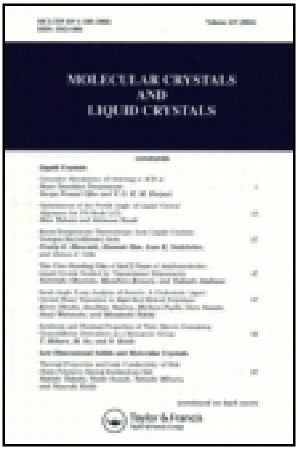

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Thermal and Structural Studies of the Different Phases of HxBPA

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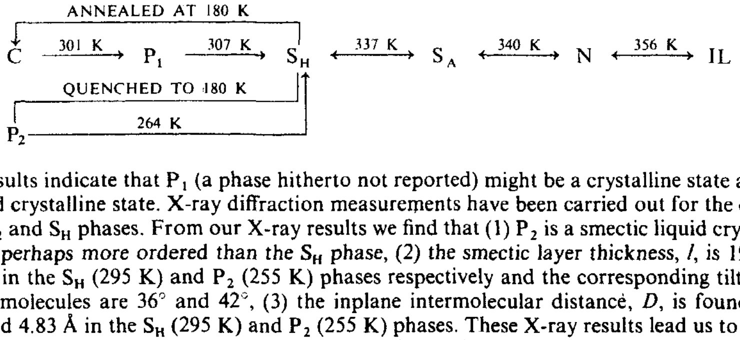
We have investigated the temperatures as well as the heats of transition involving the various crystalline and liquid–crystalline phases of HxBPA (4-*n*-hexyloxybenzilidene-4′-*n*-propylaniline) using a differential scanning calorimeter. From our observations we have arrived at the scheme of transitions given below.



Our results indicate that P_1 (a phase hitherto not reported) might be a crystalline state and P_2, a liquid crystalline state. X-ray diffraction measurements have been carried out for the crystalline, P_2 and S_H phases. From our X-ray results we find that (1) P_2 is a smectic liquid crystalline phase, perhaps more ordered than the S_H phase, (2) the smectic layer thickness, l, is 19.7 and 18.2 Å in the S_H (295 K) and P_2 (255 K) phases respectively and the corresponding tilt angles of the molecules are 36° and 42°, (3) the inplane intermolecular distance, D, is found to be 5.19 and 4.83 Å in the S_H (295 K) and P_2 (255 K) phases. These X-ray results lead us to believe that the P_2–S_H transition is related to the onset either of a rotational motion of the molecule or of static or dynamic disorder of the end hydrocarbon chains. Some preliminary Raman scattering work done with HxBPA support the latter conjecture. The X-ray measurements have been made at several temperatures between −20° and 40°C to determine the temperature variation of l and D.

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I INTRODUCTION

HxBPA is reported[1] to have three liquid crystalline phases, smectic H (S_H), smectic A (S_A) and nematic (N), between the crystalline and the isotropic liquid state. The S_H phase is known[1] to supercool down to fairly low temperatures and to change to another phase P_2 which reverts back to the S_H phase on heating to 264 K. The nature of this phase P_2 has been hitherto unknown. In the work reported here, a careful DSC measurement was done with HxBPA to study its phase transitions and the heats of transformation, in the temperature range 180 to 380 K. A hitherto unknown phase P_1 (301 to about 307 K) has been found in these measurements. A modified scheme of transitions is proposed based on our observations. X-ray diffraction studies of HxBPA have been carried out, (1) to determine the nature of the P_2 phase which has been found to be smectic liquid crystalline and very similar to the S_H phase, (2) to obtain the temperature dependence of the smectic layer thickness, l, and of the in-plane intermolecular distance, D, in both the P_2 and S_H phases, and (3) to determine, in particular the behaviour of l and D in the vicinity of the transitions, P_2–S_H and S_H–S_A, the variation with temperature near the transition point, $T_{P_2-S_H}$, being studied both while heating and while cooling.

