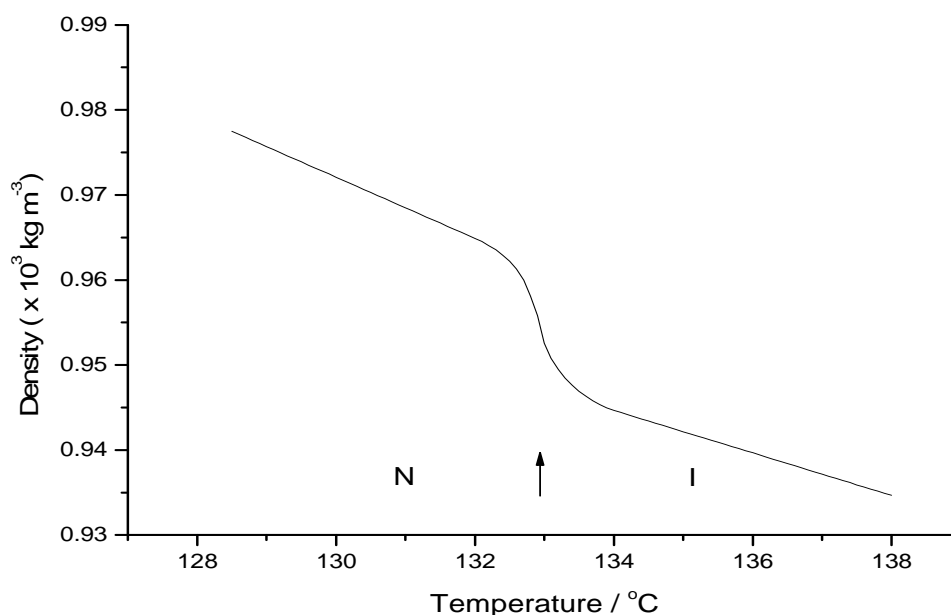


Fig.2 (a): Variation of density as a function of temperature in isotropic and nematic phases of 7.O12O.7

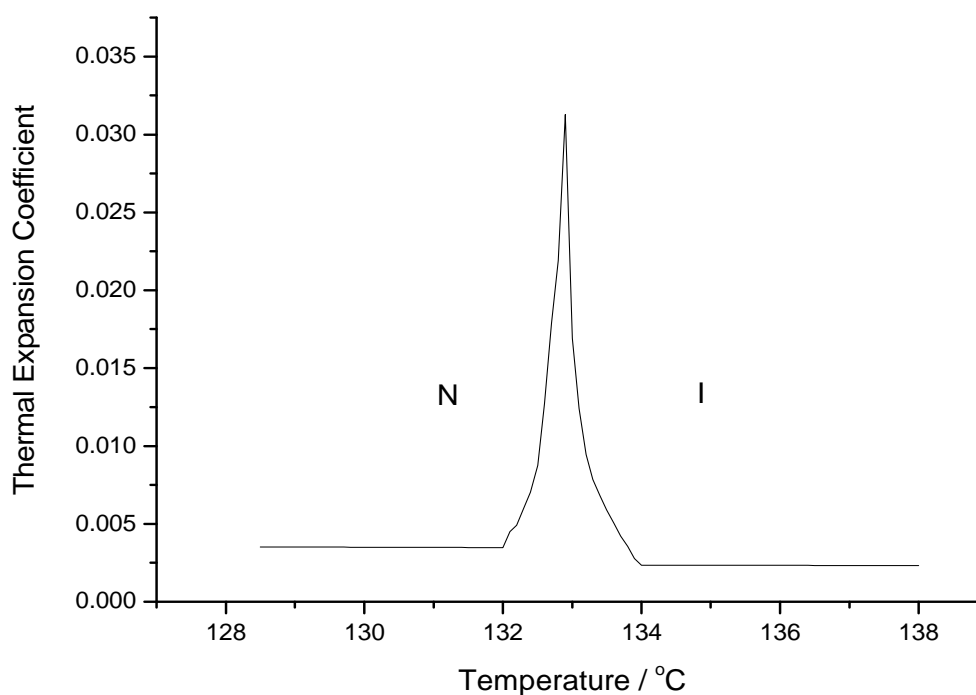


Fig.2 (b): Variation of thermal expansion coefficient at I-N transition of 7.O12O.7

