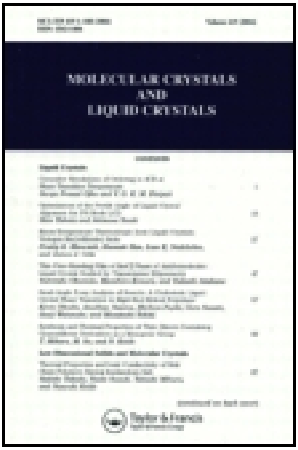

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Orientational Distribution Function and Order Parameters of Two 4′-Alkoxy-4-Cyanobiphenyls in Mesomorphic Phase

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X-ray diffraction studies on samples of 4′-Pentyloxy-4-Cyanobiphenyl and 4′-Octyloxy-4-Cyanobiphenyl over the entire mesomorphic range are reported in this paper. A magnetic field was used to align samples. The orientational distribution functions $f(\beta)$ have been calculated from the angular distribution of X-ray intensities. Orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been calculated and compared with Maier–Saupe theoretical values. Expressions for the angular part of the pseudopotentials have been obtained from the temperature variation of $f(\beta)$. The intermolecular distances D have been calculated from the experimental data and it is found that D is significantly smaller for well aligned samples. The apparent molecular length in the nematic phase and the layer thickness in the smectic phase have also been determined and are found to be about 1.4 times larger than the true molecular length in the fully extended form. This is in accordance with the findings from other cyano compounds.

INTRODUCTION

X-ray diffraction measurements on unoriented and oriented samples of two biphenyl compounds at different temperatures have been made and reported in this paper. The compounds are two homologues of the series 4′-Alkoxy-4-Cyanobiphenyl, namely pentyloxy cyanobiphenyl and octyloxy cyanobiphenyl (5OCB and 8OCB in short). The sample

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5OCB has only a nematic phase while the sample 8OCB possesses both smectic and nematic phases.

The orientational distribution function $f(\beta)$ have been calculated and the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been derived from the diffraction photographs of the oriented samples.

Intermolecular distance for the oriented and unoriented samples, length of the molecule and the layer thickness in case of Sm A have also been calculated.

Orientational distribution function and order parameters from X-ray data for several samples have been reported from different laboratories.[1,2]

The structural formula of the compounds are given below

$$CH_3 \cdot (CH_2)_4 \cdot O \cdot (C_6H_4)_2CN \quad (5OCB)$$

$$CH_3 \cdot (CH_2)_7 \cdot O \cdot (C_6H_4)_2CN \quad (8OCB)$$

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

$$\text{For 5OCB Solid} \overset{47.5°C}{\rightleftharpoons} \text{Nematic} \overset{67.5°C}{\rightleftharpoons} \text{Isotropic}$$

$$\text{For 8OCB Solid} \overset{54.5°C}{\rightleftharpoons} \text{Smectic} \overset{79.5°C}{\rightleftharpoons} \text{Isotropic}$$

By X-ray diffraction and texture studies the phase transition determined by us are as follows

$$\text{For 5OCB Solid} \underset{\sim 31.5°C}{\overset{47.5°C}{\rightleftharpoons}} \text{Nematic} \overset{67.5°C}{\rightleftharpoons} \text{Isotropic}$$

$$\text{For 8OCB Solid} \underset{\sim 35°C}{\overset{54.5°C}{\rightleftharpoons}} \text{Smectic A} \overset{67°C}{\rightleftharpoons} \text{Nematic} \overset{79.5°C}{\rightleftharpoons} \text{Isotropic.}$$

Leadbetter *et al.*[3] have determined the Smectic layer thickness of 8OCB and Alsniels *et al.*[4] have reported the X-ray critical scattering at the nematic-smectic A transition. But uptil now values of order parameters and distribution function of 5OCB and 8OCB have not been reported.

In our previous works[1,5] we have discussed details about the analysis of the equatorial arcs in the diffraction patterns of Smectic A and nematic phases to determine $f(\beta)$, the orientational distribution function.

