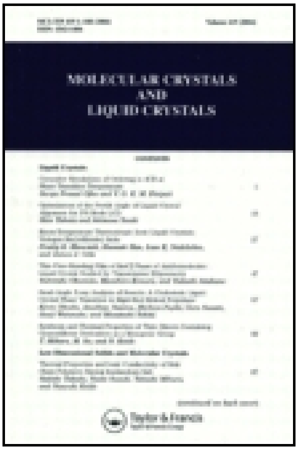

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INVESTIGATION OF RARE PHASE TRANSITIONS BY DENSITY MEASUREMENTS

B. Gogoi [a] , A. Arulsankar [a] & P. R. Alapati [a]

[a] Department of Physics, North Eastern Regional Institute of Science & Technology, Itanagar, 791 109, India

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Investigation of Rare Phase Transitions by Density Measurements

B. GOGOI, A. ARULSANKAR and P.R. ALAPATI

Department of Physics, North Eastern Regional Institute of Science & Technology. Itanagar - 791 109, India

We report here the study of nature of few rare phase transitions viz., Isotropic – Sm C, Sm C – Sm F and Sm A – Sm F transition in two homologues of α,ω-bis(4-n-alkylanilinebenzylidine-4′-oxy)alkane series using density measurements. Compound 10.O4O.10 exhibits Isotropic – Sm C, Sm C – Sm F and Sm F – Crystal phase transitions. Whereas 10.O10O.10 exhibits Isotropic – Sm A, Sm A – Sm F and Sm F – Crystal transitions. Variation of density with temperature across the phase transitions Isotropic – Sm A, Isotropic – Sm C, Sm C – Sm F and Sm A – Sm F show a jump in density confirming that all these transitions are first order in nature. However, the magnitude of the density jump is smaller than expected at some of these transitions. The calculated pressure dependence of transition temperature is also reported.

Keywords: Symmetric liquid crystal dimers; I-S_A transition; I-S_C transition; S_A-S_F transition; S_C-S_F transition

INTRODUCTION

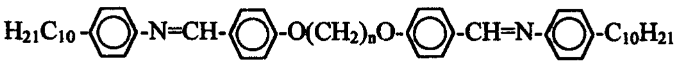
There is now a great wealth of molecular architectures known to support liquid crystal behaviour[1]. Of all these one attracting particular attention is the dimeric structure in which two mesogenic groups are linked via a flexible alkyl core. The interest in this class of mesogens stems not only from 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[2-10]. α,ω-bis(4-n-alkylanilinebenzylidine-4'-oxy)alkanes (hereafter referred to as m.OnO.m) homologous series of compounds have shown a rich smectic mesomorphism[4]. In addition to the commonly observed smectic A, smectic C, smectic B phases, the uncommon smectic F phase is also present in a number of long terminal chain length homologues. Many of the transitional properties of these dimers depend strongly on the length and parity of the spacer. In particular, the Nematic-Isotropic transition temperatures and entropies exhibit a marked alternation on increasing the spacer length. This alternation of Nematic – Isotropic transition is attenuated as the length of the spacer increases, whereas the entropy change at the transition, $\Delta S/R$, exhibits the same striking alternation but now there is little indication that this alternation decreases with spacer length. In addition, these dimers exhibit rare phase transitions viz., I-S_C, S_C-S_F and S_A-S_F transitions. As a part of our systematic study of rare phase transitions, we present here the density studies on two compounds of the m.OnO.m homologous series. These compounds are 10.O4O.10 and 10.O10O.10. Compound 10.O4O.10 exhibits I-S_C and S_C-S_F transitions where as 10.O10O.10 exhibits I-S_A and S_A-S_F phase transitions.

EXPERIMENTAL

The compounds were synthesized using the procedure given in literature[2] and repeatedly recrystallized from ethyl acetate until the transition temperatures were reproducible. The Differential Scanning Calorimetry (DSC) studies were carried out on Perkin-Elmer DSC7. Various phases exhibited by the compounds were characterized by observing their textures under a polarizing microscope attached with an indigenous hot stage. The temperature resolution of the microscopic observations was 0.1°C. Density studies were carried out with a bicapillary pyknometer[11]. The diameter of the capillary was about 0.35 mm and the accuracy in the density measurements was ±0.1 Kg. m^{-3}. The permitted cooling rate in the experiment was 2°C hr^{-1} and the temperature accuracy is ±0.1°C.

RESULTS AND DISCUSSION

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



10.O4O.10 (n=4) and 10.O10O.10 (n=10)

$$10.O4O.10 \quad K \xleftrightarrow{107.1°C} S_F \xleftrightarrow{166.3°C} S_C \xleftrightarrow{205.8°C} I$$

$$10.O10O.10 \quad K \xleftrightarrow{125.4°C} S_F \xleftrightarrow{135.2°C} S_A \xleftrightarrow{143.1°C} I$$

DSC scans of 10.O4O.10 and 10.O10O.10 show sharp melting transition which is an indication of the purity of the compound. The transition temperatures and entropy change at different transitions are in agreement with reported literature values[2].