The density variation and the variation of estimated thermal expansion coefficient ($\alpha = d \ln V / dT$, where V is the molar volume and T is temperature) with temperature for the compounds 7.O12O.7 and 8.O12O.8 are shown in Figures 2 [(a) & (b)] and 3[(a) & (b)] respectively. The molar volume of 7.O12O.7 at $(T_{NI} + 5)^\circ \text{C}$ is found to be $808.90 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ and that for 8.O12O.8 at $(T_{SmGI} + 5)^\circ \text{C}$ is $812.9 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. The percentage error in calculating the molar volume was found to be 1.82% and 2.1% for the compounds 7.O12O.7 and 8.O12O.8 respectively. The molar volume was reported to be $778.61 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ for 6.O12O.6 [12] and a comparison of this value with those obtained for 7.O12O.7 and 8.O12O.8 infers an increment of $15.15 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ per methylene unit in 7.O12O.7 and $15.33 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ in 8.O12O.8. The compound 7.O12O.7 exhibits Cr – N and N – I phase

transitions with a nematic phase thermal range of 6°C. While the compound 8.O12O.8 exhibits Cr – SmG and SmG – I phase transitions with a smectic G phase thermal range of 5°C. The value of density increases continuously with the decrease in temperature from isotropic phase, in both of the compounds studied, except at the isotropic phase to mesophase transition where a large density jump was observed.

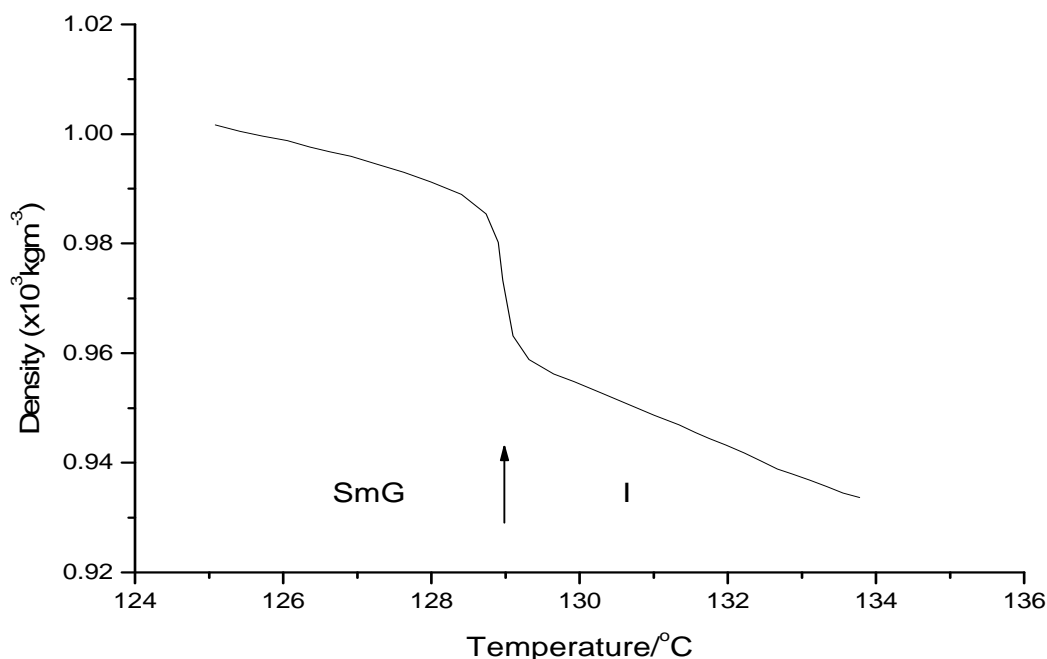


Fig.3 (a): Variation of density as a function of temperature in isotropic and smecticG phases of 8.O12O.8

