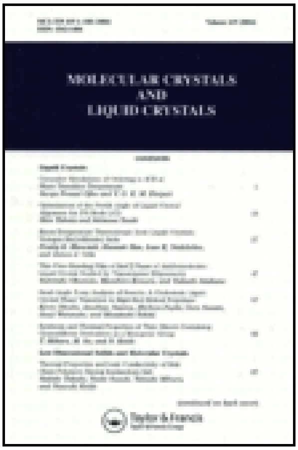

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Basana Bhattacharjee [a] , Ranjit Paul [a] & Sukla Paul [a]
[a] Department of Physics, North Bengal University, Dist., Darjeeling, West Bengal, India, 734430

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Order Parameters and Distribution Function of 4′-(*N*-(*p*-Pentyloxy Carbonyloxy-Benzylidene)Amino) Valerophenone in Smectic Phase from X-ray Diffraction Measurements

BASANA BHATTACHARJEE, RANJIT PAUL and SUKLA PAUL†

Department of Physics, North Bengal University, Dist. Darjeeling, West Bengal, India 734430

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X-ray diffraction studies of 4′-(*N*-(*p*-pentyloxycarbonyloxy-benzylidene)amino)valerophenone (PCBAV in short) oriented by a magnetic field is reported here. The compound has a smectic A phase which is identified by X-ray studies and texture studies. 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. An approximate expression for the angular part of the potential of the mean field is obtained from the temperature variation of the orientational distribution function. The value of d, the layer thickness, and D, the intermolecular distance, have been calculated. An approximate value for the translational order parameter τ_1 and average value of the root mean square displacement $\langle z^2\rangle^{1/2}$ are given. We could not get an accurate estimate of the translational order parameter due to the inaccuracy in the measurement of the intensity of the inner ring.

1. INTRODUCTION

The compound 4′-(*N*-(*p*-pentyloxycarbonyloxy-benzylidene)amino) valerophenone (PCBAV in short) has got a smectic phase over a fairly

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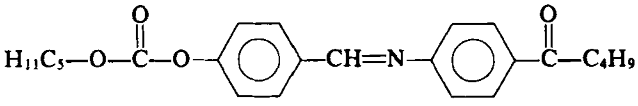
† Reprint request is to be made to Dr. (Mrs.) S. Paul, Physics Department, P.O. North Bengal University, Dist. Darjeeling, West Bengal, India-734430.

wide range of temperature. The structure of the compound is shown below.



The transition temperatures obtained from the Eastman Data Service Catalog (no. 11441) are

$$\text{Crystal} \xrightarrow{77^\circ\text{C}} \text{Smectic} \xrightarrow{115^\circ\text{C}} \text{Isotropic}$$

The phase transitions as determined by us from X-ray diffraction and texture studies are

$$\text{Solid} \underset{60^\circ\text{C}}{\overset{77^\circ\text{C}}{\rightleftharpoons}} \text{Smectic A} \overset{115^\circ\text{C}}{\rightleftharpoons} \text{Isotropic}$$

In this paper we have reported the results of X-ray studies on the oriented and unoriented samples of PCBAV in the smectic phase. 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 intensity measurements of the diffraction photographs of oriented samples. A number of experiments have been performed to calculate the order parameters for aligned nematic samples. Falgueirettes and Delord[1] have developed the use of X-ray diffraction methods to determine the orientational distribution functions of the molecular long axes $\bar{n}$ relative to the director for PAA. Recently Leadbetter *et al.*[2,3] have determined the orientational distribution function from X-ray diffraction studies both for smectic and nematic phases. Order parameters and distribution function have been calculated by Bhattacharjee *et al.*[4] for nematic phase. Some X-ray data for the mesomorphic phase of PCBAV have been reported by Bhattacharjee *et al.*,[5] but no values for $f(\beta)$ or order parameters of this compound have been published so far.

2. EXPERIMENTAL METHODS

The compound PCBAV was obtained from Eastman Kodak Company. It was recrystallized from a concentrated solution in petroleum ether and benzene and then dried over calcium chloride in a vacuum desiccator. After recrystallization no change in transition temperatures was observed.