II EXPERIMENTAL DETAILS

A Perkin-Elmer DSC-IB, differential scanning calorimeter was employed to detect the phase transitions. The sample weights used in these experiments, varied from 20 to 30 mgms and particular care was taken to ensure that the sample was not exposed to moisture or oxygen. The measurements were made at three rates of heating and cooling, viz., 4, 8 and 16°C/min. The true temperatures of transition were obtained by extrapolation to zero rate of heating or cooling. These experiments were done in the temperature range, 180 to 380 K and the transition temperature as well as the heats of transitions were obtained by averaging over the results of a number of measurements.

The X-ray experiments were done, using Ni-filtered Cu radiation ($\lambda = 1.5418$ Å) and a Laue camera modified to study scattering at small angles. The samples used were contained in capillaries (bore size varying from 0.5 mm to 1 mm), whose ends were sealed with epoxy resin. These samples were obtained in a polycrystalline state in the S_H phase by repeated quenching from the isotropic liquid state in a freezing salt bath (~ -20°C). The quenching was necessary at least once a day, as otherwise, the liquid crystal tends to have certain preferred directions of orientation in the S_H phase. The incident X-ray beam was at right angles to the capillary axis which was horizontal. The sample temperature could be varied by passing over it, nitrogen gas of suitable temperature. The rate of flow of the gas as also its temperature determined the sample temperature. Sample temperatures below room temperature were obtained by passing cold nitrogen gas, got by controlled heating of liquid nitrogen, whereas temperatures above room temperature were obtained by passing heated nitrogen gas. Using this arrangement, the sample temperature could be easily varied from −40°C to 80°C. The sample temperature was measured with the help of a Cu-Constantan thermocouple whose junction was located on the capillary. Typical exposure time for obtaining sufficiently clearly, the two rings of interest in the smectic phases, was about 30 min, and the temperature stability for this time duration was always better than ±2°C. For calibration purposes $CuSO_4 \cdot 5H_2O$ was employed. Its reflections corresponding to $(01\bar{1}, 001)$, $(12\bar{1})$ and $(1\bar{2}\bar{1})$ were used to determine accurately the distance between the sample and the film. The diameters of the Debye–Scherrer rings, seen in the X-ray photographs were obtained, using a densitometer.

III RESULTS AND DISCUSSION

A Differential Scanning Calorimetry

The DSC scans are shown in Figure 1. In the case of Run 1, the sample was cooled from room temperature (supercooled S_H phase) to 180 K and maintained there for about 90 min and then heated. In all, six transitions were observed between 180 K and 380 K. During cooling (Run 2) from 380 K to 180 K, only three peaks were obtained. In second and subsequent heating only four transitions were observed as reported elsewhere.[1] However, if the sample were cooled to 180 K and maintained there for 90 min, the results of Run 1 are reproduced. If the annealing at 180 K is carried out for a period longer than 3 hours and the sample is subsequently heated, all the peaks in Run 1 except that at 264 K are obtained. For annealing periods up to 3 hours, the intensity of the peak at 307 K grows at the cost of that at 264 K, until the latter completely disappears.

Our DSC results indicate that the S_H phase can be supercooled to below 180 K and that no glassy transition is present for temperatures exceeding 180 K, confirming the results of Uhrich *et al.*[1] It is found that the transition at 264.4 K is observed only when supercooled S_H phase is heated and not when the crystalline phase is heated. Between the crystalline and the S_H phases there are two closely occurring transitions, one very strong one at about 307 K with a weak shoulder on the low-temperature side, which can be resolved, under favourable conditions. A slight shift in the temperatures of

