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# Smectic C-to-Nematic Transition in *p*-*n*-Heptyloxybenzylidene-*p*-amino-benzoic Acid

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The results on the phase transitions in *p*-*n*-heptyloxybenzylidene-*p*-aminobenzoic acid are reported. The microscopic and X-ray studies show that the compound goes over from smectic C to nematic phase directly. The transition entropies and specific heat are determined using differential scanning calorimetry. The translational order parameter is determined using low angle X-ray intensity measurements. The tilt angle in smectic C phase is found to be 56° and is independent of temperature. The X-ray data also lead to the conclusion that the compound exists as a dimer.

## I INTRODUCTION

The preparation details of the *p*-*n*-alkoxybenzylidene-*p*-aminobenzoic acid series have been given by Dave and Patel.[1] They have also reported the transition temperatures of various phases. Recently, we undertook a study of the thermodynamic parameters of this series and reported the transition enthalpy and transition entropy data.[2] An attempt was made to systematize these results by using McMillan's theory.[3] In this paper, we present a detailed study of *p*-*n*-heptyloxybenzylidene-*p*-aminobenzoic acid ($H_p$BABA) with special emphasis on the Smectic C (SmC) → Nematic (N) transition shown by this compound. The phases were characterized by making the texture studies with a polarising microscope. The absolute specific heat data from 465 K to 496 K has been obtained using a differential scanning calorimeter (D.S.C.). X-ray diffraction studies on $H_p$BABA we made from room temperature up to 495 K mainly to determine the structural parameters of the SmC phase. The temperature dependence of the translational order parameter ($\sigma$) was obtained from X-ray intensity measurements. The temperature dependence of both $C_v$ (specific heat) and $\sigma$ were independently calculated

using McMillan's theory and were found to be in good agreement with experiment. The existence of dimers in the SmC phase of $H_p$BABA has been proposed on the basis of interpretation of our X-ray data.

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## II EXPERIMENTAL

A Leitz polarising microscope fitted with Leitz 350 hot stage was used to obtain the textures of the compound in temperature range from 300 K to 525 K.

A Perkin–Elmer DSC-1B, differential scanning calorimeter was used to measure the specific heat. The scanning for this purpose was done in three stages over the desired temperature range. First, a sapphire standard alone was scanned, then a blank determination was made without any sample and finally the sample was scanned. At any given temperature both the sample deflection and the sapphire deflection were corrected by adding or subtracting the blank deflection. The specific heat of the sample at that temperature was then calculated by the following expression:

$$\frac{\text{amplitude of deflection (sample)}}{\text{amplitude of deflection (sapphire)}} \times \frac{\text{(weight of sapphire disc)}}{\text{(weight of sample)}} \times \text{(specific heat of sapphire at that temperature)} \quad (1)$$

The weight of the sample used was 3 mg. It was heated at a rate of 8°/min using a sensitivity of 4 millical/sec.

The X-ray studies were made using Ni-filtered Cu–K$\alpha$ radiation ($\lambda = 0.15418$ nm) and a Laue camera. A voltage and current stabilized Philips PW1009 X-ray unit was used with 34 KV operating voltage and a current of 18 mA. The samples were sealed in capillaries of about 1 mm bore and were aligned by heating them to the nematic phase and then cooling them gradually in a magnetic field of $\sim$8kOe applied along the capillary axis. The X-ray pictures of the aligned samples were recorded in the temperature range from 430 K to 490 K. A specially designed heater[4] was used for this purpose, where the temperature was stable up to within 1 K. The temperature of the sample was measured with the help of a chromel-alumel thermocouple. The incident X-ray beam was at right angles to the capillary axis. In order to obtain a clear inner ring in the smectic phase, a ten minutes' exposure was found sufficient, while it was found necessary to give one hour of exposure to obtain the outer ring. In order to determine the translational order parameter ($\sigma$) from the intensity measurements of the inner ring, ten minutes' exposure was given at various temperatures. The intensity of the ring was measured using a densitometer. In addition, one hour exposure at

each temperature was given to obtain both the rings simultaneously in order to determine the tilt angle. The (111), (013) and (002) reflections of anhydrous ammonium sulphate were used to determine accurately the distance between the sample and the film.

## III RESULTS AND DISCUSSION

### A Microscopy

As the temperature was raised, the sample showed (i) the broken fan, (ii) the finger print, and (iii) Schlieren texture patterns, in that order. This confirms[5] that $H_pBABA$ goes over from Smectic C to Nematic directly, as follows:

$$\text{Cryst} \xrightarrow{436 \pm 0.5\,K} \text{SmC} \xrightarrow{477 \pm 0.5\,K} \text{N} \xrightarrow{524 \pm 0.5\,K} \text{I}$$

and not via the smectic A phase. Both heating and cooling runs yielded almost identical values for these transition temperatures indicating that supercooling, if any, was negligible.