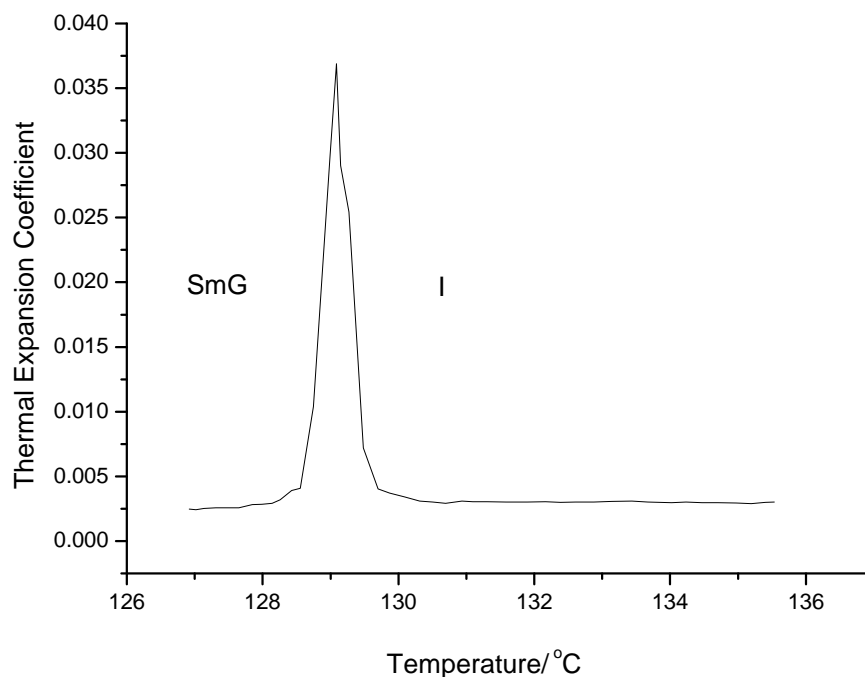


Fig.3 (b): Variation of thermal expansion coefficient at I-SmG transition of 8.O12O.8

3.1 Isotropic – Nematic transition in 7.O12O.7:

The I – N transition is accompanied by a breakdown of infinite rotational symmetry of the molecules in isotropic phase leading to the formation of nematic phase with the growth of only orientational order at the I – N transition. A

density jump of $0.01426 \times 10^3 \text{ kgm}^{-3}$ with an average absolute value of $0.9958 \times 10^3 \text{ kgm}^{-3}$ was found at the I – N transition. For the sake of comparing this density jump at I – N transition in other compounds available in literature percentage density jump was calculated at this transition. This calculated density jump ($\Delta\rho/\rho$ %) was found to be 1.49%. This jump in density and peak in thermal expansion coefficient of $310 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ confirms the strong first order nature of I – N transition in 7.O12O.7. The density jump at the transition is very large compared with those of I – N transitions in nO.m compounds (monomers) which is of the order of only 0.30 to 0.40. A comparison of the density jumps at I – N transitions of different compounds is shown in Table-1 presented later in the text. The large density jump in 7.O12O.7, in comparison with monomers, 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 terminal alkyl chains of the dimer molecule which are expected to contribute to the large entropy change at the transition. The observed entropy change ($\Delta S/R$) at this transition in 7.O12O.7 is 2.86. However, the density jump observed for 7.O12O.7 is comparable with those of other dimers at this transition [11,12]. An estimate of the pressure dependence of transition temperatures can be obtained using Clausius – Clapeyron equation

