Smectic C to Nematic Phase Transition Studies in NOBA

N. V. S. Rao* and V. G. K. M. Pisipati**

Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar, India

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The variation of density ϱ with temperature of p-n-nonyloxy benzoic acid in its isotropic, nematic and smectic-C phases is presented. The density jumps and the computed thermal expansion coefficient maxima suggest the order of the $N-S_C$ and $N-I$ transitions to be first order. The pressure dependence of the transition temperatures as computed from the Clausius-Clapeyron equation and the presence of pretransitional effects at the $N-S_C$ and $N-I$ transitions in the nematic phase are discussed.

Smectic-C (S_C) phases are very similar to smectic-A (S_A) phases as to translational and orientational order, but the molecules in S_C are tilted with respect to the layers while they are not in S_A. Chistyakov et al. [1] reported that the smectic phase of p-n-nonyloxy benzoic acid (NOBA) is S_C. However, S_C phases of different compounds can be different [2]. The major characteristics [3] which differ from one compound to another are the tilt angle and its temperature dependence, and the next mesomorphic phase on heating. NOBA belongs to one such category [3] which possesses a large but temperature independent tilt angle ~ 55° followed by a nematic phase.

Even though the nematic-smectic-C ($N-S_C$) transition is analogous to the nematic-smectic-A ($N-S_A$) transition, which was studied in considerable detail, the available information on the $N-S_C$ transition is scarce [4] and hence any information about the order of the $N-S_C$ transition, the pretranslational effects etc. will be welcome. We present here the density variation with temperature in the isotropic (I), the nematic (N) and the S_C phases of NOBA.

The density was measured using a bicapillary pyknometer [5]. The absolute error in density was ± 0.1 kg m^{-3}. The temperature control was $\pm 0.05\,°C$ for a length of time ranging from half an hour to two hours. The maximum permitted heating or cooling rate is 4 °C per hour. The cooling rate in the present experiment was 0.5 °C per hour.

The variation of the density with temperature is illustrated in Fig. 1 and that of the thermal expansion coefficient, $\alpha = d \ln V_m / dT$ with V_m = molar volume in Figure 2. The density jumps across the S_C-N and $N-I$ transitions are presented in Table 1.

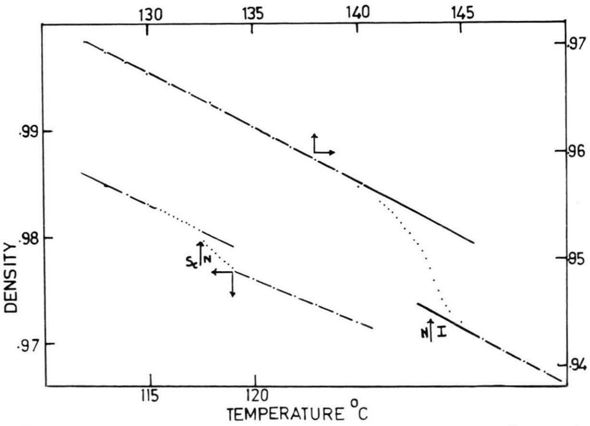

Fig. 1. Temperature variation of density, ϱ, in kg m$^{-3} \times 10^{-3}$ in smectic-C, nematic and isotropic phases.

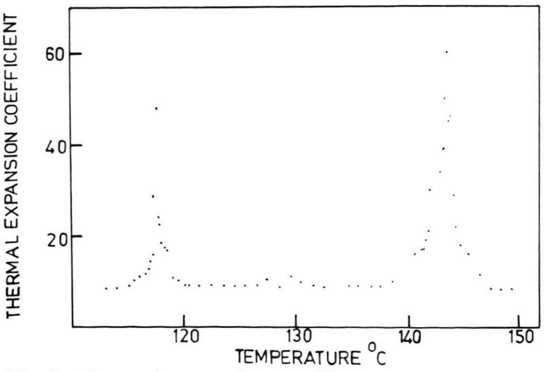

Fig. 2. Thermal expansion coefficient, α, as a function of temperature in the smectic-C, nematic and isotropic phases.

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* Department of Chemistry.

** Department of Physics.

Reprint requests to Dr. N. V. S. Rao, Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar-522510, Indien.

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Table 1. The density jumps, heats of transition and pressure dependences of the transition temperature from the Clausius-Clapeyron equation for the S_C-N and $N-I$ transitions of NOBA.

