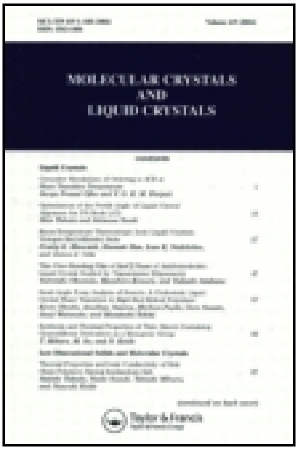

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Physical Properties of the Mesophases of 4-n-HeptyloxyBenzylidene-4′-AminoAzo Benzene (HBAAB)B

Adhikari [a] , R. A. Vora [b] & R. Paul [a]

[a] Department of Physics, University of North Bengal, Siliguri, West Bengal, 734430, India

[b] Department of Applied Chemistry, Faculty of Technology and Engineering, M.S. University of Baroda, Vadodara, India

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Physical Properties of the Mesophases of 4-*n*-HeptyloxyBenzylidene-4′-AminoAzoBenzene (HBAAB)

B. ADHIKARI$^+$, R. A. VORA* and R. PAUL$^+$

$^+$*Department of Physics, University of North Bengal, Siliguri, West Bengal-734430, India*
**Department of Applied Chemistry, Faculty of Technology and Engineering, M.S. University of Baroda, Vadodara, India*

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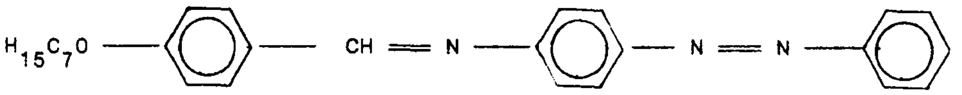
4-*n*-HeptyloxyBenzylidene -4′-AminoAzoBenzene (HBAAB) has nematic, smectic A, smectic B and three crystalline phases. X-ray diffraction studies of the aligned mesomorphic phases have been carried out to calculate orientational order parameters ($\langle P_2 \rangle$ and $\langle P_4 \rangle$), transverse correlation length (ξ), translational order parameter (τ) and layer thickness in the smectic phases or apparent molecular length in the nematic phase and intermolecular distance as function of temperature. Both nematic–smectic A (NA) and smectic A–smectic B (AB) phase transitions are found to be of the first order. The HBAAB molecules remain in the fully extended form throughout the mesomorphic range and the smectic layers are mono molecular. Orientational order parameter values in the nematic and smectic A phases have been fitted satisfactorily with the calculated values from McMillan's theory with $\alpha = 0.45$ and $\delta = 0.595$. Refractive indices (n_0 and n_e) have been measured in the nematic phase and $\langle P_2 \rangle$ calculated using Neugebauer's formula. These $\langle P_2 \rangle$ values agree within experimental uncertainties with those obtained from x-ray studies. Experimental enthalpy changes, obtained from DSC studies, have been compared with those calculated from McMillan's theory. While agreement between experimental and calculated enthalpy change at Sm $A - N$ transition is quite good, the experimental enthalpy change at $N - I$ transition is much smallar than the theoretical value. The density measurements also show a very small density change at the $N - I$ transition, making it weakly first order.

Keywords: Order parameters, x-ray diffraction, phase transition, correlation length.

1. INTRODUCTION

Study of the mesomorphic properties of liquid crystals is important both from the point of view of applicability of the liquid crystalline compound in display devices and in the study of the nature of phase transitions in condensed matter systems. In this regard x-ray diffraction studies provide a powerful tool to deduce structural informations. In the present work we have undertaken small angle x-ray diffraction study of the richly polymorphic mesogen 4-*n*-heptyloxybenzylidene-4′-aminoazobenzene (HBAAB)[1], having the structural formula shown overleaf.

