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Orientational Distribution Function and Order Parameters for 5-(4-*n*-Butylphenyl)-2-(4-Cyanophenyl)-Pyrimidine

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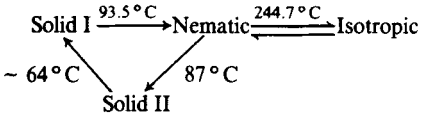
5-(4-*n*-Butylphenyl)-2-(4-Cyanophenyl)-Pyrimidine (BPCPP in short) has a very large mesomorphic range from 93.5 °C to 244.7 °C. We have reported in this paper X-ray diffraction studies of aligned sample of BPCPP over the entire liquid crystalline range, using a camera designed by us in a magnetic field of 5.8 Kilogauss. On the basis of X-ray diffraction, texture and DTA study the substance is found to have the following phase transitions



Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been determined from the calculation of $f(\beta)$, the orientational distribution function in the nematic range, $\langle P_4 \rangle$ values agrees well with the theoretical values. Agreement of $\langle P_2 \rangle$ with theoretical values is rather erratic. We are unable to explain this. Apparent molecular length L and inter molecular distances have been calculated. The molecules of BPCPP form associations in the mesophase like other cyano compounds.

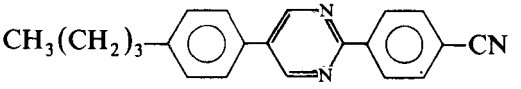
1. INTRODUCTION

5-(4-*n*-Butylphenyl)-2-(4-Cyanophenyl)-Pyrimidine (BPCPP in short) has a very large mesomorphic range from 93.5 °C to 244.7 °C. We have reported in this paper X-ray diffraction studies of BPCPP over

the entire liquid crystalline range. Single domain X-ray diffraction photographs have been obtained by using a magnetic field of 5.8 Kilogauss. We have derived the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ and also calculated the orientational distribution function $f(\beta)$ from the X-ray intensity distribution.

Intermolecular distance and apparent length of the molecule have been calculated both for the oriented and unoriented samples.

Orientational distribution function and order parameters from X-ray data for several samples have been reported from different laboratories.[1,2,4-7,11] The structure of the compound is shown below

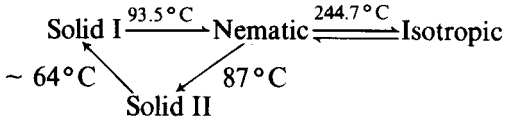


The compounds were supplied to us by M/s. F. Hoffmann-La-Roche and Co., Basel, Switzerland. According to their catalogue the transition temperature of the compounds are given below:

$$\text{Crystal} \underset{}{\overset{93.5\,^\circ\text{C}}{\rightleftharpoons}} \text{Nematic} \overset{244.7\,^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$$

Boller *et al.*[3] have synthesised the compound and studied its mesomorphic properties. Based on texture and low viscosity they have identified the mesomorphic phase as being nematic. Transition temperatures as observed by them are the same as given above.

On the basis of our X-ray texture and D.T.A. studies, we have obtained the following transition scheme for BPCPP.



The details of the analysis of the equatorial arcs in the diffraction patterns to determine $f(\beta)$, the orientational distribution function have been discussed in our previous works.[4-6]

The intensity profile $I(\beta)$ around the diffuse equatorial arc is related to the distribution function as follows[7]

$$I(\theta) = C\int_{\theta}^{\pi/2} fd(\beta)\sec^2\theta\left(\tan^2\beta - \tan^2\theta\right)^{-1/2}\sin\beta\,\mathrm{d}\beta$$

where $fd(\beta)$ describes the distribution function of a small volume having an orientation β relative to the director. It is assumed to be

same as the singlet distribution function $f(\beta)$. From the above equation using a numerical method $f(\beta)$ and hence the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ could be obtained.