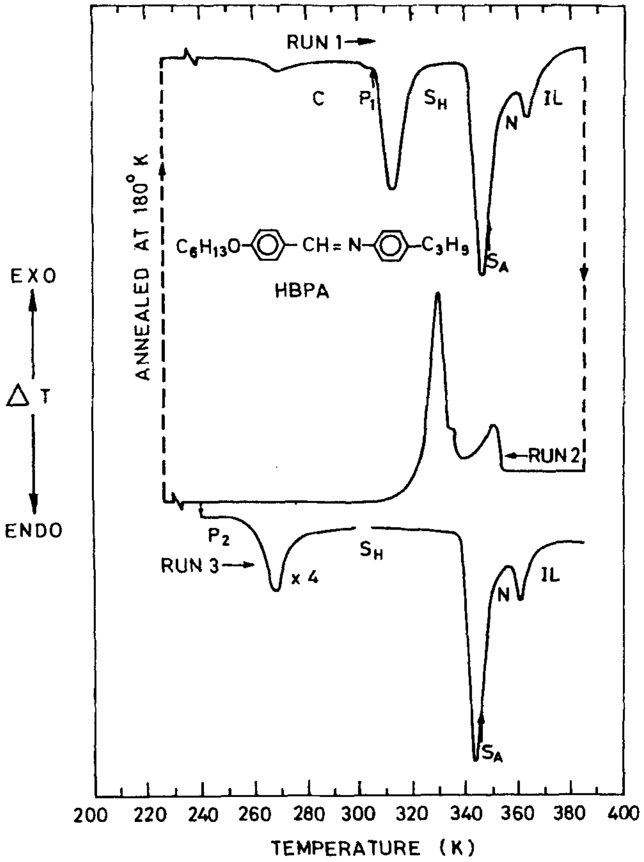

FIGURE 1 Typical DSC scans.

these two transitions was observed when the P_2 phase was present. From our results we have arrived at the modified scheme of transitions[2] shown in Figure 2. The true temperatures of transitions as well as the corresponding heats of transformation are given in Table I. The temperatures for the transitions, C–P_1 and P_1–S_H could not be obtained by extrapolation due to their spread. This spread indicated in Table I has been obtained from scans taken with heating rates (dT/dt) of 4 and 8°C/min. The extrapolated temperatures for the other four transitions differ from the corresponding ones obtained with $|dT/dt|$ of 4°C/min by 1 to 2°C, the latter being lower or higher, depending on whether the scan was taken while cooling or while heating. As is evident from this table, the heats of transitions P_2–S_H, S_A–N and N–IL and C–P_1 (not given in Table I) are relatively small, thereby indicating that no major

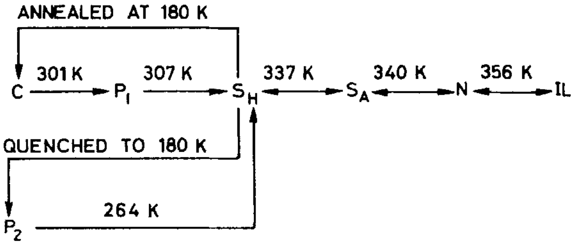

FIGURE 2 Scheme of transitions for HxBPA.

structural changes are involved in these transformations. It is therefore possible that P_1 might be crystalline while P_2 might be liquid crystalline in structure.

B X-ray Diffraction Data

Our measurements can be, in general, classified into two sets, one consisting of heating the sample from room temperature (RT) to 350 K and another involving cooling the sample from RT to 250 K and heating it back to RT. The samples used in these two sets of measurements were in the S_H phase in the poly crystalline form at room temperature (obtained as described in Section II).

Results above RT In the S_H phase, in addition to several weaker rings, we observed two strong rings, one inner ring at a scattering angle (2θ) of nearly 4° and an outer ring at a 2θ of about 20°. In the S_A phase the inner ring still remains strong and sharp, while the outer ring gets diffuse. When the sample was completely transformed to the S_A phase, the inner ring collapsed into a pair of spots and the outer ring into a pair of crescents, each pair being 180° apart. This indicates effect of strong alignment of the molecules about a

TABLE I

Nature of Transition	Temperature (K)		Heat of transition (K Cal/Mole)
	Heating	Cooling	
P_2–S_H	264.4	Not seen	0.23
C–P_1	301.2 to 301.8	Not seen	—[a]
P_1–S_H	306 to 308	Not seen	1.62
S_H–S_A	337.5	336.6	1.26
S_A–N	340.9	339.8	0.23
N–IL	356.4	356.0	0.26

[a] Not obtained due to poor resolution.