### B Differential scanning calorimetry

As reported by us earlier,[2] the D.S.C. scans yielded transition temperature values consistent with microscopy results. The transition enthalpies (in Kcal/mole) for the transitions mentioned above were calculated to be $\Delta H$(Cr-SmC) = 2.58, $\Delta H$(SmC-N) = 0.35 and $\Delta H$(*N*-I) = 1.22, respectively. The specific heat data (Table I) at different temperatures was calculated using the expression (1). The actual DSC run is shown in Figure 1.

TABLE I

Specific heat data in the region of SmC → N transition

| Temperature (K) | Specific heat (cal/deg/gm) | Temperature (K) | Specific heat (cal/deg/gm) |
|---|---|---|---|
| 468 | 0.6092 | 482 | 0.8218 |
| 470 | 0.6241 | 483 | 1.6285 |
| 472 | 0.6252 | 484 | 1.0639 |
| 474 | 0.6471 | 485 | 0.6997 |
| 476 | 0.6482 | 486 | 0.6862 |
| 478 | 0.6493 | 488 | 0.6779 |
| 480 | 0.6597 | 490 | 0.6742 |
| 481 | 0.6695 | 492 | 0.6753 |

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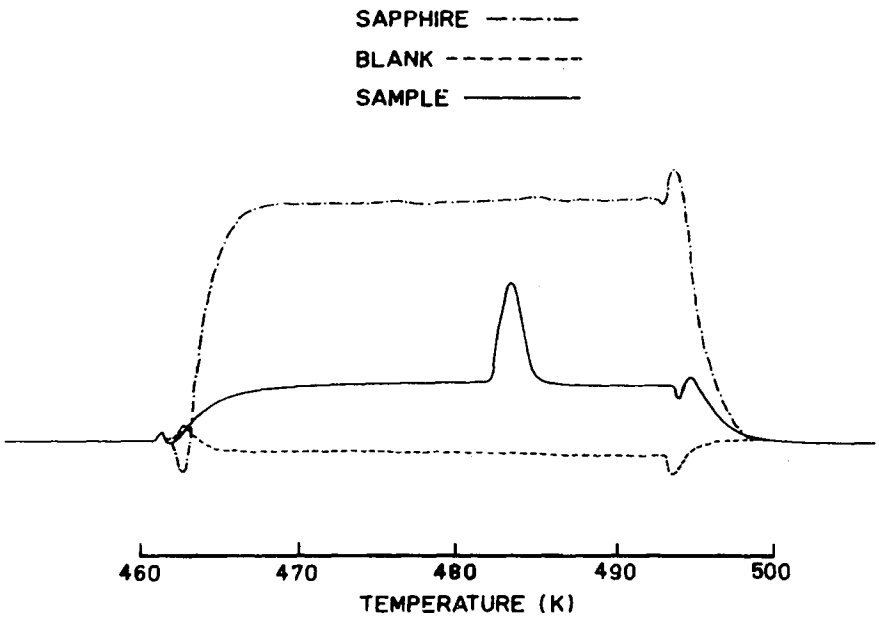


FIGURE 1 Actual DSC scans used in the measurement of absolute specific heat. Sensitivity 4 mCal/sec; heating rate 8°/min.

SmC phase should strictly be described by three order parameters,[6] viz., the translational order parameter ($\sigma$), the orientational order parameter ($\eta$) and the tilt angle ($\theta$). To date, there is no theory available, in literature, which can take into account all the three order parameters simultaneously. In view of the fact that, in general, SmC and SmA phases are not much different energetically as known from theory[7] and DSC experiments,[8] the specific heat data obtained on SmC phase was compared with the prediction of McMillan's theory for SmA, using a value of 0.80 for the McMillan's parameter $\alpha$.[2] In Figure 2, the continuous curve refers to the McMillan's theory whereas the data from Table I, after dividing by $R$ (the gas constant), is denoted by dots.

Exact specific heat behaviour in the region of N → I transition could not be obtained owing to the loss of weight of sample due to evaporation in the isotropic phase.