The normalized singlet orientational distribution function $f(\beta)$ is related to the pseudopotential $V(\beta)$ by the relation

$$f(\beta) = \exp[-V(\beta)/kT] \Big/ \int_0^{\pi/2} \exp[-V(\beta)/kT] \sin\beta \, d\beta.$$

We have best fitted our $f(\beta)$ values to the form

$$f(\beta) = Z^{-1} \exp\left[\sum_{\text{Leven}} a_L P_L(\cos\beta)\right],$$

where Z is the partition function and have obtained an expression for the angular part of the pseudopotential $V(\beta)$ up to the $P_4(\cos\beta)$ term.

2. EXPERIMENTAL

The sample BPCPP was supplied to us by M/s. Hoffmann-La-Roche and Co. The transition temperatures of the compound as observed by us by using a polarising microscope with a hot stage agreed with the literature values. The sample was used without further purification.

X-ray diffraction photographs of the sample in presence and absence of magnetic fields were taken using Ni-filtered CuK_α radiation of 1.542 Å. Photographs were taken using a high temperature X-ray camera designed to obtain the desired photographs in presence of a magnetic field.[8]

The sample was heated to isotropic phase and cooled down in the presence of a magnetic field to the desired temperature. For experiments in the supercooled region the same procedure was followed and X-ray photographs were taken. Further experimental details could be obtained from our previous publications.[4-6]

Textures of the compound were observed under the polarizing microscope. The observations were made under crossed polarizer with magnification 150 X. Phase changes were observed at 93.5 °C and 244.7 °C while heating, while cooling phase transitions were observed at 244.7 °C, 87 °C, and approximately at 64 °C. Thus whereas the transition temperatures during heating are almost the same as reported previously, those during cooling differ substantially and produce a monotropic solid phase. We could not identify the mesomorphic phase

from our texture studies alone, it could be nematic or smectic A. However, Boller *et al.*[3] called it a nematic phase and our X-ray diffraction measurements confirmed this identification.

3. RESULTS AND DISCUSSIONS

The diffraction photographs of the sample were taken at different temperatures ranging from the solid phase at room temperature to isotropic phase and also in the supercooled region, both in the presence and in the absence of the field. The photographs for the oriented and unoriented sample at 100°C are shown in Figure 1 and Figure 2 respectively. Unoriented diffraction patterns have a diffuse outer ring which give intermolecular distance d, a sharp inner ring which gives L, the apparent molecular length. Another diffuse ring at Bragg angle 5.4° is found which may be due to some intramolecular interactions.

The pattern of the oriented sample consists of two diffuse outer maxima as shown in Figure 2. The inner most ring is split into two sharp arcs. Photograph has some similarity with smectic A, but diffuse outer maxima are more like nematics. The sample could be oriented in

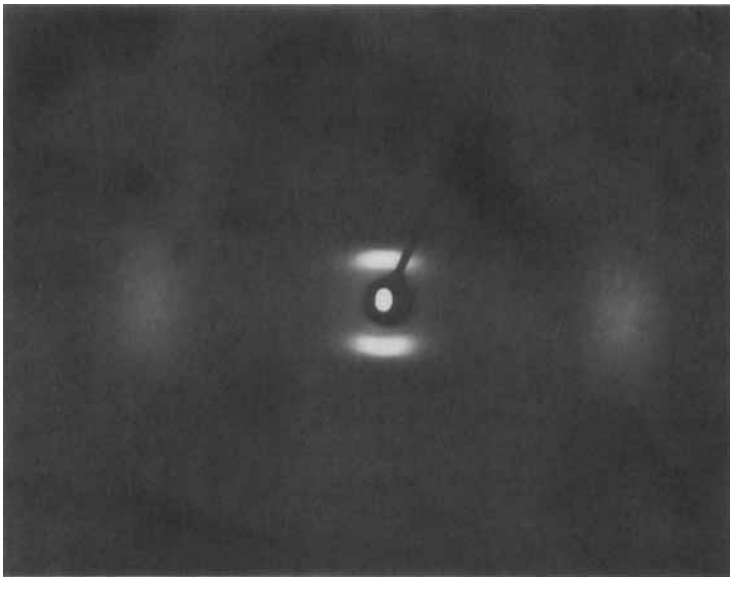


FIGURE 1 X-ray photograph of oriented sample of BPCPP at 100 °C.