preferred direction. The lines joining the pair of spots and the maxima of the pair of crescents are mutually perpendicular, as expected. The line joining the two spots (let us call this direction, **m**) makes an angle of about 30° with the horizontal (capillary axis). There is also visual evidence of this alignment effect, viz, the translucent S_H phase becomes transparent on going over to the S_A phase. On heating the S_A phase beyond the temperature, T_{S_A-N}, the alignment is retained, as is evident from the X-ray photograph in this phase. However, the inner ring in the nematic phase is also diffuse, as expected. If one obtains the preferred direction of orientation of the molecules by assuming it to be perpendicular to the line joining the maxima of the outer crescents,[3] then we find that in the nematic phase, this direction is parallel to the capillary axis and changes reversibly by an angle of about 30° at the S_A–N transition. It is, of course, assumed that this preferred direction is in a plane perpendicular to the incident X-ray beam, and this assumption is reasonable because of the maxima in the crescents being 180° apart. When the S_A phase was cooled to the S_H phase, it was found that the direction of the smectic planar normal remains almost the same, while the extent of molecular alignment becomes less. This is seen by the grouping of spots in the inner ring around **m**, the direction already defined.

The smectic layer thickness, l, in all three phases is calculated from the diameter of inner rings. In the S_H and S_A phases, the Bragg reflection condition, $2l \sin \theta = \lambda$, was used. In the nematic phase, the parameter l is the apparent length of the molecule defined as the average distance between the electron density minima at the ends of the molecule and is calculated using the relation,[4]

$$\lambda = l \sin 2\theta \tag{1}$$

which is valid for complete orientational order with the molecules being aligned perpendicular to the incident beam. The value of l calculated thus is about 23 Å. Apriori one does not know the extent of orientational order in this phase and hence we have also calculated the value of l, using the relation,[4]

$$1.229\lambda = 2l \sin \theta \tag{2}$$

which is valid, if the molecules are oriented at random. In this case, l, turns out to be about 28 Å. The value of the in-plane intermolecular separation, D, in the S_H phase is obtained from the diameter of the strong outer ring using the Bragg condition and assuming a hexagonal arrangement of molecules[5] in the smectic layers ($\lambda = \sqrt{3}D \sin \theta$). In the S_A and nematic phases (in the nematic phase, D corresponds to the average intermolecular distance perpendicular to the long axes of the neighbouring molecules) D has been calculated from the distance between the maxima of the two outer crescents using the relation[6]

$$1.117\lambda = 2D \sin\theta \tag{3}$$

The values of l and D in the different phases have been plotted as a function of temperature in Figure 3. In the S_H phase, both l and D increase with temperature though the slope is very small. Least squares fit of straight lines to the points in the S_H phase for temperatures up to 333 K has been done, and the lines are shown in Figure 3. The slope of l is found to be 5.2×10^{-3} Å/K whereas that of D is seen to be 1.1×10^{-3} Å/K. In the region of temperature 333 to 337 K, l increases from 20 to 24 Å, the latter being the smectic layer thickness found in the S_A phase. This value of l in the S_A phase is less than the molecular length, L, calculated according to the model given by de Vries[4] to be 24.44 Å. Such a difference between the values of l in the S_A phase and L has been found in other liquid crystals also[6] and the difference is considered as being due to overlap of the molecules in neighbouring smectic layers. If this is assumed, the overlap length would be 0.44 Å. In the nematic phase, l calculated using Eq. (1) has been plotted on the graph. These values are also less than L. However, the value 28 Å of l, calculated using Eq. (2), is much larger than that of L. Eq. (1), thus seems to be more applicable in this case, indicating that the extent of molecular