HBAAB has nematic, smectic A, smectic B and several crystalline phases. Results of our x-ray diffraction experiment on magnetically aligned samples of HBAAB have



been analysed to determine the structural and orientational order parameters (OOP) throughout the mesomorphic range. Translational order parameter (τ) in the smectic phases of this compound has been determined from second order reflections in the meridional direction. Refractive index measurements for HBAAB have also been carried out by us in the nematic phase only and the OOP values determined therefrom have been compared with those obtained from x-ray diffraction studies. The experimentally determined order parameters have been fitted to McMillan's theory for the smectic A phase[2,3]. Density and DSC studies of isotropic – nematic (NI), nematic–smectic A (NA) and smectic A – smectic B (AB) phase transitions have also been carried out and results discussed.

2. EXPERIMENTAL

The synthesis and DSC study of HBAAB took place at the Department of Applied Chemistry, M. S. University of Baroda and all other experimental work was conducted at the Department of Physics, University of North Bengal. An examination of this compound by optical microscopy and differential scanning calorimetry has led to the following phase behaviour:

$$\begin{tikzcd}
\text{Cryst. 1} \arrow[r, "107\,^\circ\text{C}"] & \text{Sm B} \arrow[r, leftrightarrow, "125\,^\circ\text{C}"] \arrow[d, "89\,^\circ\text{C}"] & \text{Sm A} \arrow[r, leftrightarrow, "150.5\,^\circ\text{C}"] & \text{N} \arrow[r, leftrightarrow, "167.5\,^\circ\text{C}"] & \text{I} \\
\text{Cryst. 3} \arrow[u, "55\,^\circ\text{C}"'] & \text{Cryst. 2} \arrow[l, "73\,^\circ\text{C}"']
\end{tikzcd}$$

Texture study of this compound were done under a polarising microscope equipped with Mettler FP80/82 Thermosystem. The compound on cooling from the isotropic phase showed a marbled texture, often found in the nematic phase. Below the nematic phase a simple fan-shaped texture, typical of the smetic A phase was observed. On further cooling smectic A to smectic B phase transition took place, marked by the occurrence of small transition bars which gradually gave way to the smectic B mosaic texture with strong paramorphic boundaries[4]. On further cooling no flow could be observed in the sample, indicating that the compound has gone to the crystalline phase. From x-ray diffraction studies three different types of solid phases could be identified in the low temperature range. However, we have not tried to characterise the solid phases in this paper.

The experimental set up and the procedure for order parameter determination from x-ray diffraction[5] and refractive index[6] studies have been described in detail in our earlier publications. The x-ray diffraction patterns were recorded photographically on a flat plate camera using nickel filtered Cu K_α radiation of mean wavelength $\lambda = 1.5418\,\text{Å}$. Samples were aligned using a magnetic field of about 3 Kilogauss for x-ray diffraction experiment. To obtain better accuracy in the measurement of layer thickness, x-ray diffraction photographs of inner spots were taken with sample to film distance increased to about 9 cm. The x-ray films were scanned linearly and circularly by using a Zeiss micro-densitometer (model MD 100) and the optical density values were converted to x-ray intensity data following a standard procedure[7]. The outer rings of the x-ray diffraction photographs in the smectic B phase being very sharp, we scanned the film linearly at first and from these readings the values of x-ray intensities along the circular arc were calculated. Refractive indices were measured by a thin hollow prism method, sample being surface aligned by rubbing. Due to absorption of the extraordinary beam in the smectic phases of this compound, it has not been possible to measure the extraordinary refractive index (n_e) in those phases. The ordinary refractive index (n_0) could be measured throughout the mesomorphic range.