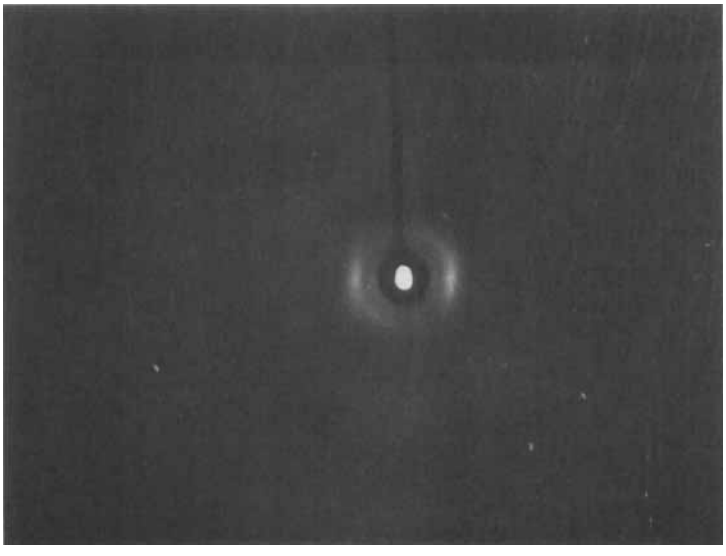


FIGURE 2 X-ray photograph of unoriented sample of BPCPP at 100 °C.

very low magnetic field unlike any smectic compound. Therefore, the phase is a nematic one.

X-ray diffraction patterns at 80 °C of the monotropic phase cooled in the absence and presence of a magnetic field are shown in Figure 3 and Figure 4 respectively. Figure 3 shows the presence of several sharp well defined outer rings and a sharp inner ring. In Figure 4, we get equatorial maxima in the outer rings. The ring at 5.4° Bragg angle splits into four maxima. The inner most ring breaks up into two well defined diffraction spots. The presence of these spots implies that monotropic phase has some mesomorphic character. The interesting feature is that in the meridian direction additional spots of almost equal intensity appear at lower angles. These spots are definitely the Bragg's diffraction maxima originating from the smectic like layers, the molecules being perpendicular to the layers. Bragg's spacings for these spots are found to be 22 Å and 39 Å respectively. Existence of a mixture of domains of bilayered smectics and partially overlapped bilayered smectics may be a possible explanation for the occurrence of these spots. The length of the molecule in its fully extended form is found to be 19.3 Å from our stereo model unit. When the sample is cooled to 59 °C in magnetic field we get a photograph (Figure 5) of polycrystalline solid phase and is distinctly different from the phase at 80 °C (Figure 4).

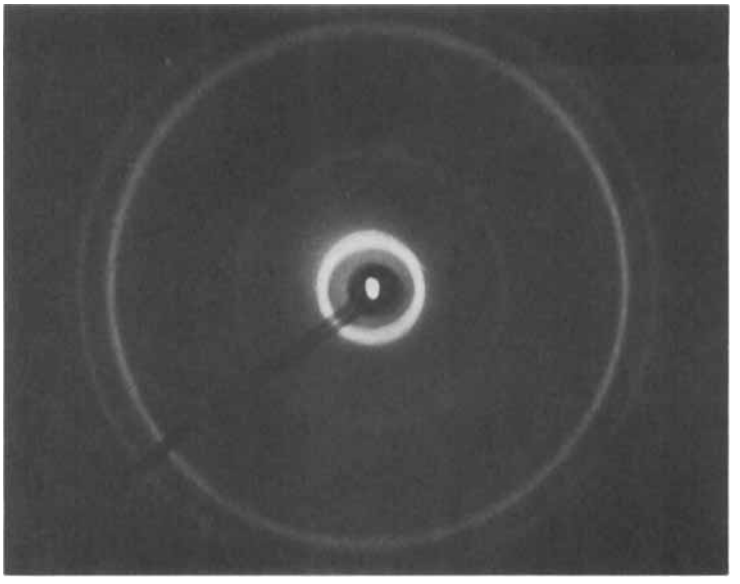


FIGURE 3 X-ray photograph of a sample of BPCPP at 80 °C, in absence of magnetic field.