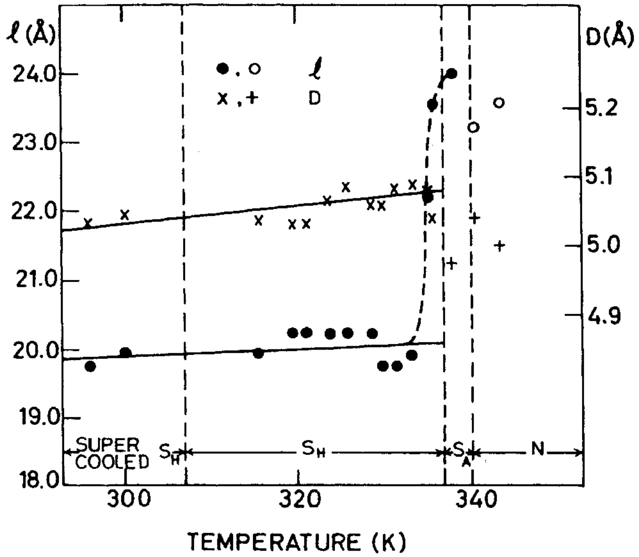

FIGURE 3 Temperature dependence of l and D for $T > 295$ K. Open circles are values of l in the nematic phase, obtained using Eq. (1). The results given as + are values of D calculated using Eq. (3). The straight lines are those obtained by least squares fit, to the experimental values of l and D in the S_H phase.

alignment, is large but incomplete. The value of D in the S_A phase, calculated using Eq. (3) is smaller than that in S_H phase, near the transition, as has also been observed in the case of some other liquid crystals.[5] This decrease could be just apparent and might have resulted from calculating D, using equations that are obtained by making assumptions which are not completely justified. In the nematic phase, although one observes a slight increase in D values, these are still lower than those obtained in the S_H phase, near the transition temperature $T_{S_H-S_A}$.

The molecular tilt angle, θ_t (the angle made by the preferred direction of orientation of the molecule with the smectic planar normal) can be calculated from the relation, $\cos\theta_t = l/L$, assuming that there is no overlap of molecules belonging to neighbouring smectic planes. However if one assumes that the overlap length of 0.44 Å observed in S_A phase, remains unchanged in the S_H phase, then $\cos\theta_t = l/(L - 0.44)$. The value of θ_t, calculated using these two relations are shown in Figure 4 as a function of temperature. θ_t decreases very slowly with temperature up to 333 K. It is seen from the inset that for $T > 333$ K, θ_t rapidly decreases, the decrease being to zero, when one assumes the overlap length of 0.44 Å. By extrapolation the value of θ_t is found to

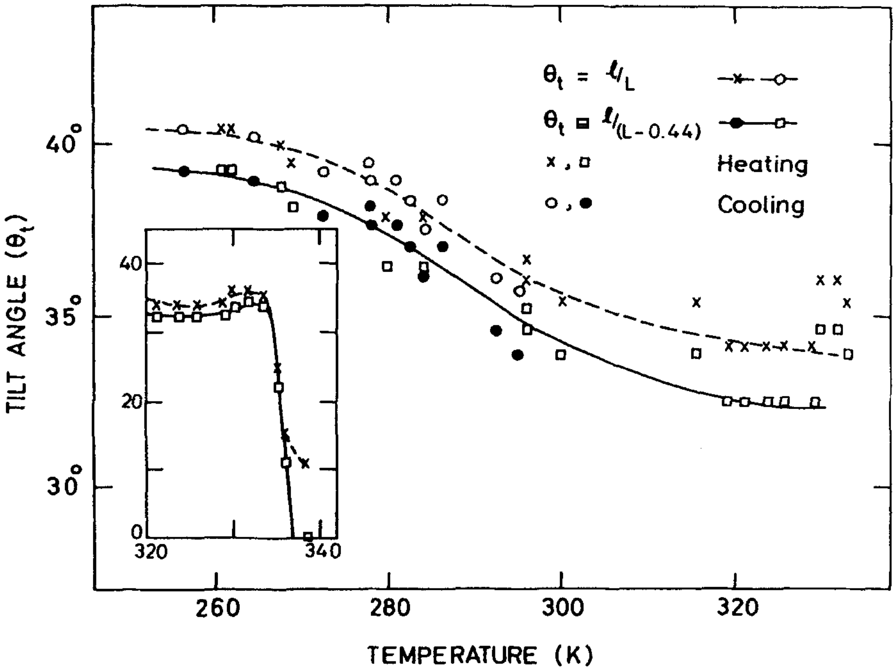

FIGURE 4 Variation of θ_t with temperature. The inset shows the behaviour of θ_t near the transition point, $T_{S_H-S_A}$. The full line and dashed line curves are guides to the eye.