### C X-ray studies

The X-ray photographs in the SmC phase showed two inner crescents from the diameter of which the interplanar spacing was calculated to be 2.868 nm. As shown in Figure 3, the maxima of the outer ring were found to be tilted

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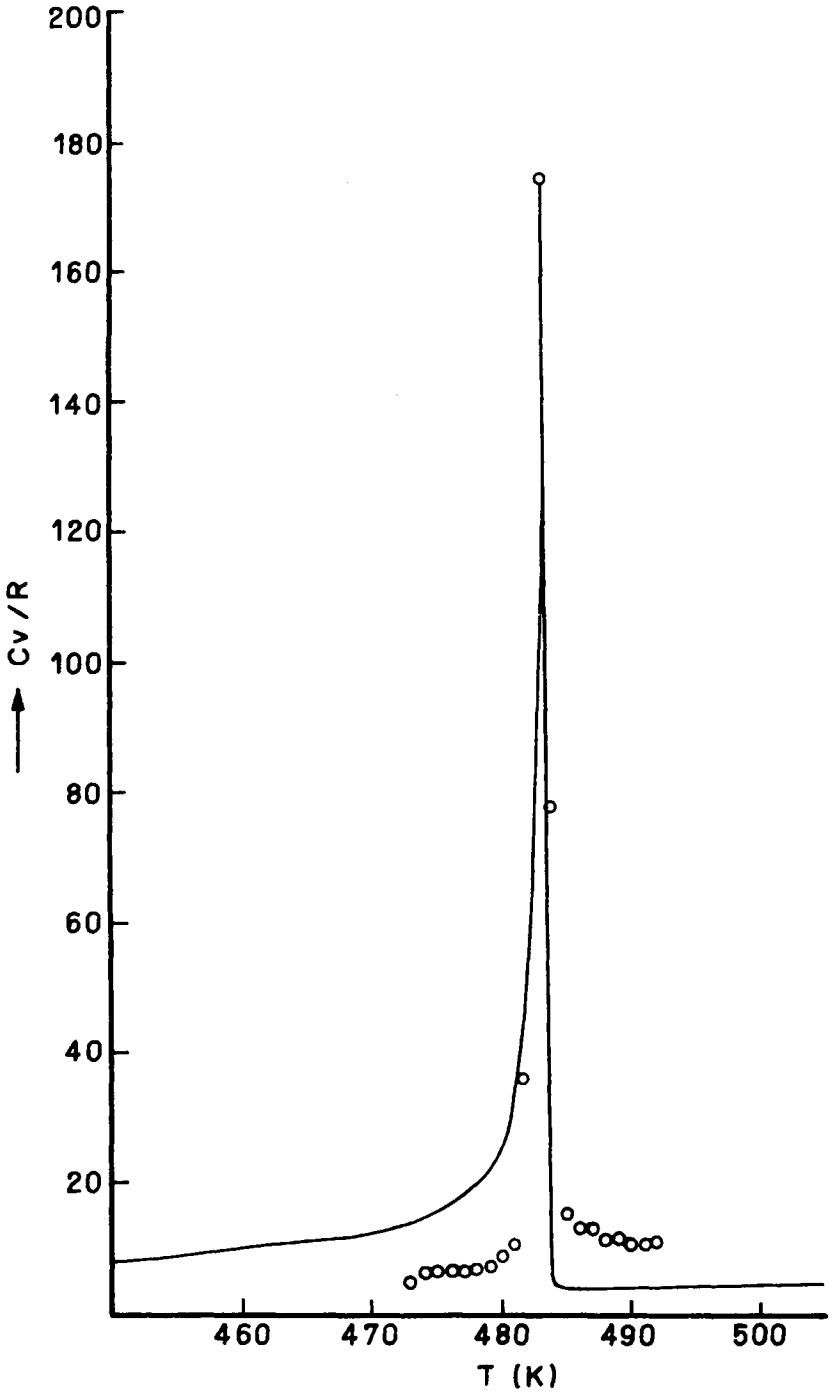


FIGURE 2 Specific heat vs temperature. $R = 1.986$ Cal/deg mole. Circles are the experimental points. The continuous line is the theoretical curve based on McMillan's Theory.

