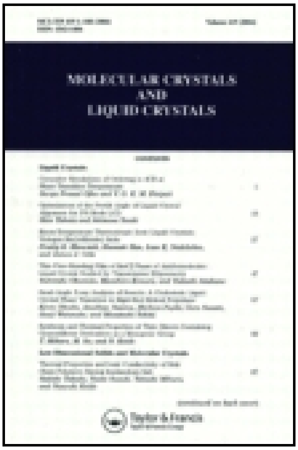

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Density, Refractive Index and Ultrasonic Velocity Studies Involving N(p-n-Hexyloxy Benzylidene) p-n-Octyl Aniline

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Density, Refractive Index and Ultrasonic Velocity Studies Involving N(p-n-Hexyloxy Benzylidene) p-n-Octyl Aniline

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The density, refractive index and ultrasonic velocity dependence on temperature for N(p-n-hexyloxy benzylidene) p-n-octyl aniline, 60.8, is presented. The compound exhibits smectic B, smectic A, nematic and monotropic smectic G phases between the solid and isotropic liquid phases. The nematic—isotropic and smectic A—smectic B phase transitions are found to be first order. The interesting nematic—smectic A transformation is confirmed to be a first order from the observed results. An estimate of the pressure dependence of the phase transition temperatures using the volume and enthalpy data are presented. A comparison of these results with other reported results in the homologous series of n0.m compounds are also discussed.

INTRODUCTION

Recent phase transition studies[1-6] inferred both first and second order transitions in n0.m compounds viz., N(p-n-alkoxy benzylidene)p-n-alkyl anilies and two phase coexistence phenomena at the nematic-

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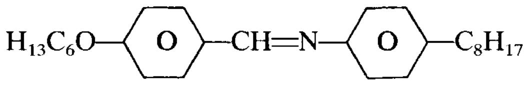
smectic A, smectic A—smectic B[7] and smectic C—smectic B transitions.[8] The homologues of N(p-n-hexyloxy benzylidene)p-n-alkyl anilines exhibit different mesomorphic behaviour i.e., 60.1 exhibit nematic—smectic B, 60.2 nematic—highly ordered smectic G, 60.4 nematic—smectic A—smectic B—smectic G, 60.8 nematic—smectic A—smectic B—monotropic smectic G. Previous studies in 60.4,[10] 70.1[11] and 70.4[12] exhibited first order nematic—smectic A transition, while 50.8 and 50.10[1-3] a weak first order nematic—smectic A transition. We present here the results of density, ultrasonic velocity and refractive indices in nematic, smectic A and smectic B phases of N(p-n-hexyloxy benzylidene) p-n-octyl aniline 60.8.

EXPERIMENTAL

60.8 was prepared by condensation of p-n-hexyloxy benzaldehyde (0.1 mole) and p-n-octyl aniline (0.1 mole) following the procedure similar to that described earlier.[12] The density, ultrasonic velocity and refractive indices measurements were carried out following previous publication.[1,10] The transition temperatures in °C and the identified phases are presented below



$$\begin{tikzcd}
\text{solid} \arrow[r, "28"] & \text{smectic B} \arrow[r, leftrightarrow, "65.3"] \arrow[dl, leftrightarrow, "14"] & \text{smectic A} \arrow[r, leftrightarrow, "81"] & \text{nematic} \arrow[r, leftrightarrow, "82.2"] & \text{isotropic} \\
\text{smectic G} \arrow[u] & & & &
\end{tikzcd}$$

RESULTS AND DISCUSSION

The temperature dependence of the density, ultrasonic velocity and refractive indices in N(p-n-hexyloxy benzylidene) p-n-octyl aniline 60.8 in the isotropic, nematic, smectic A and smectic B phases are displayed in Figures 1, 2 and 3. No hysteresis was observed in heating and cooling cycles. A sudden jump in density (($\Delta\ \rho/\rho$) = 0.43%) and an anomalous decrease in the ultrasonic velocity (0.6%) were observed at the nematic—isotropic transition temperature. The transition temperatures observed by these methods coincided with that by the thermal microscopy within 0.1°C and reported data. The ther-