3. RESULTS AND DISCUSSION

Orientational order parameters (OOP) $\langle P_2 \rangle$ and $\langle P_4 \rangle$, as obtained from our x-ray data, have been plotted as function of temperature for HBAAB in Figure 1. It is seen from Figure 1 that the nematic-smectic A phase transition is of the first order, since the values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ change abruptly in passing from the nematic to the smectic A phase. Figure 2 shows the x-ray diffraction photograph of a monodomain sample in the smectic B phase at 123 °C, with the incident x-ray beam parallel to the smectic layers. The resultant x-ray diffraction photograph shows the presence of elongated bars of relatively intense diffuse scattering on both sides of the equatorial maxima. The widths of these bars are quite sharp. The smectic A–smectic B transition is also marked by sharp discontinuities in the order parameter values indicating first order phase transition. The OOP values in the nematic and smectic A phase of HBAAB show significant temperature dependence, while the order parameter values in the smectic B phase of this compound are found to be almost independent of temperature. The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values within the smectic B phase are also relatively higher than the neighbouring smectic A phase. This seems to indicate that the smectic B phase of this compound is of the crystal B type[8] unlike the hexatic B phase which undergoes a second order hexatic-B to smectic A phase transition[9]. It may be mentioned that although the approximation[10] used for calculating $\langle P_2 \rangle$ and $\langle P_4 \rangle$ is not valid for $\langle P_2 \rangle \gtrsim 0.8$, we are still reporting these order parameter values due to scarcity of available data on smetic B phase in the literature. These values at least give an estimation of the degree of order of a liquid crystal within the smectic B phase.

We tried to fit the experimental order parameter values for HBAAB to those calculated from McMillan's theory for smectic A phase[2,3], using the potential parameters $\alpha(=0.45)$ and $\delta(=0.595)$ as adjustable constants and the theoretical curves

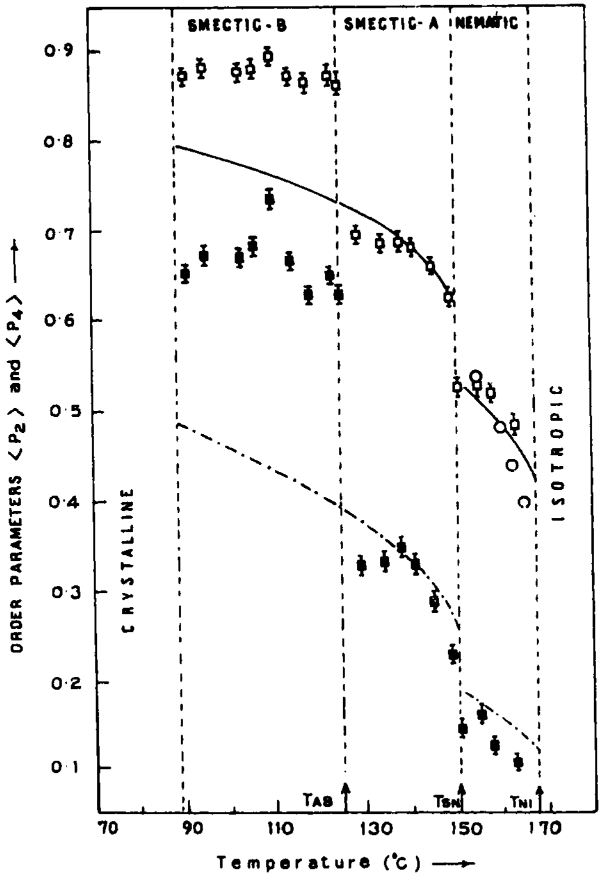


FIGURE 1 Temperature dependences of $\langle P_2\rangle$ and $\langle P_4\rangle$ for HBAAB. Key to symbols: (□) x-ray data for $\langle P_2\rangle$; (■) *x*-ray data for $\langle P_4\rangle$; (○) refractive index data for $\langle P_2\rangle$; Solid line is theoretical $\langle P_2\rangle$ from McMillan's potential with $\alpha = 0.45$, $\delta = 0.595$; dashed line is theoretical $\langle P_4\rangle$ from McMillan's potential. T_{NI} = nematic-isotropic transition temperature; T_{SN} = smectic A-nematic transition temperature; T_{AB} = smectic A-smectic B transition temperature. Vertical bars show estimated errors.

are shown in Figure 1. The agreement of the experimental $\langle P_2\rangle$ and $\langle P_4\rangle$ values with the theoretical values is fairly good in the nematic and smectic A phases of HBAAB. The order of the nematic–smectic A phase transition as obtained experimentally is also reproduced from the theoretical calculations. However, agreement between the experimental order parameter values and those calculated from McMillan's theory in the smectic B phase is poor for the obvious reason that McMillan's theory is not applicable to smectic B phase.