X-ray diffraction photographs were taken at different temperatures in the presence and absence of a magnetic field using Nickel filtered copper K_α radiation of wavelength 1.542 Å. A high temperature X-ray camera designed in our laboratory has been used to obtain the desired photographs in presence of a magnetic field.[6]

The temperatures were measured and regulated with an accuracy of ±0.5°C with the help of a thermocouple inserted in the block containing the sample. The sample in the form of bead was kept in the central hole on a non-magnetic stainless steel sample holder. Flat plate photographs were taken at different temperatures with exposure time 2 to 3 hours. The sample in the smectic phase was aligned by heating it to isotropic liquid and then cooling it down to the desired temperature in the presence of a magnetic field. The field was applied throughout the exposure time. Photographs were taken at different temperatures in a field of 5.8 Kilogauss. This magnetic field was found to be sufficiently strong to produce a monodomain sample as seen from the sharpness of the inner spots of the photograph with magnetic field (Figure 1). A photograph taken with a higher field of 6.5 kilogauss gave substantially the same pattern. Further details of the experimental technique have been given in our previous paper.[4]

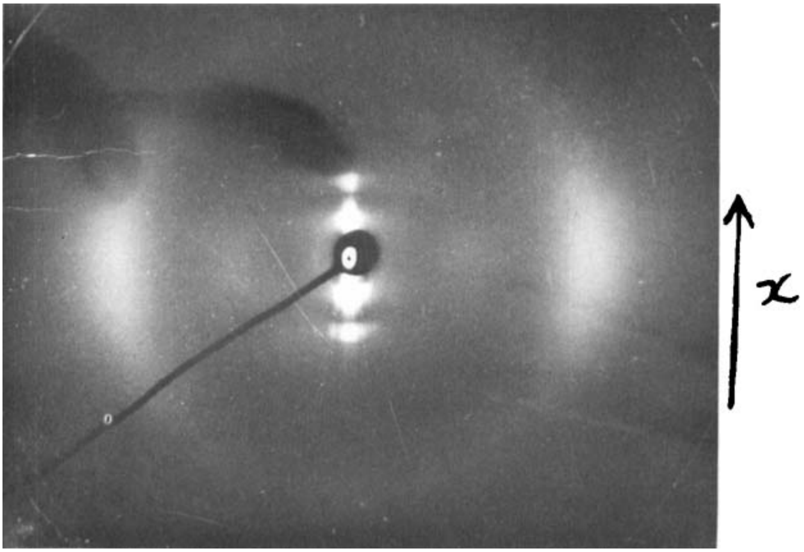


FIGURE 1 X-ray diffraction photograph of oriented sample of PCBAV at 69°C. Magnetic field (5.8 Kilogauss) used for orientation is in the x direction.

Texture and DSC studies

The texture of the compound was observed under polarizing microscope. The observations were performed under crossed polarizers with magnification 150×. Solid crystals were melted on clean glass surfaces and cover slip was used. While heating, phase changes were observed at 77°C and 115°C as given in literature. During cooling, smectic to solid phase transition was observed at 60°C. Focal conic texture of smectic A was observed during heating.[7] Both focal conic and simple fan shaped textures of smectic A were observed during cooling. We had not been successful with our conoscopic observations, so we cannot say defintely whether the phase is uniaxial or biaxial, but so far as the texture study is concerned the smectic phase is identified to be A. X-ray photographs as in Figure 1 also indicate that the phase is smectic A. DSC (differential scanning calorimetry) was done for the substance, phase changes were observed at the same temperatures as mentioned above.