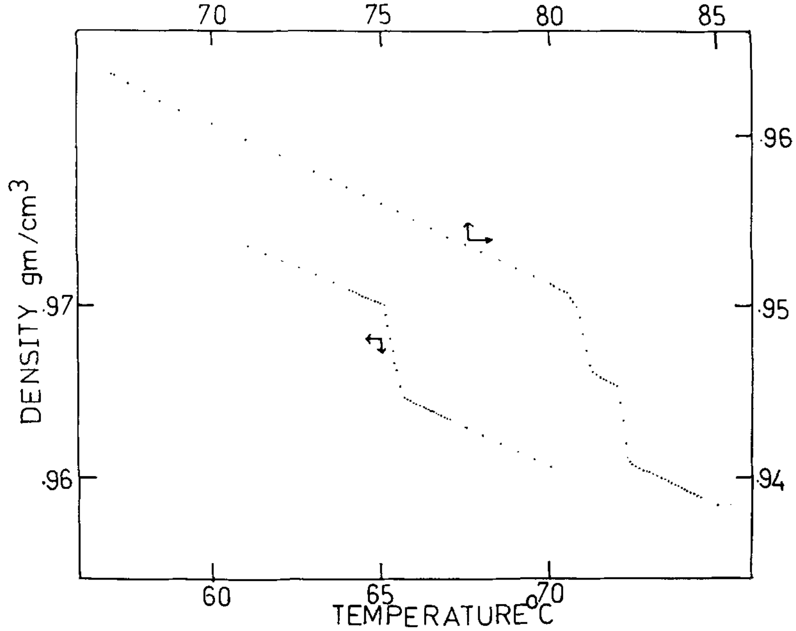


FIGURE 1 Temperature dependence of density in nematic, smectic A and smectic B phases of 60.8.

mal expansion coefficient (α = *d* ln V/dT; V = molar volume) variation with temperature is illustrated in Figure 4. The observed results at this transition are in accordance with the previously reported results. The estimated pressure dependence of transition temperature using the Clausius-Clapeyron equation (dT/dp) = $T_t(\Delta V/\Delta H)$ is 37 K/k bar.

The nematic—smectic A transition is considered to be interesting in the homologues of n0.m compounds because this transition is first order in some compounds while it is second order in some other compounds. The DSC studies inferred[13] large enthalpy at this transition. The density jump (Δ ρ/ρ) at the N − S_A transition from the extrapolated curves is 0.4%. This value is in agreement with the jumps observed at this transition in 60.4 (0.23%),[10] 70.1 (0.43%),[11] 70.4 (0.46%)[12] and 70.5 (0.25%)[14] and suggests analogous nature of the transition. The heating or cooling rate in the transition region is 0.1°C/ hour. The width of the transition region is 0.2°C. The sample in the bulb appeared as a two phase mixture in the entire transition range. The thermal expansion coefficient maxima suggests a first order transition (Figure 4). The McMillan parameter T_{NA}/T_{NI} = 0.997 is also