become zero at $T = 337$ K, which is the value of the transition temperature, $T_{S_H-S_A}$ obtained from our DSC measurements. It therefore seems that the relation $\cos \theta_t = l/(L - 0.44)$ is more valid than the relation, $\cos \theta_t = l/L$, for the calculation of θ_t for HxBPA.

Since it seems reasonable to assume that the tilt angle in the S_H phase of HxBPA is mainly determined by Van der Waal's interactions between the phenylene groups of neighbouring molecules in the smectic planes,[7] θ_t will be strongly dependent on the positional order of the molecules in these planes. From our results on θ_t it would then seem that the positional order is almost unchanged in the S_H phase for temperatures up to 333 K, while it is rapidly lost as the temperature increases from 333 to 337 K. There is a slight increase in θ_t (due to a slight decrease in l) for temperatures just below 333 K and the reason for this is not understood.

The reason for the reversible change in the preferred direction of orientation of the molecules in the vicinity of the transition S_A–N, is not understood. Since the direction of the smectic planar normal remains more or less unchanged as one cools the sample, through the transition point $T_{S_A-S_H}$, we can deduce that it is the preferred direction of orientation of the molecules which changes by an angle equal to the molecular tilt angle when the sample is cooled through $T_{S_A-S_H}$.

Results below RT These measurements were made with samples in the supercooled S_H phase and in the P_2 phase. No changes were observed in the main features of the diffraction photographs when one cooled the sample from the supercooled S_H phase at RT to the P_2 phase at 240 K. The photographs consist of a strong inner ring and a strong outer ring, and several weaker rings, similar to those observed in the S_H phase. This shows that P_2 is a liquid crystalline phase, very similar to the S_H phase in structure, consistent with the indications of our DSC results. However, cooling the sample below 260 K produced a small but noticeable expansion in the strong outer ring (and hence a decrease in D) and a change in the relative intensities of the weak rings. While heating, these effects disappear for $T > 270$ K. The strong inner ring gradually expands (showing that l decreases and hence θ_t increases) as one cools the sample, and this behaviour is reversed while heating. The values of l and D have been calculated from these X-ray measurements, as was done earlier for the S_H phase.

The temperature dependence of l and D are shown in Figure 5, for both the cooling and heating runs. It is found that a decrease in both l and D are found as the temperature is reduced. Least squares fit of straight lines has been done to the points obtained only from the cooling runs and the best fits are shown as solid lines in Figure 5. In the case of l, the points obtained from both heating and cooling runs are fitted fairly well by the calculated line with a