3. THE DISTRIBUTION FUNCTION FOR THE ORIENTATION OF THE LONG MOLECULAR AXES

The analysis of the equatorial arcs in the diffraction pattern of S_A phase to determine $f(\beta)$, the orientational distribution function, have been done in the same way as described in our previous paper.[4] The appearance of arcs is assumed to arise from differently aligned regions with the local director $\bar{m}$ making an angle β with the average director $\bar{n}$. The intensity profile around the arc, $I(\theta)$ under this approximation can be written as,[3]

$$I(\theta) = C\int_{\beta=\theta}^{\beta=\pi/2} f_d(\beta) \sec^2\theta(\tan^2\beta - \tan^2\theta)^{-1/2} \sin\beta d\beta$$

where $f_d(\beta)$ describes the distribution function for the orientation β of a local cluster of the molecules which are assumed to have mutually perfect alignment and is expected, therefore, to be the same as the singlet distribution function $f(\beta)$. The above equation has been used to obtain $f_d(\beta)$ and hence the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$. A computer programme has been written by us to calculate $f(\beta)$ using the experimental values of $I(\theta)$, the detailed discussion of which is given in our paper on CPHB[4]. The normalized singlet orientation distribution function $f(\beta)$ is related to the pseudopotential $V(\beta)$ by the relation[8]

$$f(\beta) = \exp[-V(\beta)/kT] \bigg/ \int_0^{\pi/2} \exp[-V(\beta)/kT] \sin \beta d\beta \tag{1}$$

We have best fitted our $f(\beta)$ values to the form[8]

$$f(\beta) = Z^{-1} \exp\left(\sum_{L \text{ even}} a_L P_L(\cos \beta) \right), \tag{2}$$

where Z is the partition function, and thus obtain an idea about the pseudopotential. In our previous work[4] we also calculated the order parameters following Vainshtein,[9] but in the present paper we have omitted that calculation because of its approximate nature.

Translational order parameter of smectic A

Smectic A liquid crystals possess both orientational and translational order. Theory of smectic A order parameters have been proposed by a number of investigators. It was pointed out by McMillan[10] that the smectic layer distribution functions are directly related to the intensity of the layer reflections. The distribution function normal to the layers may be written[3]

$$f(z) = \frac{1}{d}\left(1 + \sum_{l=1}^{\infty} 2\ \tau_l \cos\,(2\pi lz/d) \right), \tag{3}$$

with

$$\tau_l = \langle \cos\,(2\pi lz/d) \rangle,$$

where d is the layer spacing, z is the displacement of the molecular center in the direction perpendicular to the layer plane and τ_l is the translational order parameter. The intensity of the (00l) layer reflection is

$$I(00l) = C\ \tau_l^2\ \langle \mathrm{F}(00l) \rangle^2, \tag{4}$$

where $F(00l)$ is the structure factor for a perfect layer and C is a constant.

For a gaussian distribution

$$F(z) = [2\pi\ \langle z^2 \rangle]^{-1/2} \exp[-z^2/2\ \langle z^2 \rangle] \tag{5}$$

$$\begin{aligned} \tau_l &= \langle \cos\,(2\pi lz/d) \rangle \\ &= \exp[-2\pi^2 l^2\ \langle z^2 \rangle / d^2] \\ &= \tau_1^{l^2} \end{aligned}$$

Equation (4) shows that intensity of the first order layer reflection is proportional to the smectic order parameter τ_1^2. If two or more reflections are observed then assumption of a constant value of $\langle F(00l)\rangle$ and a gaussian form for $f(z)$ enables us to obtain τ_1 and $\langle z^2\rangle^{1/2}$. In the S_A phase of PCBAV two layer reflections are observed as shown in the Figure 1. The inner ring is very close to the stop. We could not get an accurate value of the translational order parameter due to the inaccuracy in the measurement of the intensity of the inner ring.

However, we measured $I(002)$ and $I(001)$ at 69°C. The intensities were corrected for Lorentz and polarization factors. Use of the Equation (4) gives $\tau_2/\tau_1 = 0.7870$ and assumption of a gaussian distribution for $f(z)$ gives $\tau_1 = 0.9233$ and $\langle z^2\rangle^{1/2} = 1.56$ Å.