The intensity profile $I(\theta)$ around the diffuse equational arc is related to the distributed function as follows,[6]

$$I(\theta) = \int_{\beta=0}^{\pi/2} f_d(\beta) \sec^2 \theta \, (\tan^2 \beta - \tan^2 \theta)^{-1/2} \sin \beta d\beta \tag{1}$$

where $f_d(\beta)$ describes the distribution function for the orientation β of a small volume relative to the director $\bar{n}(\beta = 0)$. The assumption has been made in obtaining the above expression that the molecules are rigid and rod like. It was shown that $f_d(\beta)$ may be expected to be close to the true singlet orientational distribution function $f(\beta)$. From the above equation using a numerical method[1] $f(\beta)$ 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 by the relation

$$f(\beta) = Z^{-1} \exp[-V(\beta)/kt] \tag{2}$$

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

$$f(\beta) = \exp[\Sigma a_L P_L(\cos \beta)] \tag{3}$$

for L even and thus obtained L an idea about the nature of the pseudopotential. In our previous paper[5] we have calculated the translational order parameter in smectic A phase of PCBAV from the second order layer reflection. However, the second order layer reflection from 8OCB in Smectic A phase is very weak (almost absent) and so we have not attempted to calculate the translational order parameter in the present paper.

EXPERIMENTAL METHOD

The samples 5OCB and 8OCB were supplied to us by M/s. Hoffmann-La-Roche and Co., Basel, Switzerland. Both the substances were purified by recrystallizing from acetone and was then dried in a vacuum desiccator. X-ray diffraction photographs of both the samples in presence and absence of magnetic fields were taken using Ni-filtered CuK$_\alpha$ radiation of wavelength 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.[7]

The sample in the nematic phase was aligned by heating it to the desired temperature in the presence of magnetic field of 5.8 kilogauss using an electromagnet and 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 the magnetic field. Further, experimental details could be obtained from our previous work.[1,5]

From polarizing microscopic study,[5,8] it is found that the sample 5OCB possesses typical thread like texture of nematic phase over the whole range of temperature and the sample 8OCB shows focal conic and fan textures of Smectic A phase and thread like texture of nematic phase. The transition temperatures as observed by us are given in introduction of this paper.

RESULTS AND DISCUSSIONS

(a) Intermolecular distance, apparent molecular length and layer thickness

The X-ray diffraction photographs of the samples 5OCB and 8OCB at different temperatures (starting from solid phase at room temperature to isotropic phase and also in the supercooled mesomorphic phase) were taken both in the presence and in the absence of the aligning magnetic field. The photographs of 5OCB in the presence of the magnetic field show typical pattern of oriented nematic phase having two diffuse outer maxima and two inner maxima perpendicular to the outer

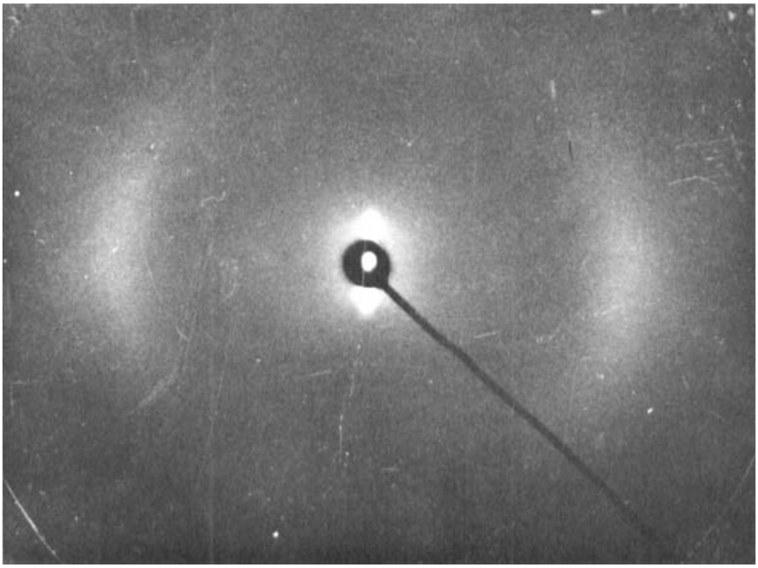

FIGURE 1 X-ray diffraction photograph of an oriented sample of 8OCB in the smectic phase at 40°C.

pair. Having two different phases, the photographs of 8OCB in the presence of the magnetic field show two different patterns. Whereas the photographs in the nematic phases are similar in nature to those obtained from 5OCB to the smectic phase photographs consist of two diffuse outer maxima (showing disordered structure within the layer) and two sharp inner spots from (001) reflection. The line joining the inner spots is perpendicular to the line joining the outer maxima indicating that the mesophase concerned is of Smectic A type (Figure 1).