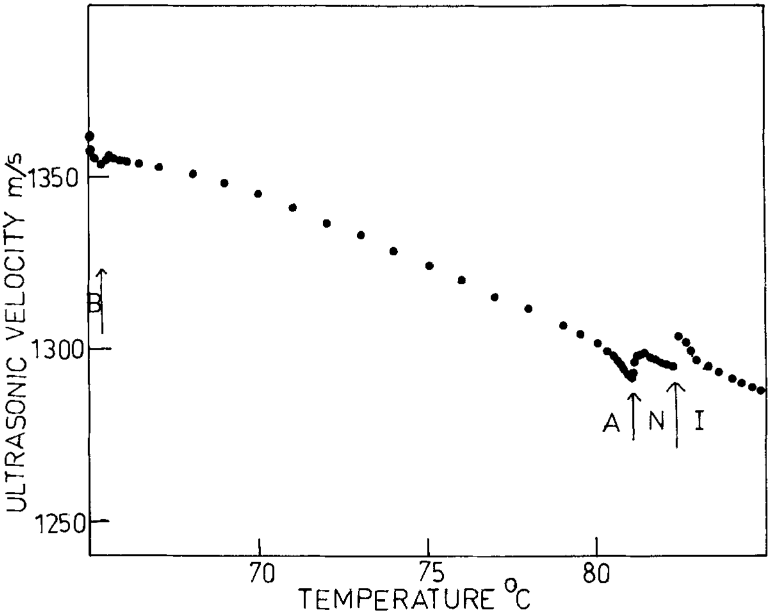


FIGURE 2 Temperature dependence of ultrasonic velocity in nematic smectic A and smectic B phases of 60.8.

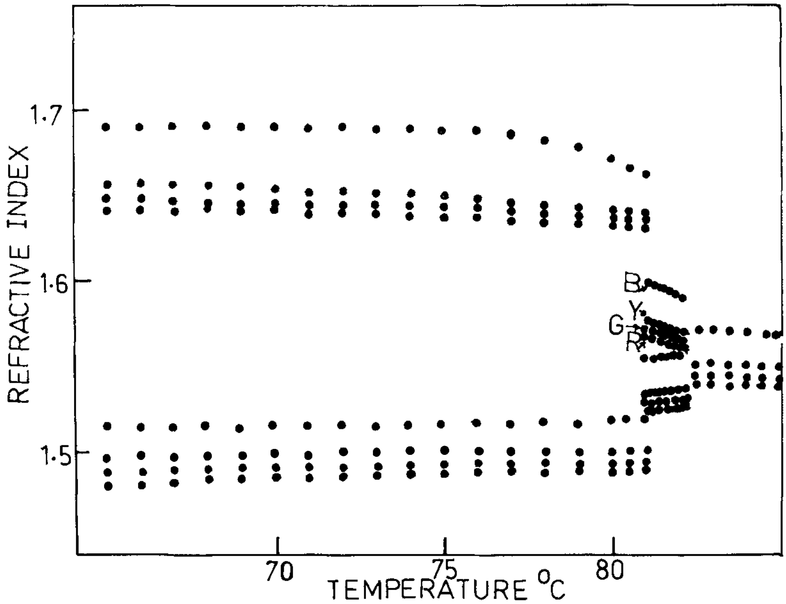


FIGURE 3 Temperature dependence of refractive indices in nematic smectic A and smectic B phases of 60.8.

in the range of critical value reported differentiating the first and second order transitions. The value of this parameter slightly differs from the values reported for the systems 4-n-pentylbenzenethio- 4-alkoxybenzoate ($\bar{n}$S5)[15,16] and alkylcyanobiphenyl (nCB)[16,17] where the tricritical point occurs when $n = 10$, and $n = 9$ with $T_{NA}/T_{NI} = 0.986$ and 0.994 respectively. However, this is in agreement with the reported value for 70.7 which also exhibits a first-order N − S_A transitions.[4] The pressure dependence of transition temperatures estimated from the volume and enthalpy data is presented in Table I along with the data at this transition from different methods in this homologous series. The temperature dependence of refractive indices (Figure 3) and birefringence clearly supports the first order nematic—smectic A transition. The jump in birefringence at this transition is more than the absolute value of birefringence in the nematic phase. Further the coexistence of nematic—smectic A phases was inferred by the observation of refracting rays characteristic of both nematic and smectic A phases. The crystalline smectic B—smectic A transition was inferred by the observation of transition bars across the fans at the S_A-S_B transition followed by fans with a reduced number of discontinuities.[18] The density jump across this transition is ($\Delta\ \rho/\rho$