We have also determined the translational order parameter (τ) for HBAAB, in the smectic phases from our experimental data where the second order meridional reflections were present, using a procedure described by Leadbetter and Norris[10]. These are compared with the values obtained from McMillan's theory in Figure 3.

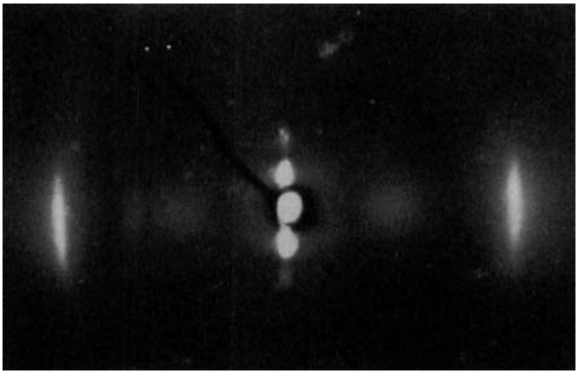


FIGURE 2 X-ray diffraction photograph of the oriented sample in the smectic B phase of HBAAB at 123°C.

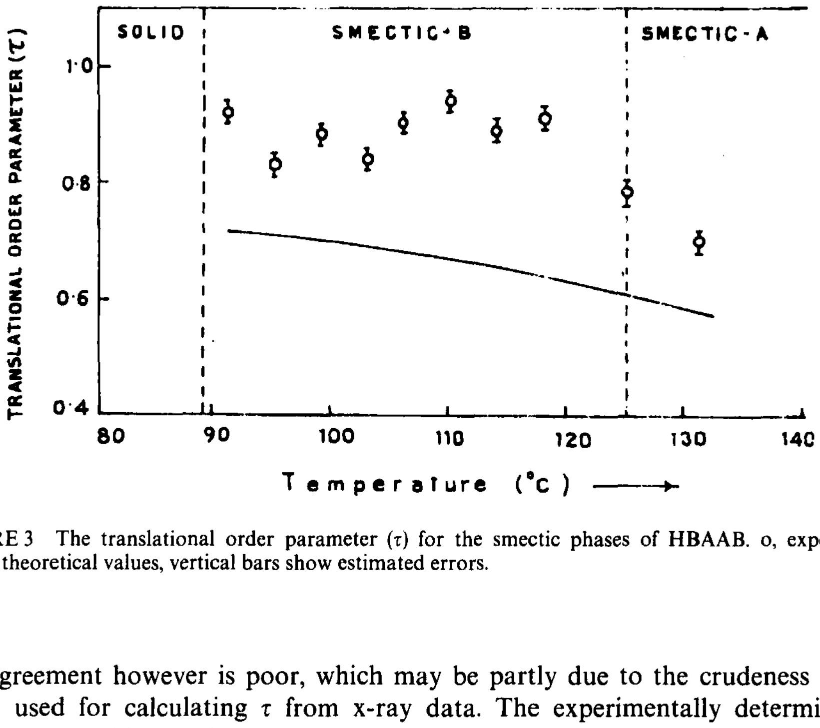


FIGURE 3 The translational order parameter (τ) for the smectic phases of HBAAB. o, experimental;——, theoretical values, vertical bars show estimated errors.

The agreement however is poor, which may be partly due to the crudeness of the model used for calculating τ from x-ray data. The experimentally determined τ values are very high in the smectic B phase which is as expected.