Intermolecular distances *D* for oriented (in presence of the magnetic field) and unoriented (in absence of the magnetic field) samples the apparent length of the molecules *l*, and the layer thickness *d* in the case of the smectic phase of 8OCB at different temperatures have been calculated using expressions given by deVries.[9] Variation of *D* with temperature and magnetic field are shown in Figure 2 and Figure 3 for 5OCB and 8OCB samples respectively. It is found that for both the samples

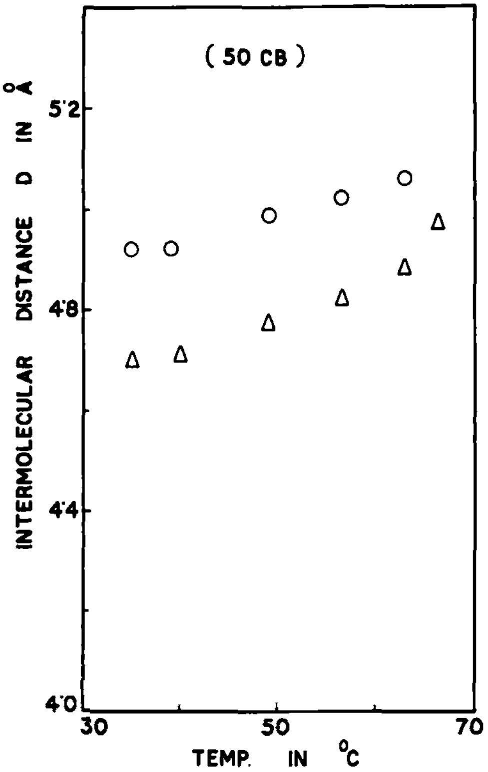

FIGURE 2 Variation of intermolecular distance *D* with temperature for 5OCB; triangles: with magnetic fields; circles: without magnetic field.

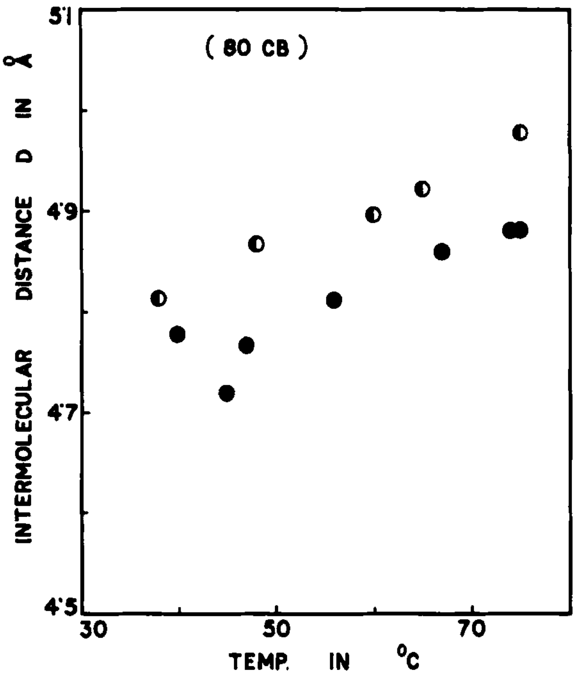

FIGURE 3 Variation of intermolecular distance D with temperature for 8OCB; closed circles: with magnetic field; half closed circles: without magnetic field.

the application of magnetic field causes a decrease in the intermolecular distance. This is in accordance with our previous finding in PCBAV.[5]

The apparent decrease in the value of D in magnetic field is not an artifact arising from the geometry of diffraction. We have determined the locus of the maximum intensity of the outer crescent in the X-ray diffraction photographs from aligned samples and find that the locus is part of a circle within experimental inaccuracy of about 0.5%. For about half the circle intensities are too low to make meaningful measurements of the maximum. Since the difference in D values with and without magnetic field is between 2 and 3%, we think we are observing a real change in D.

D also changes with increasing temperature and remains fairly constant in the supercooled state. No change in D value is observed in 8OCB at the Nematic–Smectic phase transition.