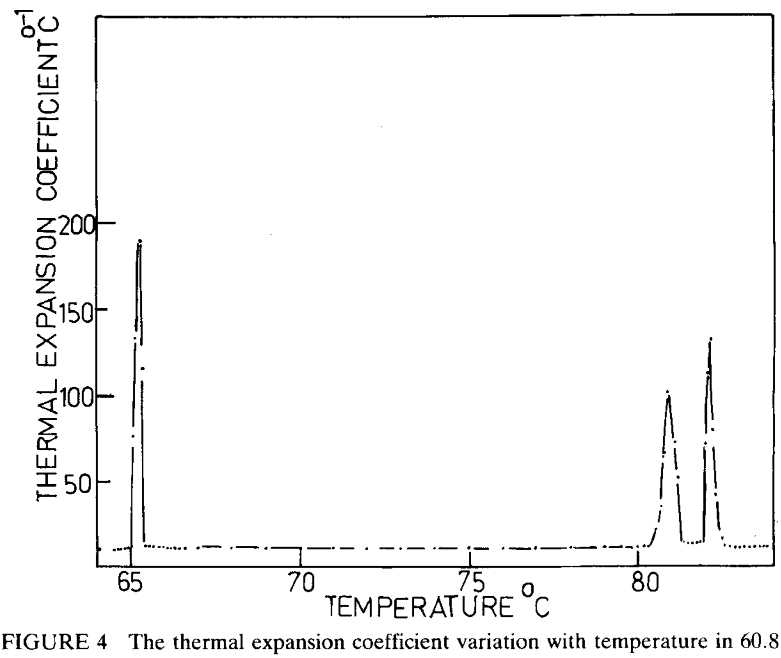


FIGURE 4 The thermal expansion coefficient variation with temperature in 60.8.

TABLE I

Pressure dependence of nematic—smectic A transition temperatures

Name of the compound	Abbreviation	Nature of data	$\Delta T_t/\Delta P$ K/k.bar	T_{NA}/T_{NI}	References
N(p-n-hexyloxy benzylidene) p-n-butyl aniline	60.4	volume-enthalpy	19.7	0.976	8
N(p-n-heptyloxy benzylidene)p-n-butyl aniline	70.4	volume-enthalpy	21.9	0.994	10
N(p-n-heptyloxy benzylidene) p-n-pentyl aniline	70.5	volume-enthalpy	21.9	0.989	12
N(p-n-pentyloxy benzylidene) p-n-octyl aniline	50.8	volume-enthalpy	11.6	0.977	2
N(p-n-butyloxy benzylidene) p-n-octyl aniline	40.8	P-T	17.1	0.958	13
N(p-n-hexyloxy benzylidene) p-n-octyl aniline	60.8	present work	31.8	0.997	—

= 0.51%) is smaller than the jumps in 50.8 (0.79%) and 50.10 (0.76%) while it is greater than the jumps in 80.8 (0.24%)[19] and 80.4 (0.4%).[15,20] The large density increase between the smectic A and crystalline smectic B phase does not however correspond to a step function instead an almost linear behaviour with a finite slope is observed. This indicates the existence of an impurity broadened two phase region between 65.1°C and 65.4°C. The broadening can be explained as being due to two phase coexistence which occurs commonly[7,21] and does not require pretransitional effects. Moreover the transition from disordered molecular arrangement inside the layers of smectic A to the ordering in smectic B might be the origin of the two phase coexistence. Although it is conceivable that impurities can convert an otherwise second order transition into first order transition there is absolutely no reason to believe that this effect is occuring here. For example the complete absence of pretransitional phenomena expected for second order transition weighs heavily against such hypothesis. The pressure dependence of transition temperature from volume—enthalpy data is 25.8 K/k bar. The inference from the ultrasonic velocity variation with temperature by a dip, which is rather broad at the transition temperature also supports the density results. In refractive indices measurements the optical rays were rather blurred in the transition region. However after the transition the extraordinary and ordinary rays were observed in the smectic B phase.

Acknowledgments

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