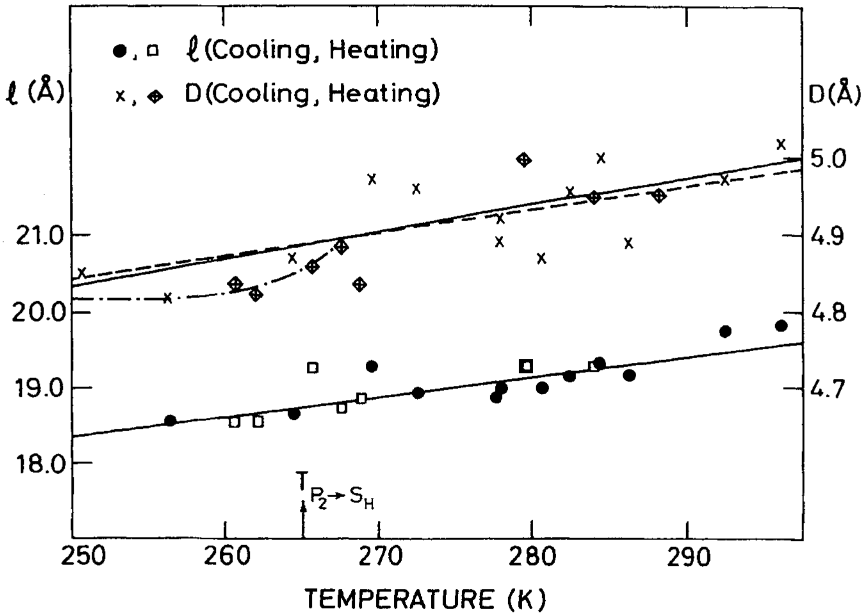

FIGURE 5 Temperature dependence of *l* and *D* for $T < 295$ K. The straight lines are those obtained by least squares fit to results obtained by cooling runs. The dashed line is similarly obtained, but by omitting *D* values for $T < 270$ K. The dot-dashed curve is a guide to the eye.

slope of 2.6×10^{-2} Å/K. It is also found in this case that even if we exclude points below the transition temperature, $T_{P_2-S_H}$ (264.4 K), the slope of this line is changed very little. In the case of *D*, the calculated line whose slope is 3.3×10^{-3} Å/K does not fit the points below 270 K, whereas above this temperature, results of both heating and cooling runs agree fairly well with this line, although their scatter is rather large. If in this case, one excludes the points below the temperature, $T_{P_2-S_H}$ while fitting, the slope of the least square fitted line is reduced to a value of 2.0×10^{-3} Å/K. This is seen as the dashed line in Figure 5. It seems to us that the results of the heating runs follow a behaviour as shown by the dot-dashed curve, for $T < 270$ K. The *D* values obtained from the heating run indicate that *D* increases from 4.82 Å to 4.9 Å in the temperature range 250 to 269 K. Above 269 K, *D* follows the dashed line obtained by fitting. It is also found that all values of *D* below the transition, $T_{P_2-S_H}$ are less than 4.85 Å. It is known[5,8] that in some lipids, when the hydrocarbon chains are frozen parallel to each other, the intermolecular distance is 4.85 Å. If one assumes that a similar distance results for *D*, when the hydrocarbon chains in HxBPA are also frozen parallel to each other, one can conjecture that the transition P_2–S_H is caused by the onset of static or dynamic disorder in these chains. Results of preliminary Raman scattering experiments[9] carried out with HxBPA support this conjecture. It is found that the value of D never exceeds 5.1 Å in both the supercooled and normal states of the S_H. This rules out the possibility of collective rotational motion of the molecules in the S_H phase, since this motion can only take place for $D > 5.12$ Å.[5]

The variation of θ_t with temperature in the supercooled S_H and P_2 phases are also shown in Figure 4, for both the heating and cooling runs. θ_t has been calculated using the two relations mentioned earlier. The curves drawn are only guides to the eye. It is found that θ_t decreases smoothly with increasing temperature in the whole range studied. In the S_H phase at room temperature values of θ_t obtained from the two relations are 36° and 34.5°, both values being higher than the value of 30° quoted by Uhrich *et al.*[1]

IV CONCLUSIONS

1) We have given a revised scheme of transitions for HxBPA in which a new phase P_1 has been incorporated. It seems that transition C–P_1 does not involve any major structural change.†

2) We have obtained evidence to show that P_2 is a liquid crystalline phase, structurally similar to the S_H phase. In the P_2 phase, the hydrocarbon chains are probably frozen parallel to each other and the transition to the S_H phase might be due to the onset of static or dynamic disorder of these hydrocarbon chains.

3) In the transition S_A–S_H, it is the preferred direction of orientation of the molecule that changes and not the direction of the smectic planar normal.

4) In the S_A phase, the molecules in the neighbouring smectic planes are found to overlap to the extent of 0.44 Å.

5) The molecular tilt angle, θ_t, changes gradually from about 40° at 250 K to about 33° at 330 K, but falls very rapidly above 334 K, becoming zero at 337 K which is the transition temperature, $T_{S_H-S_A}$.

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† Some X-ray diffraction measurements that we have carried out since have, indeed, confirmed this.

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