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

Name of the compounds	Density jump at N – I transition ($\Delta\rho/\rho$)%	Estimated value of dT_i/dP (K/kbar)	Reference
7.O12O.7 [α,ω -bis-(4-n-dodecylaniline benzylidene - 4'-oxy) heptane]	1.49	49.80	Present work
6.O12O.6 [α,ω -bis-(4-n-dodecylaniline benzylidene - 4'-oxy) hexane]	2.09	98.7	12
CB.O10O.10[α -(4-cyano biphenyl-4'-yloxy)- ω -(4-n-decylanilinebenzylidene-4'-oxy)decane]	1.04	26.83	11
TB5A [terephthal-bis-pentylaniline]			
TB7A[terephthal-bis-heptylaniline]	0.356	56.05	13
5O.5 [N-(p-n- pentyl benzylidene)-p-n-pentylaniline]	0.351	60.07	13
5O.6[N-(p-n- pentyl benzylidene)-p-n-hexylaniline]	0.34	36.50	14
5O.8[N-(p-n- pentyl benzylidene)-p-n-octylaniline]	0.30	33.00	14
6O.8[N-(p-n- hexyl benzylidene)-p-n-octylaniline]	0.25	26.30	14
	0.43	37.0	15

$$\frac{dT_t}{dP} = T_t \frac{\Delta V}{\Delta H}$$

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 49.80 K/kbar for 7.O12O.7. A comparison of the dT_i/dP values for different compounds including 7.O12O.7 and monomers is presented in Table 1. In the table a comparison of density jump and the estimated pressure dependence of transition temperatures was made between the schiff base monomers and schiff base dimers, which are reported in the present studies. This comparison was relevant because the schiff base monomers of nO.m series are the precursors of the schiff base dimers studied. From this comparison it is clear that the density jump at the I – N transition is higher compared with the monomers but in good agreement with our previous work for similar kind of liquid crystal dimer. Whereas the estimated value of the pressure dependence of the I – N transition is comparable with those of TB5A and TB7A and is significantly smaller than that observed for 6.O12O.6.

3.2 Isotropic – SmecticG transition in 8.O12O.8:

The isotropic to smecticG transition is a very rare kind of phase transition and is an example of a transition between a completely disordered liquid phase to a well-defined three- dimensional structure in smectic phase. At this transition, the infinite rotational symmetry of the isotropic phase is broken with the development of a long-range three dimensional positional correlation as well as a three- dimensional bond orientational order. The isotropic - smecticG transition in 8.O12O.8 is accompanied by a density jump of 0.0264 kgm^{-3} with an average value of density 0.9755 kgm^{-3} . The percentage density jump was calculated and found to be 2.7% at this transition. This large density jump and peak in thermal expansion coefficient ($\alpha=368 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$) indicating the transition to be first order transition. In our study, it is observed that the density jump is much less, than what would have been expected for a transition of entropy change ($\Delta S/R$) was 9.79. However, this density jump is found to be higher compared to the smecticA to isotropic transition and smecticC to isotropic transition of the same series of dimers (10.O10O.10, 10.O4O.10) [16, 17]. The density jump is also higher than the isotropic to smecticG transition of 10.O12O.10 [18]. It may be due to the dimensionality and crystal structure order change is different at the isotropic to smecticG transition. Also it could be due to the terminal chain length. This value is different from the values at the onset of smectic A, C and F directly from isotropic liquid. It is noticed that the dimensionality and the crystal structure change is different (from smecticA, C and F) at the isotropic to smecticG transition resulting in a larger density

jump. It is due to the fact that the isotropic phase is completely disordered state where the molecules are randomly oriented but the Smectic G phase is a phase of three dimensional structure with considerable disorder i.e., the layer distribution is not sharp as in the case of crystals. The decreasing trend of the density jump with the increase of the flexible spacer length irrespective to type of transition is in agreement with that reported [19] in the case of TBNA and 12O.m series[20] where this type of behaviour was reported for increasing terminal chain length (the spacer length). Moreover, at this transition the infinite rotational symmetry of isotropic phase is broken with the growth of three-dimensional positional correlation of bond orientational order [21]. The calculated pressure dependence of transition temperature is found to be 117. 70 K/kbar which is larger than that at any transition in these dimers reported so far.

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