Phase Transition Studies across Isotropic-Smectic A and Smectic A-Smectic F Phases in 90.4

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The temperature dependence of the density of N(p-n-nonyloxy benzylidene)p-n-butylaniline (90.4) is studied. The compound exhibits smectic A, smectic F and smetic G phases. The isotropic-smectic A (IA) and smetic A-smectic F phase transitions are found to be first order. The calculated thermal expansion coefficient and differential scanning calorimetry support the density results. The density jumps, associated enthalpies and the estimated pressure dependence of the transition temperatures for IA transitions in other compounds are also presented.

N(p-n-alkoxybenzylidene)p-n-alkylanilines (abbreviated as ${}_nO_m$ compounds, n and m representing the number of carbon atoms in the alkoxy and alkyl chains, respectively) form a well studied homologous series [1–4], the importance of which is exposed in [5–9]. Very little is reported on N(p-n-nonyloxy benzylidene)p-n-butylaniline, 90.4 [4, 10], the only material known to exhibit a smectic A-smectic F (AF) transition. Most microscopic, miscibility and X-ray studies [1, 4] indicate that this material possesses a smectic F phase. The idenifications, however, were made before the smectic I phase was discovered. The X-ray studies indicated that the phase in question may be smectic I [11]. However, the smetic I phase differs from the smectic F phase primarily in the direction of tilt of the quasi hexagonal molecular packing with the hexagon either tilted towards an apex (smectic I) or an edge (smectic F) of the hexagon. The AF transition involves a change of the lath like molecules in the smectic A layered phase to the smectic F phase, characterised by two order parameters: a tilt parameter and a six-fold bond orientational order parameter. Thus the AF transition exhibits a simultaneous onset of both types of order. Further, the data about the isotropic-smectic A (IA) transition are rather meagre. This transition involves the growth of a periodic translational order in a layered arrangement and a long rage orientational order of the molecules.

In this work, the density variation with temperature, the associated density jumps and the enthalpies across the phase transitions are studied in order to estimate the thermal expansion coefficient, the pressure dependence of the transition temperatures and pretransitional effects in 90.4.

Experimental

The density variation with temperature of 90.4 was studied following the experimental method described in [9]. The density measurements are accurate to ±0.0001 g/cm^3. The sample was prepared by condensation of p-n-butylaniline (0.1 mole) and p-n-nonyloxybenzaldehyde (0.1 mole) in presence of a few drops of glacial acetic acid. After refluxing the reactants for four hours, the solvent was removed by distillation under reduced pressure. Later, the pure white compound was recrystallised from absolute ethanol until the observed transition temperatures became constant. The transition temperatures were determined

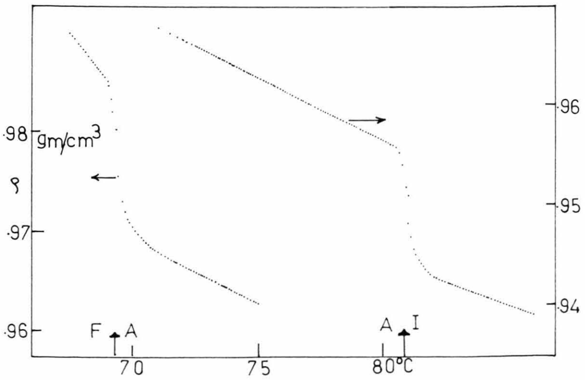

Fig. 1. Variation of density (ϱ) with temperature of 90.4.

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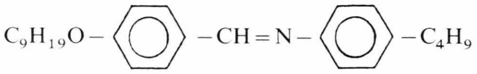
by textural observations using a Hertel-Reuss superpan polarizing microscope attached with a hot stage. The transition temperatures are accurate to ± 0.1 °C.

Results and Discussion

The transition temperatures observed by thermal microscopy, density and DSC are given below. The molecular formula along with the heats of transition are also given.



$C_9H_{19}O-C_6H_4-CH=N-C_6H_4-C_4H_9$

Solid	Smectic G	Smectic F	Smectic A	Isotropic
Microscopic data	50 °C	66 °C	68.2 °C	80.9 °C
Density data		67 °C	69.2 °C	80.9 °C
DSC data	50 °C	64.6 °C	67.8 °C	80.9 °C
Literature data	50 °C	67 °C	69.5 °C	82 °C
Enthalpy (J/mole)	–	159	3859	6320

The literature data are from [4]. However, differences of a few degrees occur in [1] and [2].

The variation of the density (ϱ) and thermal expansion coefficient (α) with temperature are displayed in Fig. 1 and 2, respectively. The molar volume of 90.4 in the isotropic liquid at $T_{\mathrm{AI}} + 5$ °C is 403.8×10^{-6} m^3 mol^{-1}. Assuming additivity of the molar volumes in nonyloxybenzylidene alkyl anilines [12] and alkoxybenzylidene butylanilines [5], the estimated methylene group contributions are 16.3 m^3 mol^{-1} and 16.2 m^3 mol^{-1}, respectively, which are in reasonable agreement with the contribution of the methylene unit to the molar volume of the isotropic liquid in the other homologous series [13].