The transverse correlation length, ξ, has been determined from linear scan of the diffraction peaks along the equatorial direction in the nematic and the smectic A phase of HBAAB. The x-ray intensity profile, which was first corrected for the use of a flat film, was next deconvoluted for finite width of the collimator based on a method of substitution of successive foldings[11]. The deconvoluted intensity profile

$I(q)$ was fitted to a lorentzian form with a quadratic background viz,

$$I(q) = \frac{a_1}{a_2 + (q - q_0)^2} + a_3 q^2 + a_4 q + a_5, \tag{1}$$

q being the magnitude of the scattering vector. a_1, a_2, a_3, a_4, a_5, and q_0, are the fitting parameters. The correlation length is defined as $\xi = 2\pi(a_2)^{-1/2}$. Figure 4 shows the temperature variation of ξ in the smectic A and nematic phase of HBAAB. The same procedure in the smectic B phase could not be carried out since the corrected intensity profile almost exactly matched the primary beam profile, implying very large value value of ξ. It seems from Figure 4 that the correlation length varies continuously across the nematic–smectic A transition and does not diverge as in a second order phase transition. The rapid increase in ξ in the nematic phase near the smectic A–nematic transition is due to smectic fluctuations.

Figure 5 shows the density variation of HBAAB in the temperature range 90 °C to 174 °C. Also shown in the same figure is the birefringence $\Delta n (= n_e - n_0)$ at wavelength $\lambda = 5780$ Å, in the nematic phase only of HBAAB. From the temperature variation of density it is seen that there are discontiniuties in the density values at

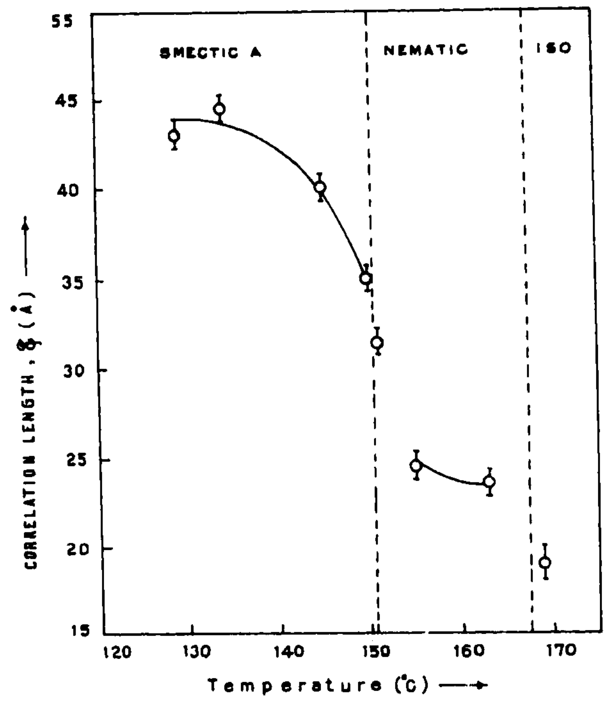


FIGURE 4 Variation of transverse correlation length ξ with temperature in the nematic and smectic A phases of HBAAB. Vertical bars show estimated errors. Solid line is guide to the eye only.

the nematic–smectic A and smectic A–smectic B transition temperatures implying first order phase transitions in both the cases.

Orientational order parameter values obtained on analysing the refractive index and density data, as a function of temperature (in the nematic phase) using Neugebauer's procedure[12] are also shown in Figure 1. It is seen from Figure 1 that there is a rapid decrease in the order parameter values obtained from refractive index measurements close to the nematic – isotropic transition temperature T_c. This may be due to the fluctuation of the director, which is more pronounced near the transition temperature[13]. The order parameter values obtained from x-ray diffraction and refractive index studies agree quite well within experimental uncertainties.

Results for the temperature dependence of the apparent molecular length i.e., density wave parallel to the director in nematic phase (l) and layer thickness in smectic phase (*d*) are given in Figure 6. It is seen that the layer thickness in the smectic phases and the apparent molecular length in the nematic phase are almost equal and temperature independent. The mean value of *d* or l is (26.15 ± 0.12)Å which is in close agreement with the molecular model length of 26.45Å, (in the completely extended form), indicating absence of molecular associations throughout