4. 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. The photographs in the smectic range were taken both in presence and absence of magnetic field. Procedure for alignment in magnetic field is given in section 2 of this paper..Typical diffraction photographs of oriented and unoriented samples are shown in Figure 1 and Figure 2, respectively. Diffraction patterns of unoriented samples show a sharp inner ring with its second order and a diffuse outer ring, typical of smectic C or smectic A type. The pattern of the oriented sample consists of two diffuse outer maxima, which shows that the structure within the layers is undoubtedly disordered. The (001) and (002) diffraction spots are sharp. From the diffraction pattern of the oriented sample it is obvious that the smectic phase is of A type. The line joining the outer maxima is perpendicular to the line joining (001) maxima; which shows that molecules are perpendicular to the smectic planes.

Average distance between neighboring molecules (D) and layer spacing (d) are calculated from X-ray diffraction photographs as given by deVries.[11] Temperature dependence of these parameters have also been discussed by him.[12,13] Variation of the lateral spacing D with temperature is shown in Figure 3. It is seen that the application of magnetic field causes a decrease in the intermolecular distance. With the help of a stereo model unit (Prentice Hall, Inc., West Nyack, N.Y. 10984) we have measured the molecular length L in their completely extended

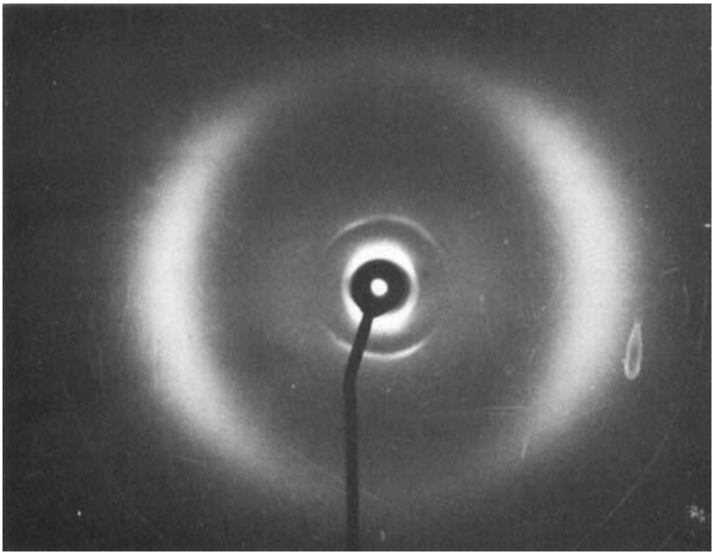


FIGURE 2 X-ray diffraction photograph of a sample of PCBAV at 95°C without application of magnetic field.

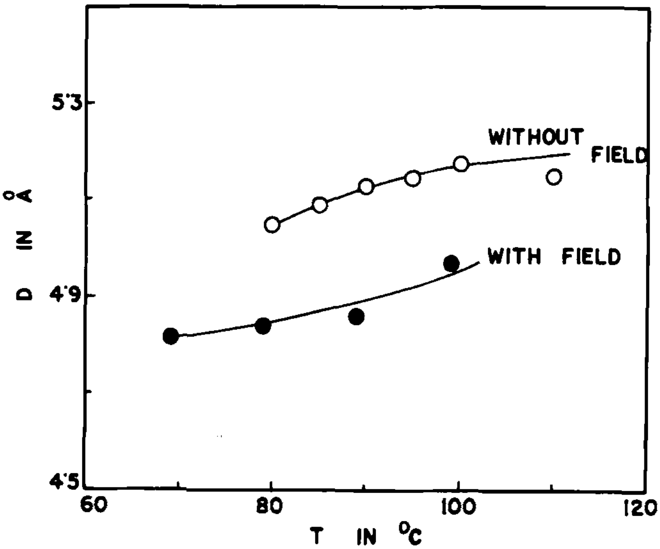


FIGURE 3 Variation of intermolecular distance, *D*, with temperature, ○ without magnetic field, ● with magnetic field.

form and found the value to be 26 Å. The experimental *d* value decreases with increasing temperature and it varies between 27.3 Å at 80°C to 25.5 Å at 110°C. It seems that as temperature rises the thermal vibrations of the flexible part of the molecule cause a decrease in the layer thickness.