The variation of density as a function of temperature and the variation of estimated thermal expansion coefficient (α = dlnV/dT where V is molar volume) with temperature for 10.O4O.10 and 10.O10O.10 are shown in figures 1 and 2 respectively.

Isotropic to Smectic A Transition (10.O10O.10)

The Isotropic – Smectic A transition in 10.O10O.10 is inferred as a first order transition with a significant jump in density as well as indicated by a peak in thermal expansion coefficient. Besides the higher slope of the density value for S_A phase compared to the isotropic phase indicates the dense packing and higher structural ordering in the S_A phase than in the isotropic phase. Further, coexistence of isotropic and smectic A phase is observed for 0.9°C (which suggest the simultaneous development of orientational and translational order) but large part of density jump is completed within 0.2°C. The observed density jump ($\Delta\rho/\rho$%) across the I-S_A transition is 2.26% and falls on higher side of reported values so far[18]. The

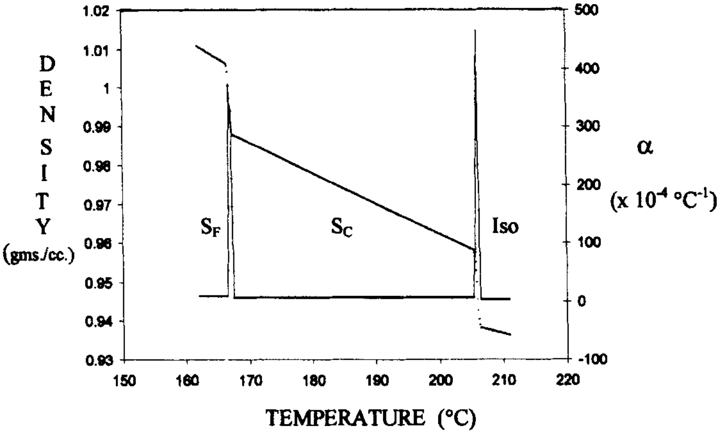


FIGURE 1 Density and Thermal Expansion Coefficient variation with temperature in isotropic, smectic C and smectic F phases of 10.O4O.10

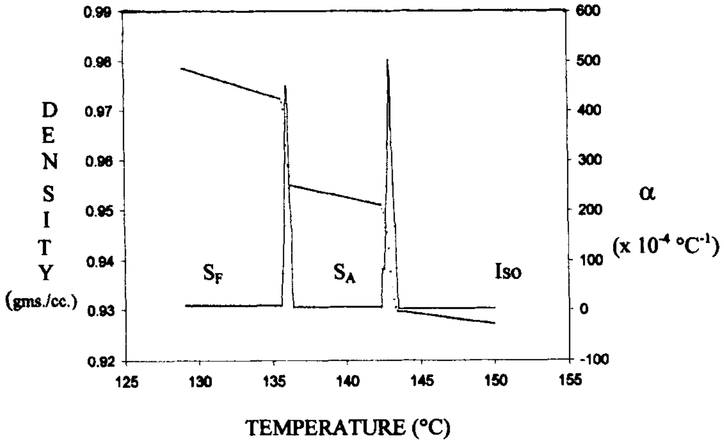


FIGURE 2 Density and Thermal Expansion Coefficient variation with temperature in isotropic, smectic A and smectic F phases for 10.O10O.10.

minimum and maximum density jump reported so far across I-S_A transition are

0.35% and 2% respectively. A comparison of density jump, transition enthalpy and estimated pressure dependence of transition temperature of different compounds (monomers) and dimers are presented in Table 1.

Isotropic to Smectic C transition (10.O4O.10)

The Isotropic – Smectic C (I-S_C) transition is accompanied by a large jump in density. Further, the coexistence of isotropic and smectic C phases is observed for 0.9°C. However, the significant jump in density at the transition is completed within 0.4°C. The observed density jump of 2.09% and a thermal expansion coefficient maxima ($\alpha = 451 \times 10^{-4}$ °C^{-1}) confirm the transition to be first order transition. The slope of the density plot (calculated away from the phase transition i.e., in the thermally sTable linear region) is found to attain a higher value with the growth of the relatively densely packed smectic C phase. The observed density jump is found to be comparable to that for other compounds and highest across the I-S_C transition reported so far. A comparison of the density jump across I-S_C transition is presented in Table 2.

TABLE 1 Density jump and heat of transition of some compounds at Isotropic-smectic A transition

COMPOUND	$\Delta\rho/\rho$%	ΔH/J mol^{-1}	References
10.O10O.10	2.26	20515.34	Present work
7.O4O.7	1.57	17665.73	15
7.O5O.7	0.95	9046.68	15
Di-n-hexadecyl 4,4'-azoxy cinnamate	0.40	4764	14
Di-n-undecyl 4,4'-azoxy cinnamate	0.35	5555	14
Di-n-undecyl 4,4'-azoxy-α-methyl cinnamate	1.21	8565	14
n-amyl-4(4-n-dodecyloxybenzylidene amino) cinnamate	1.28	8414	14
N-(4-n-Heptyloxybenzylidene)4'-n-octylaniline	1.04	5870	23
N-(4-n-octyloxybenzylidene)4'-n-butylaniline	1.11	5680	22
Terephthalylidene-bis-p-n-decylaniline	1.82	7080	18
Terephthalylidene-bis-p-n-octylaniline	0.96	5670	16
Di-ethyl 4,4'-azoxy dibenzoate	2.00	5442	24

TABLE 2 Density jump of some compounds at Isotropic-smectic C transiton.