	$\Delta\varrho/\varrho$	ΔH kcal/mole [6]	dT_t/dP K/kbar	dT_t/dP K/kbar [7]
Smectic-C to nematic	0.23	0.4	13.5	23.9
Nematic to isotropic	0.88	0.6	37.8	27.3

The pressure dependences of the S_C-N and $N-I$ transition temperatures are estimated using the Clausius-Clapeyron equation

$$(dT_t/dP) = T_t(\Delta V/\Delta H), \tag{1}$$

where T_t is the transition temperature, P the pressure, ΔV the volume change associated with the transition and ΔH the heat of transition. The computed (dT_t/dP) values from our ΔV values and heats of transitions taken from [6], along with reported data [7], are presented in Table 1. The (dT/dP) value of 13.5 K/kbar obtained for the S_C-N transition of NOBA is in good agreement with the values obtained for this transition in various compounds (12 K/kbar from pressure studies [8] and 14.8 K/kbar from volumetric studies [9] on p,p′-di-n-heptyloxy azoxy benzene, which exhibits S_C with temperature independent tilt angle and nematic mesophases, 17.8 K/kbar from pressure studies for $\overline{7}S5$ [10]). However the present value is in disagreement with the value 23.9 K/kbar from pressure studies on NOBA [7]. We believe that the discrepancy must arise from the following reasons: a) Prolonged time taken to carry out the density measurements, b) different purities of the sample for which ΔH was taken [7] and our sample. Chou and Carr [11], from conductivity and dielectric measurements, found that NOBA changes its conductivity anisotropy from positive to negative after heating for 2−3 hours. The change in conductivity anisotropy has been attributed to the purity of the sample. The jump in density at the transition, $\Delta\varrho/\varrho$, is 0.23%. The results obtained after 24 hours heating were in quantitative agreement with the results from the first run. However a shift in transition temperature by 0.2 °C after repeated heatings was observed.

The value of 37.8 K/kbar for the $N-I$ transition from our density measurements is larger than the value of 27 K/kbar obtained from the pressure-transition temperature studies.

The smectic-C phase should be described by three order parameters, viz. the translational order parameter, the orientational order parameter and the tilt angle [12]. Pretransitional effects are found to be present in the vicinity of the $N-S_C$ and $N-I$ transitions in the nematic phase. This may be due to the generation of dimeric structures to form cybotactic groups in attaining an equilibrium below the $N-I$ transition. The same phenomena of development of translational order and tilt angle in the S_C phase at the $N-S_C$ transition, when the nematic transforms into the S_C phase can explain the pretransitional behaviour. Pretransitional effects are also reported by Chou and Carr [11].

The maxima in the thermal expansion coefficient computed from the density results, which are displayed in Fig. 2, support the transition to be first order. It should be stressed that our data are not consistent with a logarithmic singularity. Indeed, these data have been fitted to a simple power-law form given by

$$\alpha = A t^{-X} + B \quad \text{for} \quad T > T'_{NC},$$

$$\alpha = A' t^{-X'} + B' \quad \text{for} \quad T < T_{NC}$$

with T_{NC} fixed at T_m, the temperature of the maximum thermal expansion coefficient α. For $T > T_{NC}$, $x = 0.00011$, $A = 3.49$, $B = -3.49$ and for $T < T_{NC}$, $x' = 0.00007$, $A' = 3.49$, $B' = -3.49$ are obtained.

The density jump across the nematic-isotropic transition is $\Delta\varrho/\varrho = 0.88\%$ for NOBA. This is a fairly high value when compared to the values observed for $N-I$ transitions in most other compounds [13, 14]. However, high values, $\Delta V_K/V_{n,K} = 0.73\%$ for 4-methoxy cinnamic acid [13], $\Delta\varrho/\varrho = 1.28\%$ for p-n-octyloxy benzoic acid [15] and $\Delta\varrho/\varrho = 0.97\%$ for p-n-heptyloxy benzoic acid [15], seem support the idea that higher density jumps occur in aromatic carboxylic acids exhibiting nematic phases, and these exhibit intermolecular hydrogen-bonding to form the monomer-dimer equilibrium in these acids. Yakhmi et al. [16] also observed higher order in the nematic phase of the two lower homologues, i.e. p-n-butoxy and p-n-amyloxy benzoic acids.

They predicted higher order parameters in nematic phase and also higher transition energies at the N–I transition temperatures for all the p-n-alkoxy benzoic acids. Our reults support the idea that hydrogen bonding and the resulting monomer-dimer equilibrium plays an important role in these compounds. The maxima of the thermal expansion coefficient and the density jump support a first order N–I transition in this compound.

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