In earlier paper[5] based on only X-ray data, we have reported that PCBAV seems to have B, C and A phases. But later on, texture studies and DSC results did not confirm this. We repeated the whole experiment both in the absence and in the presence of magnetic field and identified the mesophase to be smectic A.

Normalized orientational distribution functions $f(\beta)$ as a function of β at different temperatures, as obtained from experimental intensity values, are shown in Figure 4. We expect, as temperature decreases, the

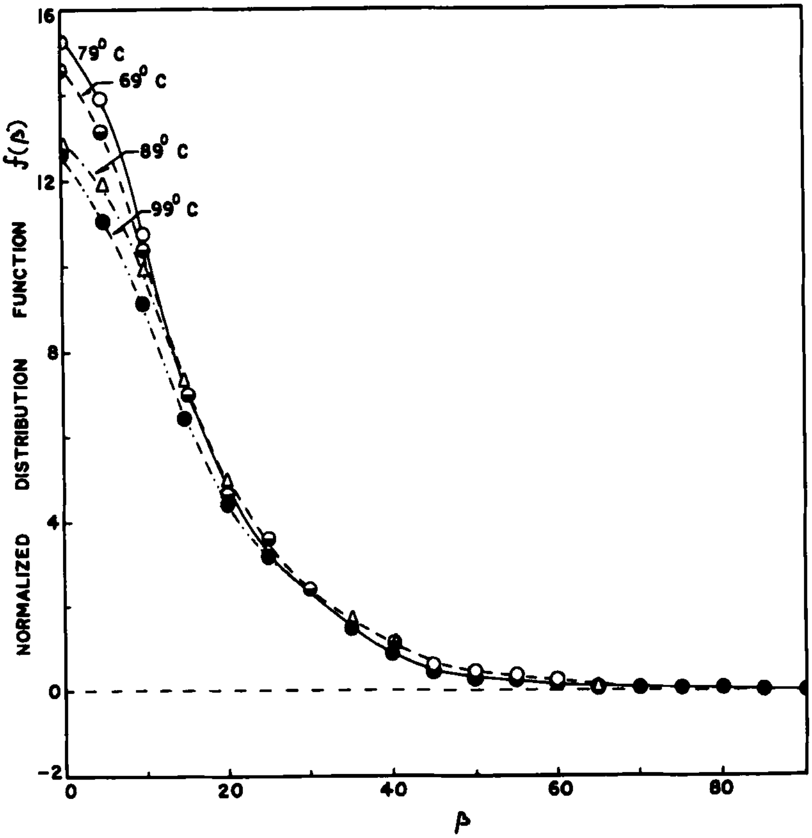


FIGURE 4 Normalized orientational distribution function $f(\beta)$ against angle β, at ◒ 69°C, ○ 79°C, △ 89°C, ● 99°C.

function to become more peaked at $\beta = 0°$. Our $f(\beta)$ curves generally conform to this idea, except that the curve at 69°C is less peaked than that at 79°C. Since DSC, X-ray and texture studies do not show any phase transition between 79°C and 69°C while cooling PCBAV at 69°C is in smectic A phase. However, we are unable to explain the cause of this anomaly.

Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at different temperatures are shown in Figure 5 together with the Maier-Saupe (MS) mean field theoretical values. The experimental order parameter values are estimated to be accurate within ±.02. Both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values are found to be larger than MS theoretical values.[8] Anomalous nature of the $f(\beta)$ at 69°C is reflected in the values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at that temperature. Leadbetter and Wrighton[2] have calculated $\langle P_2 \rangle$ values in the smectic A phase for TBBA and 408 from X-ray diffraction data. Contrary to our observations, they found that the experimental $\langle P_2 \rangle$ values are lower than MS theoretical values. According to them, simple mean field theory does not predict correctly the magnitude and temperature dependence of $\langle P_2 \rangle$ for smectic phase.