The IA transition is accompanied by a significant density jump ($\Delta\varrho/\varrho$) of 1.23% and a large thermal expansion coefficient peak value of 39×10^{-3} °C^{-1}, indicating the first order nature of the IA transition. The larger density jump across the IA transition than across the isotropic-nematic and isotropic-cholesteric transitions [14] is due to the commencement of S_A phase, which has greater structural ordering than the nematic or the cholesteric liquid crystalline phases. The density jump across the IA transition in this compound falls on the higher side of the density jumps reported across this transition in other compounds (Table 1) [5–8, 14–16].

The estimated thermal expansion coefficient $\alpha = \mathrm{d}(\ln V)/\mathrm{d}T$, where V is the volume, which is higher in

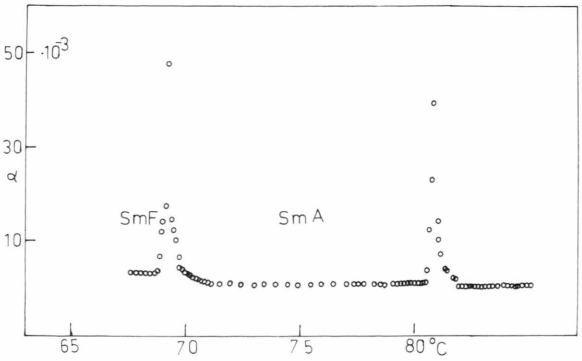


Fig. 2. Variation of thermal expansion coefficient (α) with temperature of 90.4.

Table 1. Density jumps, enthalpies and $\mathrm{d}T_t/\mathrm{d}P$ values across the AI transition in different compounds.

Compound	T_{AI} °C	$\Delta\varrho/\varrho$ %	ΔH J/g	$\mathrm{d}T_t/\mathrm{d}P$ K/k · bar
Di-n-hexadecyl 44′-azoxy cinnamate	135	0.4	6.05	26.7
Di-n-undecyl 44′-azoxy cinnamate	160.2	0.35	8.59	34.9
Di-n-undecyl 44′-azoxy α-methyl cinnamate	85.7	1.21	12.70	18.9
n-amyl 4(4-n-dodecyloxy benzylidene amino)cinnamate	137.2	1.28	16.60	33.7
Diethyl 4-4′ azoxy dibenzoate	123	2.0	15.90	43
Terephthalylidene bis (p-n-octyl aniline)	202.4	0.96	11.10	42
Terephthalylidene bis (p-n-decyl aniline)	190.2	1.82	12.53	72.2
N(p-n-heptyloxy benzylidene)p-n-octylaniline	83	1.04	14.4	27.3
N(p-n-octyloxy benzylidene)p-n-octylaniline	86.2	0.73	–	–
N(p-n-octyloxy benzylidene)p-n-butylaniline	81.2	1.1	15.53	26.5
N(p-n-nonyloxy benzylidene)p-n-butylaniline	80.9	1.2	16.60	39.5

the smectic A phase (13×10^{-4} °C^{-1}) is slightly higher than in 80.4 (12×10^{-4} °C^{-1}) [5], the lower homologue of 90.4. Further, the higher value of α in the smectic A phase than in the isotropic phase suggests higher ordering, implying closer packing of the molecules. Visual observations across the IA transition indicated a significant physical change in the bulb of the dilatometer. It is associated with the uniformly growing smectic A phase from the isotropic phase, the phase transformation ranging within about 1.4 °C, and 90% of the transformation is complete within 0.3 °C. The material in the bulb appeared as a two phase mixture, with the transparent isotropic liquid being layered above the translucent smectic A phase in the lower part of the bulb.

Pressure dependences of the IA transition temperatures for different compounds, obtained by using the Clausius-Clapeyron equation $\mathrm{d}T_t/\mathrm{d}P = T_t(\Delta V/\Delta H)$, where T_t is the transition temperature, ΔV the molar volume changes and ΔH the enthalpy change, are presented in Table 1. It is apparent from these data that the pressure dependence of IA transition temperatures are at variance, and it can be argued that this must be due to the different experimental conditions in determining the volume jumps and enthalpy values (rate of cooling or heating). The AF transition is found only in the compound 90.4 of the $_n\mathrm{O}_m$ homologous series.

The density jump and thermal expansion coefficient maxima across the AF transition inferred a first order transition. The density jump ($\Delta\varrho/\varrho$) across this transition is found to be 1.44% and is compatible with the observed large enthalpy change. It is much higher than the density jumps either across the IA transition in this compound or the AB and CF transitions in other compounds ($\Delta\varrho/\varrho$ across the AB transition is 0.4% in 80.4 [5], 0.76% in 50.8 [17] and 50.10 [18], and less prominent in 60.4 [9] and 70.1 [19]. Across the CF transition ($\Delta\varrho/\varrho$) is 0.39% in 50.5 [20] and 1.04% in TBOA [7]). The thermal expansion coefficient, which is higher in the smectic F phase ($\alpha = 32 \times 10^{-4}$ °C^{-1}) than in the smectic A phase (13×10^{-4} °C^{-1}) indicates the closer molecular packing in the smectic F phase leading to rigidity of the molecules.

The $\mathrm{d}T_t/\mathrm{d}P$ value estimated from the molar volume change and heat of transition for this AF transition (48 K/k · bar) is slightly higher than the $\mathrm{d}T_t/\mathrm{d}P$ value for the CF transition in both TBOA and 50.5 (43 K/k · bar), or the CI transition in TBDA (43 K/k · bar) [8], and nearly equal to the value for the AB transition in 50.8 (49 K/k · bar).

Acknowledgements

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