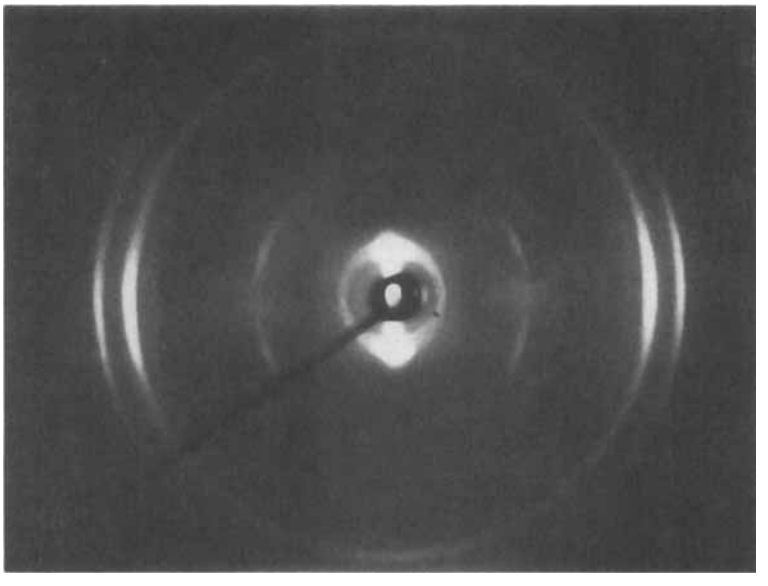


FIGURE 4 X-ray photograph of a sample of BPCPP at 80 °C cooled in presence of 5.8 K.gauss magnetic field.

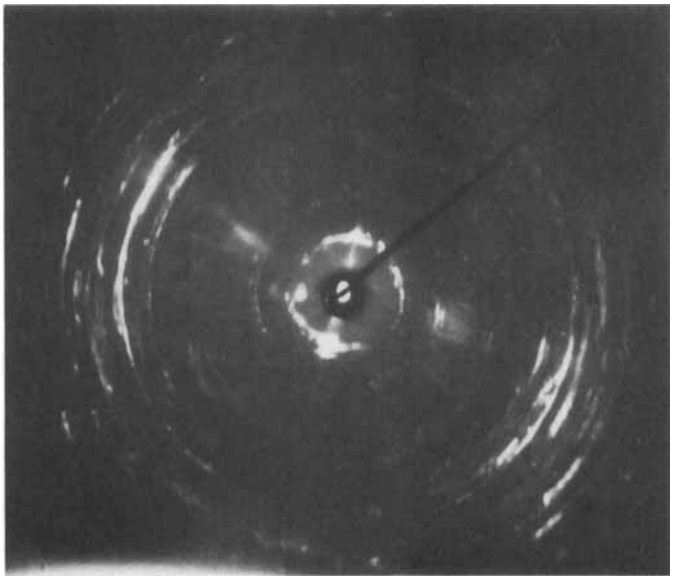


FIGURE 5 X-ray photograph of a sample of BPCPP at 59 °C (supercooled phase) cooled in presence of magnetic field.

X-ray patterns at 80 °C for both aligned and non-aligned samples show that the structure is analogous to the structure of smectic E phase, the molecules being perpendicular to the layers. These well defined rings indicate a high degree of order and pronounced molecular arrangement within strata. From the powder pattern we tried to determine an elementary orthorhombic or hexagonal unit cell (c axis parallel to the long molecular axis, perpendicular to a and b). But all the lines could not be explained from this unit cell. Non orthogonal arrangement may possibly explain this, but the lines are too few to interpret the data assuming non-orthogonality. The presence of the ring at Bragg angle 5.4° which splits into four maxima also remains unexplained.