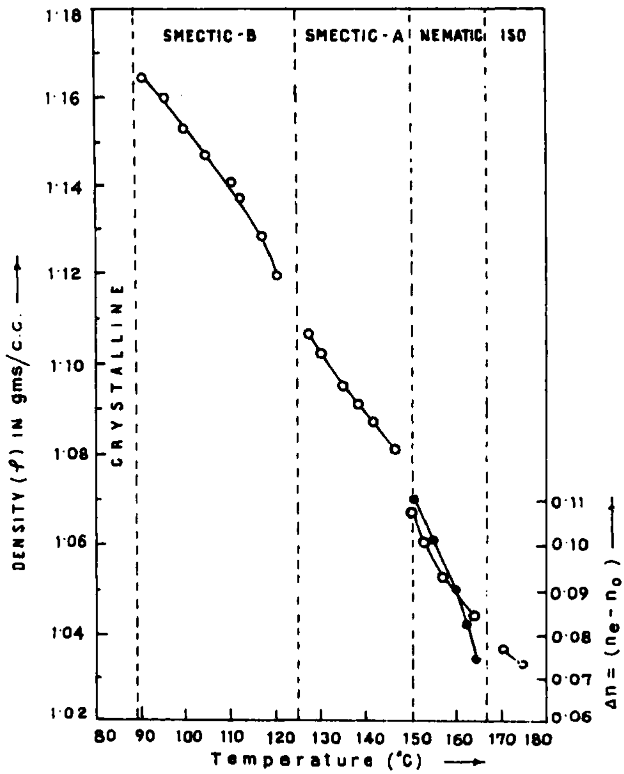


FIGURE 5 The density and birefringence (Δn, in the nematic phase) values of HBAAB as functions of temperature; ○ density values; ● birefringence values. Lines drawn are guide to the eye only.

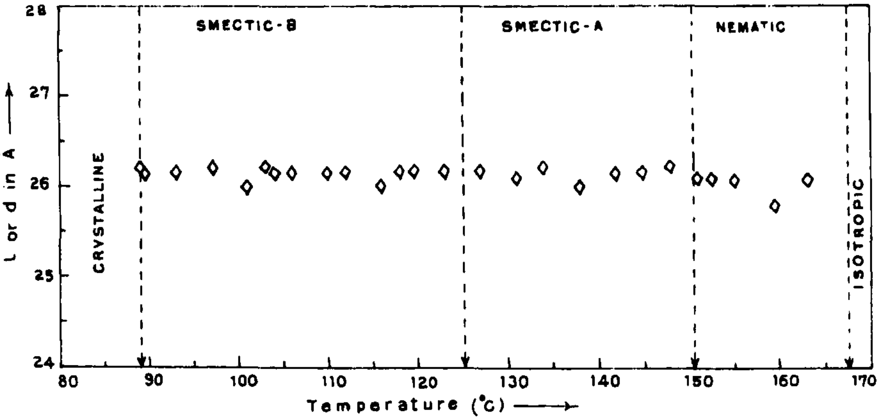


FIGURE 6 Variation of layer spacing (*d*) or apparent molecular length (*l*) with temperature. Estimated error is ± 0.15Å throughout the measured range.

the mesomorphic range of HBAAB. This also implies that the molecules are in completely extended form in the mesophases inspite of the presence of rather long and flexible heptyl chain. In Figure 7 we have plotted the variation of the intermolecular distance, D, with temperature for HBAAB. The D values are found to increase with increasing temperatures, accompanied by abrupt jumps at the smectic B-smectic A and smectic A-nematic transition temperatures again indicating the order of the transition in these to be first order. The D values in the nematic phase are found to increase with increasing temperatures which is probably due to increased thermal vibrations.

Figure 8 shows the DSC curve for HBAAB during cooling, and the enthalpy changes at the isotropic-nematic, nematic-smectic A and smectic A-smectic B phase transitions are listed in Table I. We have calculated ΔH_{SN}, the enthalpy change at the smectic A-nematic transition temperature (T_{SN}), from McMillan's theory taking the values of α and δ from the best fit theoretical curve to the experimental x-ray $\langle P_2 \rangle$ data (refer Figure 1). ΔH_{SN} is calculated from the following expression

$$\Delta H_{SN} = \frac{1}{2T^*_{SN}} [(\eta_S^2 - \eta_N^2) + \alpha\delta\tau^2 + \alpha\sigma^2)]\, NKT_{SN} \qquad (2)$$