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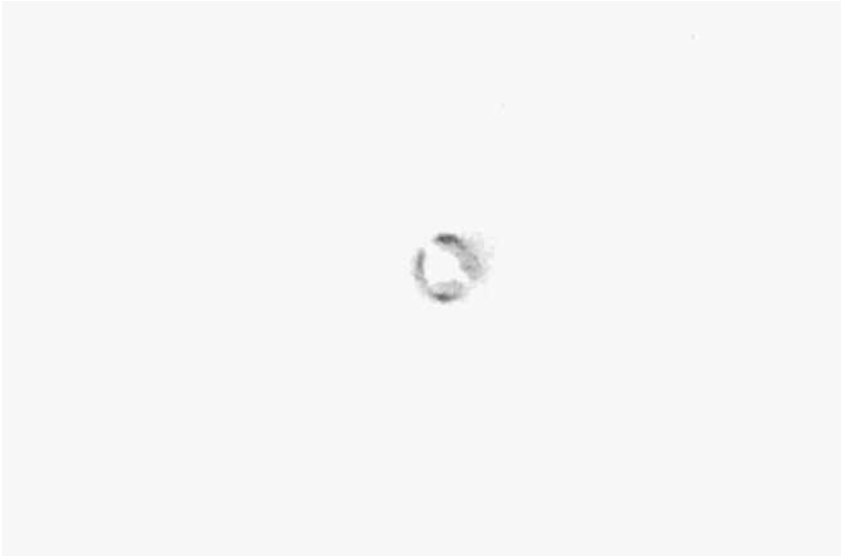

FIGURE 3 The tilt angle ($\theta$) as determined from the inclination of maxima of the outer ring with respect to the maxima of inner crescents.

with respect to the maxima of the inner crescents, from which the tilt angle $\theta$ was estimated to be 56°. From the radius of the outer ring the intermolecular spacing in a smectic plane was calculated to be 0.529 nm. The tilt angle $\theta$ did not vary with temperature, except in the transition region, indicating that the compound goes over from SmC to Nematic directly and not via SmA. In the region of SmC → N transition it was observed that the inner crescents became four spots, as shown in Figure 4, which is characteristic of a SmC phase.[9] A slight increase in temperature ($\sim$1–2 K) yielded only two intense spots which were at right angles to the maxima of outer ring implying thereby that the tilt angle $\theta$ has become zero. This feature is shown separately in Figure 5. The increase in intensity of inner spots was experimentally observed a number of times and is not accidental. Also, it is important to note that there was no change in the diameter of the inner crescents as they became spots.

In accordance with the McMillan's theory the intensity of the inner ring should be proportional to $\sigma^2$.[10] The peak value of the densitometer tracing for the inner crescents was taken to be proportional to the indensity ($I$) at each temperature. A plot of $\sigma$ vs. $T/T_{NI}$ is shown in Figure 6. In this, the continuous curve represents the $\sigma$ calculated using McMillan's theory, whereas the dots relate to experimental data. The latter were determined by normalising $\sqrt{I}$ value with the theoretical $\sigma$ value at 453 K. The observed

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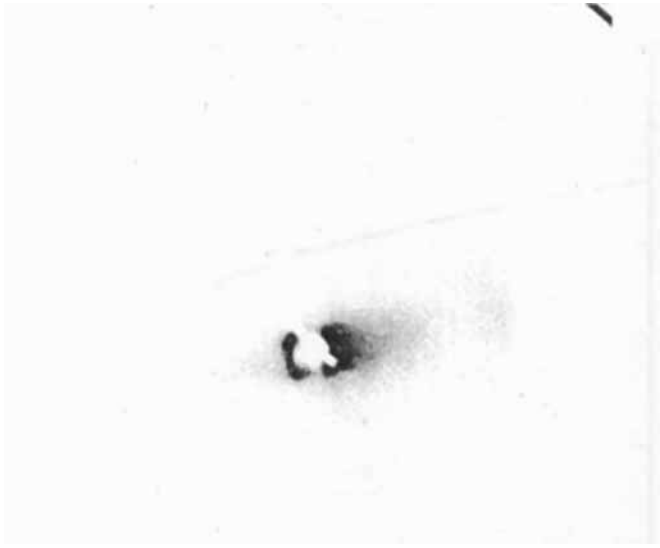

FIGURE 4 Inner ring in the region of the SmC → N transition showing four spots.

FIGURE 5 The rise in intensity of the two inner spots and their change in orientation leading to $\theta = 0$.