Although it is evident from the X-ray pattern that the monotropic phase is smectic E like, texture studies showed a solid like phase. Moreover at the supercooled transition temperature an abrupt change of volume was observed and the sample seemed to be highly viscous. From the DTA study it was found that the heat of enthalpy of this transition is typical of mesomorphic to solid transition (about 3.5 K.cal/mole, during cooling). We therefore, conclude that the compound has a monotropic phase which we designate as a smectic E like

TABLE I

Bragg spacing in the supercooled phase (cooled from nematic in 4.6 K.Gauss field)

Temp. °C	Sr. No. of diffraction rings/spots	Diameter (cm)	Bragg Angle in deg.	Bragg spacing in Å	Reflection
	1	6.845	14.068	3.17	Equatorial section
	2	5.28	11.208	3.96	
	3	4.705	10.091	4.40	
	4	2.455	5.429	8.14	
69 °C	Outer spots	0.89	1.989	22.19	Meridional Section.
	Inner spots	0.50	1.118	39.45	
	1	6.88	14.129	3.15	Equatorial Section
	2	5.305	11.256	3.95	
	3	4.73	10.140	4.37	
	4	2.465	5.450	8.11	
	5	0.92	2.055	21.47	
80 °C	Outer spots	0.90	2.011	21.94	Meridional Section
	Inner spots	0.52	1.163	37.93	

solid phase. Bragg angles from the diffraction lines of this phase at two different temperatures and the corresponding spacings calculated from the Bragg's law are listed in the Table I. The outermost ring is very weak and is absent in the print reproduced in Figure 3 and Figure 4.

The intermolecular distance d and the apparent length of the molecules L, have been calculated using the expression given by de Vries.[9] The variations of d and L with temperature are shown in Figure 6 and Figure 7 respectively. As temperature increases inter-

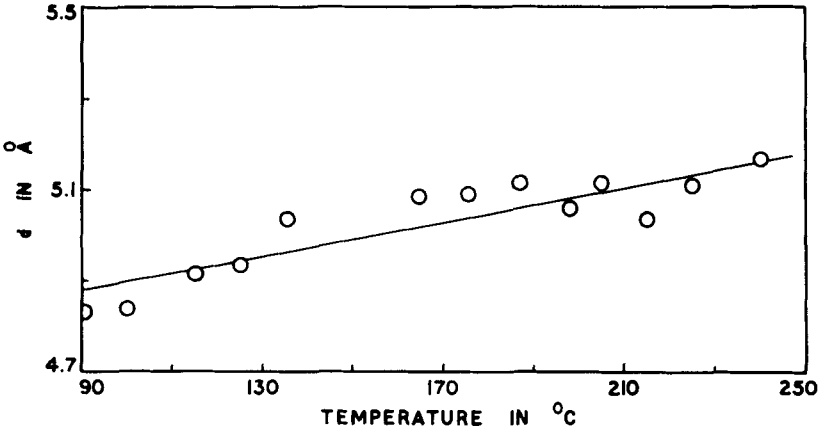


FIGURE 6 Variation of intermolecular distance d with temperature.