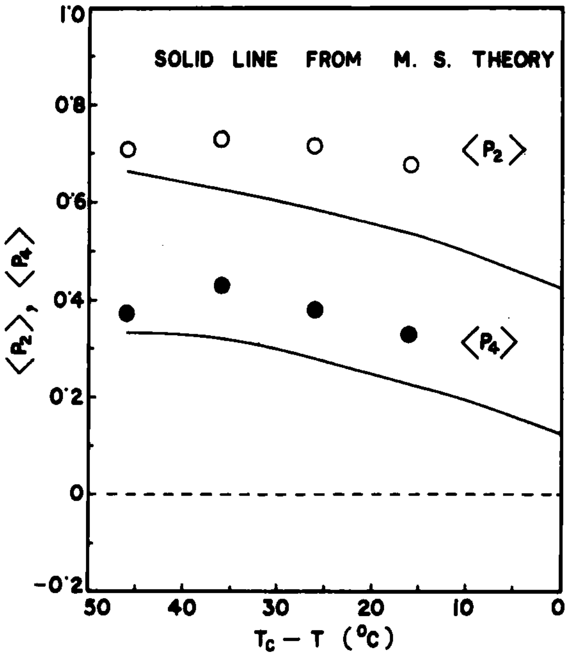


FIGURE 5 Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ against $(T_C - T)$, ○ $\langle P_2 \rangle$, ● $\langle P_4 \rangle$. Full lines from Maier-Saupe mean field theory.

We have calculated the angular part of the mean field potential written in the form

$$V(\beta) = \sum_{L \text{ even}} b_L \langle P_L \rangle P_L(\cos \beta)$$

from least squares fitting to $\ln f(\beta)$ values (Eq. 2). The coefficients b_L are assumed to be temperature independent in view of small temperature range of only 30°C. Taking all four temperature data, the pseudopotential can be written as (up to $P_4(\cos \beta)$ term).

$$\begin{aligned} V(\beta)/k = &-(2447 \pm 211) \langle P_2 \rangle P_2(\cos \beta) \\ &+(1063 \pm 699) \langle P_4 \rangle P_4(\cos \beta) \end{aligned}$$

So, it is seen that the standard deviation for b_2 is reasonable while that of b_4 is large, suggesting the breakdown of the idea of the Legendre polynomial expansion of the pseudopotential. This is in accordance with out earlier results on a nematic liquid crystal.[4]

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References

1. P. Delord and J. Falgueirettes, *C.R. Hebd. Sean. Acad. Sci. Paris*, **260**, 2468 (1965).
2. A. J. Leadbetter and P. G. Wrighton, *J. Physique Colloq.*, **40**, C3-234 (1979).
3. A. J. Leadbetter and E. K. Norris, *Molecular Physics*, **38**, 669 (1979).
4. B. Bhattacharjee, S. Paul and R. Paul, *Molecular Physics*, **44**, 1391 (1981).
5. B. Bhattacharjee, A. Zeminder and S. Paul, *Proc. Nucl. Phys. & Solid State Phys. Symp. (India)*, **21C**, 420 (1978).
6. B. Jha and R. Paul, *Proc. Nucl. Phys. & Solid State Phys. Symp. (India)*, **19C**, 481 (1976).
7. D. Demus and L. Richter, *Texture of Liquid Crystals*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (1978).
8. E. B. Priestly, Peter J. Wojtowicz and Ping Sheng, *Introduction to Liquid Crystals*, Plenum Press, New York (1975), Chapters 3 & 4.
9. B. K. Vainshtein, *Diffraction of X-rays by Chain Molecules*, Elsevier Publishing Co., Amsterdam (1966).
10. W. L. McMillan, *Phys. Rev.*, **A6**, 936 (1972).
11. A. de Vries, *Mol. Cryst. Liq. Cryst.*, **10**, 219 (1970).
12. A. de Vries, A. Ekachai and N. Spielberg, *J. Physique Colloque*, **40**, C3-147 (1979).
13. A. de Vries and S. B. Qadri, *Liquid Crystals*, Editor Chandrasekhar, Heyden; London (1979), p. 179.