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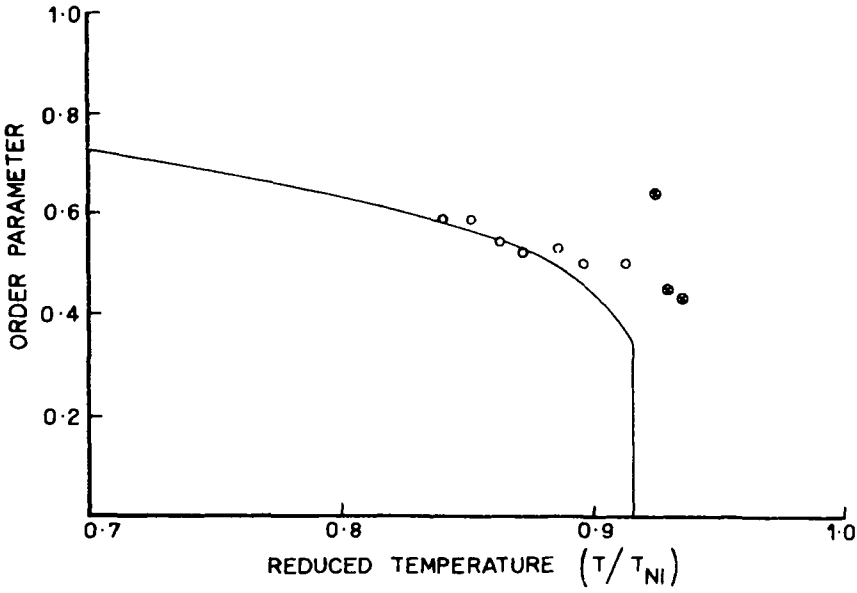


FIGURE 6 Translational order parameter vs reduced temperature. Continuous curve is the theoretical curve based on McMillan's theory. Note the increase in intensity shown by experimental points indicating the pretransition effect.

feature of a sudden increase in the intensity near the transition is separately shown by crosses in Figure 6.

The length of $H_p$BABA molecule was calculated, using standard bond-lengths and bond-angles, to be 2.3 nm. Considering that there is a tilt angle ($\theta$) of 56°, one should expect a value of ~1.29 nm for the interplanar spacing. But the observed interplanar spacing, as mentioned earlier, was 2.868 nm. This discrepancy can be accounted for if one assumes the formation of dimers of the type shown in Figure 7. The calculated total length of such a dimer, using the hydrogen bond length (0.276 nm) and the Van der Waal radii of the end-hydrogen atoms (0.12 nm each) is 5.12 nm. The SmC interplanar spacing (2.863 nm) as calculated from this dimer length, using the observed tilt angle of 56°, is in good agreement with the observed value. Preliminary IR studies at room temperature have shown a broad band from 1800 to 3500 $cm^{-1}$. This normally is characteristic of hydrogen bonding and perhaps supports the idea of formation of dimers in our compounds. The dimer structure shown in Figure 7 would obviously lead to a cancellation of the central dipole moments (arising from COOH groups), leaving only the end dipole moments. According to McMillan's theory,[11] whenever the molecular structure is dominated by two outboard dipole moments, SmC phase results.

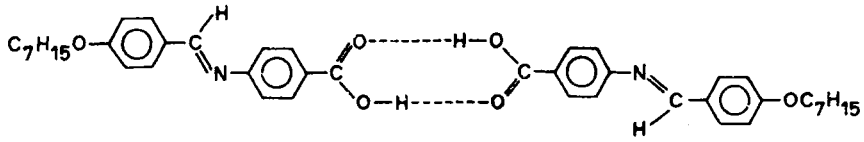

FIGURE 7 Anticipated structure of the dimer molecule.

From this, it appears that the SmC phase in $H_p$BABA is a consequence of dimer formation. This is further supported by the observation of SmC phase in *p-n*-alkoxybenzoic acid series.[9,12]

Lastly, our observation that the diameter of the inner ring remained same as $\theta$ became zero near the SmC → N transition is surprising because as $\theta$ goes to zero one would expect the interplanar spacing to increase thereby causing a reduction in the inner ring diameter from 1.05 cm to 0.56 cm. This anomaly can be explained if one assumes that there is a sudden decrease in the concentration of dimers at the SmC → N transition, the interplanar spacing now being determined by the increased monomer concentration. In fact, using an extension of Maier–Saupe theory, we have recently been able to show that there can be a sudden decrease (as high as 20%) in the concentration of dimers at the N → I transition in the case of *p-n*-alkoxybenzoic acids.[13] A reference to such a possibility was made by Carr[12] based on the dielectric measurements. Attempts are now being made by us to extend similar calculation to SmC → N transition also.

## IV CONCLUSIONS

The specific heat and the structure of $H_p$BABA phases were studied as a function of temperature. The main conclusions are:

a) Both microscopy and X-ray studies have shown that $H_p$BABA goes over from SmC to nematic directly and not via SmA phase.

b) X-ray data can be explained only if one assumes the formation of dimers.

c) The SmC → N transition appears to be accompanied by a sudden decrease in the concentration of dimers.

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