where $T^*_{SN} = kT_{SN}/v \cdot \tau$, σ and η_S, the order parameter in the smetic A phase, is calculated at a temperature just below the smectic A-nematic transition temperature; while η_N, the order parameter in the nematic phase, is calculated at a temperature just above the transition temperature. It is clear from Table I, that the behaviour of ΔH_{SN} at the NA transition is reproduced by the theory quite well. Following similar procedure we have calculated the enthalpy change at the nematic -isotropic phase transition as well. The experimental enthalpy change for nematic -isotropic phase transition is much smaller than the calculated value as seen in Table I. It seems that

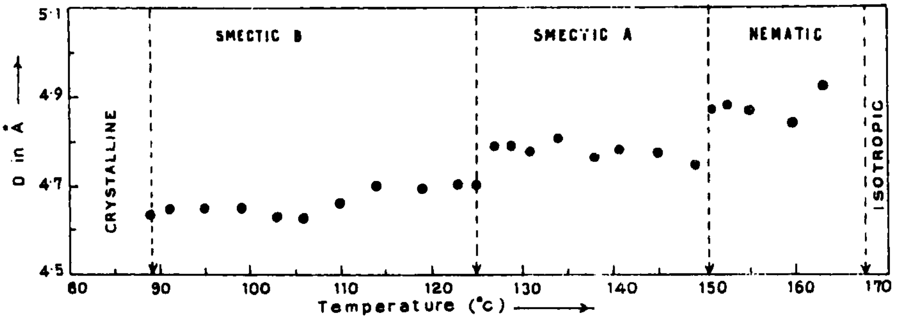


FIGURE 7 Variation of intermolecular distance D with temperature. Estimated errors are smaller than the size of the symbols used.

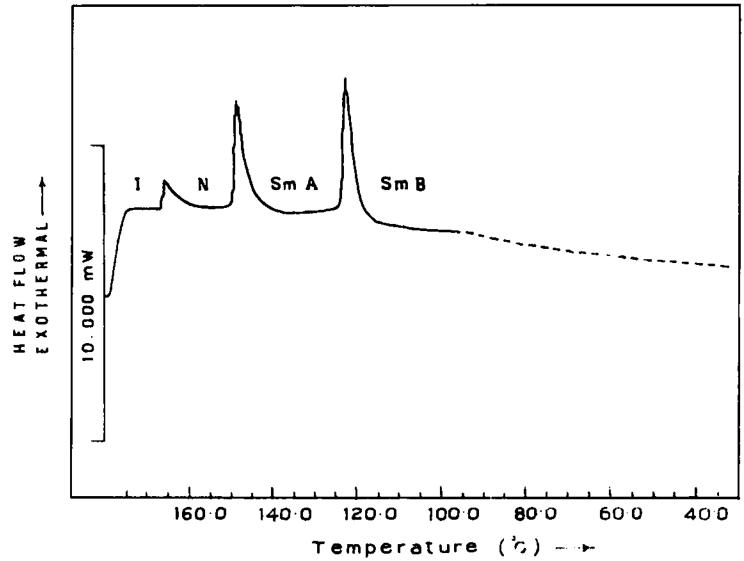


FIGURE 8 The DSC scan of HBAAB during cooling. I denotes isotropic phase, *N* denotes nematic phase, Sm A denotes smectic A phase and Sm B denotes smectic B phase.

TABLE I

Enthalpy change associated with different phase transition of HBAAB

Temp. in °C	ΔH(J/G) Experimental	ΔH(J/G) Calculated
125.0	2.223	–
150.5	3.557	3.040
167.5	0.857	3.912

entropy change at the smectic A – nematic transition is much greater than that at the nematic – isotropic transition. This is also evident from Figure 5 which shows that the density change at nematic – isotropic transition is very small making the transition weakly first order. Such behaviour regarding smectic A-nematic and nematic-isotropic phase changes in a liquid crystalline mixture has also been reported[14]. No calculations of smectic B to smectic A enthalpy change is possible due to unavailability of suitable model theory for this phase transition.

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