Compound	$\Delta\rho/\rho\%$	Reference
10.040.10	2.09	Present work
Terephthalylidene-bis-p-n-dodecylaniline	1.13	12
Terephthalylidene-bis-p-n-tetradecylaniline	1.20	13
Terephthalylidene-bis-p-n-hexadecylaniline	0.75	13
4,4'-di-n-octadecyloxy azoxybenzene	1.94	14
4,4'-azoxy α-methyl cinnamate di-n-hexadecylester	1.35	14

The observed density jumps across the I-S_C transition are found to be higher than those across I-S_A transition and lower than that across I-S_F ($\Delta\rho/\rho$ = 2.14% in 10O.14[19]) phase transitions. It is due to the growth of characteristic intermediate smectic C order (in between structural orders that grow across I-S_A and I-S_F transitions) from the isotropic liquid. The estimated pressure dependence

$$\frac{dT_t}{dP} = T_t\left(\frac{\Delta V}{\Delta H}\right)$$

Where T_t - Transition temperature.

ΔV - Molar volume change associated with the transition.

ΔH - Heat of transition.

for I-S_C transition temperatures using Clausius-Clapeyron equation is found to be 36.67 K/k bar in 10.040.10 and is compared with that of other Isotropic-mesophase transition of other compounds (monomers) as well as with that of I-S_A transition in other dimers in Table 3.

The estimated pressure dependence of transition temperature of 36.67 K/k bar for 10.040.10 is in agreement with the values reported for the I-S_C transition in other compounds whereas it is lower when compared with other isotropic-mesophase transition in other compounds.

Smectic C to Smectic F Transition (10.O4O.10)

A large density jump of 1.83% and a thermal expansion coefficient peak value of 370 x 10^{-4} °C^{-1} characterize S_C-S_F transition to be a first order transition. This is also consistent with the large entropy change ($\Delta S/R = 4.10$) observed at the transition in DSC studies. It may be noted that the large thermal range of (39°C) smectic C phase in 10.O4O.10 is expected[20] to unlock the high temperature two-fold biaxial mode from the exponentially growing six-fold hexatic continuous symmetry resulting into a second order transition (against the observed first order S_C-S_F transition as in the case of two dimensional melting of crystals). The existence of S_C-S_F tricritical point where the order of the transition changes from second order to first order was discussed in a study of TB5A[21]. The estimated pressure dependence of S_C-S_F transition is found to be 39.66 K/k bar. This value is found to be comparable with that of 5O.5 ($dT_t/dP = 42.5$ K/k bar) and TB0A ($dT_t/dP = 43$ K/k bar)[25] and lower than that reported for 9O.6 and 9O.8[26].

Smectic A to Smectic F Transition (10.O10O.10)

The smectic A – smectic F transition is inferred by a large jump in density in 10.O10O.10. The observed density jump is 1.80%. This density jump along with a large thermal expansion coefficient peak value of 450 x 10^{-4} °C^{-1} for 10.O10O.10 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 so far on which density studies were reported across smectic A – smectic F transition are 7.O4O.7, 7.O5O.7 and 9O.4 in which observed density jumps were 0.55%, 0.62% and 1.42% respectively[15,25]. The density jump observed for 10.O10O.10 at the

TABLE 3 Pressure dependence of transition temperature of some compounds at Isotropic-mesophase transition.

Compound	Transition	T_C/°C	dT_i/dp (K/k bar)	Reference
10.O4O.10	I-S_C	205.8	36.67	Present work
10.O10O.10	I-S_A	143.1	39.71	Present work
7.O4O.7	I-S_A	212.1	29.08	15
7.O5O.7	I-S_A	142.3	30.07	15
Terephthalylidene-bis-p-n-dodecylaniline	I-S_C	180.2	35.3	12
Terephthalylidene-bis-p-n-tetradecylaniline	I-S_C	170.0	33.03	13
Terephthalylidene-bis-p-n-hexadecylaniline	I-S_C	160.0	29.99	13
Terephthalylidene-bis-p-n-octylaniline	I-S_A	202.4	42.00	16
Terephthalylidene-bis-p-n-nonylaniline	I-S_A	199.0	91.5	17
Terephthalylidene-bis-p-n-decylaniline	I-S_A	190.2	72.2	18
4,4'-di-n-octadecyloxyazoxy benzene	I-S_A		27.1	14
4,4'-azoxy α-methyl cinnamic di-n-hexadecylester	I-S_A		30.1	14

$S_A - S_F$ transition is higher than that reported so far for other compounds. The estimated pressure dependence of transition temperature is found to be 45.76 K/k bar. This value is in good agreement with that reported as 48 K/k bar for 9O.4[25] and smaller than that for 7.O4O.7 and 7.O5O.7.

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