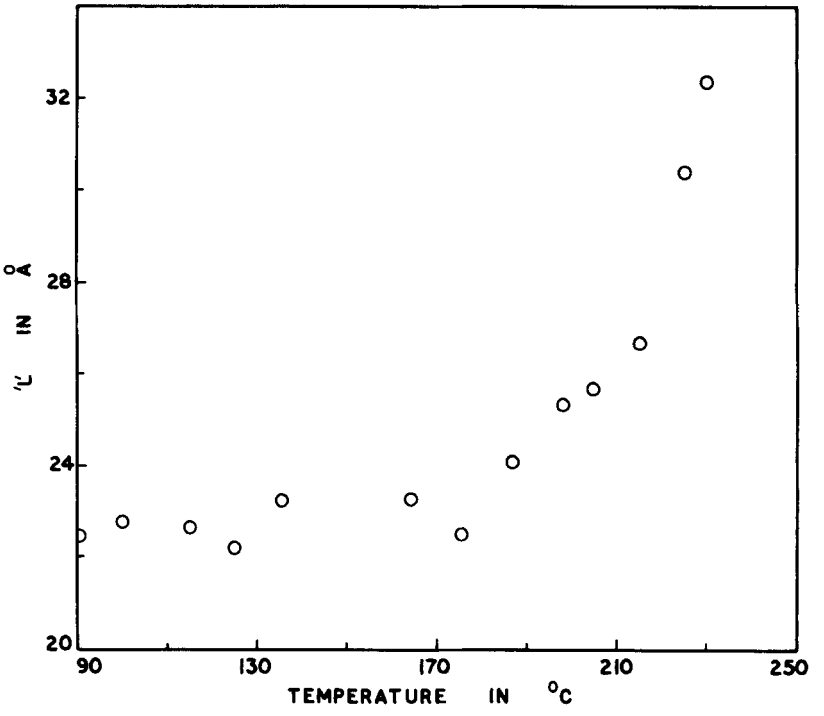


FIGURE 7 Variation of apparent molecular length L with temperatures.

molecular distance d increases. The value of L, the apparent molecular length, changes slowly with temperature in the low temperature region, but it increases sharply at about 185°. The DTA scan, however, did not show any peak at this temperature, showing that no first order phase transition occurs. The L values changes from 22.4 Å at 90.5°C to 32.3 Å at 240°C. Since these values are larger than the model molecular length (19.3 Å) the molecules of BPCPP forms associations in the mesophase like most cyano compounds. The ratio of apparent molecular length to the model molecular length is less than 1.4 at the lowest temperature.

Cladis *et al.*[10] have proposed a model of a partial bilayer with overlapping of the aromatic systems for several cyano compounds. In the case of BPCPP a complete overlap of the rigid parts of the two molecules gives an apparent length of the dimer approximately equal to 22 Å which is almost equal to the experimental value at 90.5°C. This shows that the dipolar charge separation in BPCPP may be spread over whole of the rigid part of the molecule. At higher

temperatures (near 185 °C) the extent of overlap starts reducing giving rise to a rapid increase in L probably due to thermal excitation.

Variation of the normalized orientational distribution function $f(\beta)$ with β as obtained from $I(\theta)$ at 115 °C is shown in Figure 8. The temperature dependence of the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in the nematic range is shown in Figure 9, together with Maier-Saupe's molecular field predictions. The order parameters are estimated to be accurate to within ± 0.02. Unlike other compounds[4,5,6,11] the $\langle P_4 \rangle$ values of BPCPP agree well with theoretical Maier-Saupe values. Agreement of $\langle P_2 \rangle$ values with the theoretical values is rather erratic.

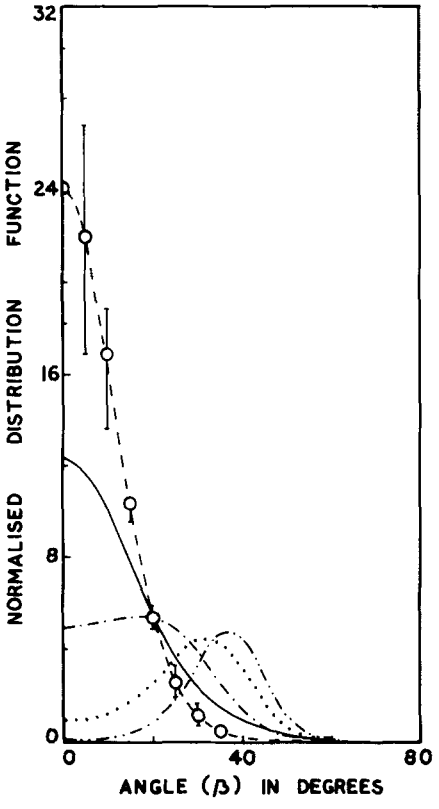


FIGURE 8 Normalized orientational distribution function $f(\beta)$ against angle β for BPCPP at 115 °C. Calculated $f(\beta)$ value; ——— from X-ray data, - - - - - - from pseudopotential $V(\beta)/k = -(4300 \pm 1050)\langle P_2 \rangle P_2(\cos\beta)$, · · · · from pseudopotential $V(\beta)/k = -4300\langle P_2 \rangle P_2(\cos\beta) + 4800\langle P_4 \rangle P_4(\cos\beta)$, —·—·—·— from pseudopotential $V(\beta)/k = -4300\langle P_2 \rangle P_2(\cos\beta) + (4800 + 1900)\langle P_4 \rangle P_4(\cos\beta)$, -·-·-·- from pseudopotential $V(\beta)/k = -4300\ \langle P_2 \rangle P_2(\cos\beta) + (4800 - 1900)\langle P_4 \rangle P_4(\cos\beta)$.

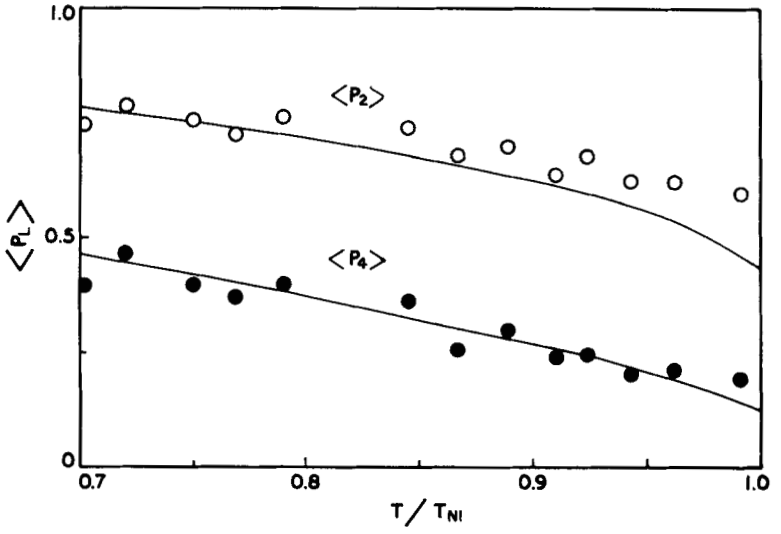


FIGURE 9 Variation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for BPCPP with temperature, —Maier Saupe theoretical values.

Anomalous nature of the $f(\beta)$ values at some temperatures are reflected in the $\langle P_2 \rangle$ values. We are unable to explain the cause of this.

We have calculated the angular part of the mean field potential in the form $V(\beta) = \Sigma_{\text{Leven}} b_L \langle P_L \rangle P_L(\cos\beta)$ for L up to 10. The coefficients b_L are calculated from a_L values for a wide range of temperature. But the variation of the coefficient b_L with temperature is not systematic. As the variation of density with temperatures is not available the coefficient b_L is taken to be constant. The calculation leads to the pseudopotential responsible for orientational ordering in this compound as

$$V(\beta)/k = -(4300 \pm 1050)\langle P_2 \rangle P_2(\cos\beta) + (4800 \pm 1900)\langle P_4 \rangle P_4(\cos\beta)$$

The above equation has the form proposed by Humphries *et al.*[12] It is seen that standard deviations of both b_2 and b_4 are very large. BPCPP has a nematic phase over a wide range of temperature and the approximation that density values are constant at all temperatures may be an explanation for these large standard deviations.

We have calculated $f(\beta)$ from this potential as well as by neglecting the $P_4(\cos\beta)$ term. All these values are shown in Figure 8. The

orientation distribution function obtained by us from the X-ray diffraction data do not agree well with the distribution function generated from the commonly accepted molecular field potential even after including the $P_4(\cos\beta)$ term. The probable cause of this discrepancy may be the same as those discussed in our earlier papers.[4,6]

Acknowledgments

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