The dependence of l on temperature is not very pronounced, it varies from 24 Å to 25 Å in the case of 5OCB. The length L of 5OCB molecule in its completely extended form is found to be 17.5 Å with the help of a stereomodel unit. Thus l/L value is about 1.4 which is in accordance with some earlier works[1,10] on cyano compounds. The increase in apparent length may be due to the association in the nematic phase molecules having large dipole moment. The variation of the layer thickness d with temperature in the smectic phase of 8OCB is very slight and its average value is approximately 32.6 Å. The length of the molecule of 8OCB in its fully extended form is 23.5 Å. The ratio d/L is again about 1.4. Leadbetter *et al.*[3] also found the same result for 8OCB and some other cyano compounds. This shows that a bilayer structure must be formed in the smectic phase of 8OCB. In the nematic phase of 8OCB the value of l is found to be 31.75 Å. The reason for the difference between the apparent and the measured length of the molecule is the same as for 5OCB.

(b) Distribution function and order parameters

Variation of $f(\beta)$ with β as obtained from $I(\theta)$ for 5OCB at 49° is shown in Figure 4. The corresponding $f(\beta)$ vs β plot for 8OCB at 74°C (nematic phase) is given in Figure 5. For both 5OCB and 8OCB it was found that the orientational distribution function spreads out at higher temperatures as anticipated.

The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for 5OCB and 8OCB at different temperatures are shown in Figure 6 and Figure 7 respectively. The order parameter values are estimated to be accurate within ±.02 except in the case of supercooled 8OCB where the uncertainty is somewhat greater. The first order Smectic A–Nematic phase transition in 8OCB is observed at 67°C which is clearly indicated by discontinuities in $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values.[13]

Experimental $\langle P_2 \rangle$ values for both the compounds are found to be larger than Maier–Saupe (MS) theoretical values. As explained earlier[1] this may be due to short range dipole–dipole interactions. Experimental $\langle P_4 \rangle$ values for 5OCB and the nematic phase of 8OCB are lower than the MS values. This discrepancy in $\langle P_4 \rangle$ values is not unusual.[1] In the smectic phase of 8OCB experimental $\langle P_4 \rangle$ values seem to agree with MS values within experimental uncertainty.

As in our earlier paper,[1] we have calculated the mean field potential for rigid cylindrical molecules in the form

$$V(\beta) = \sum_{L\ \mathrm{even}} b_L \langle P_L \rangle P_L(\cos\beta) \tag{4}$$

The coefficients b_L, which are calculated from a_L values (Eq. 3), are assumed to be temperature independent in view of narrow temperature

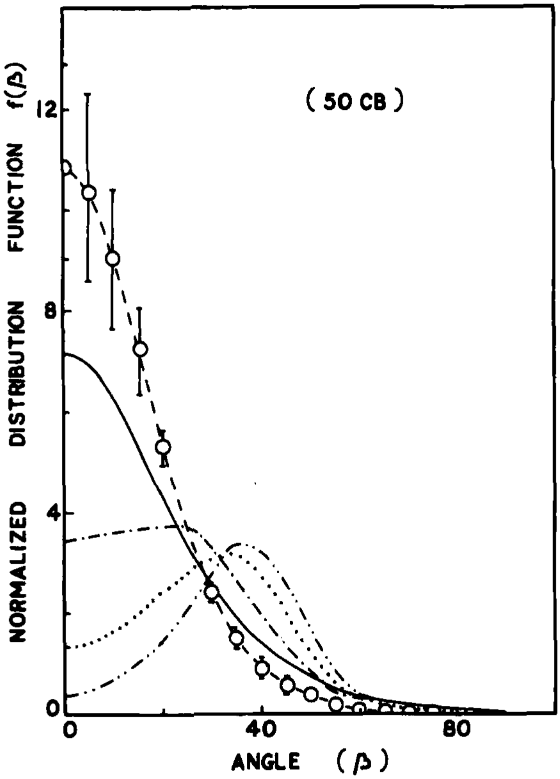

FIGURE 4 Normalized orientational distribution function $f(\beta)$ against orientation angle β for 5OCB at 49°C. Calculated $f(\beta)$ values: ——from X-ray data; ------from pseudopotential, $V(\beta)/k = -(2460 \pm 350)\langle P_2\rangle P_2(\cos\beta)$; ········from pseudopotential, $V(\beta)/k = -2460\langle P_2\rangle P_2(\cos\beta) + 3900\langle P_4\rangle P_4(\cos\beta)$; —··—··—from pseudopotential, $V(\beta)/k = -2460\langle P_2\rangle P_2(\cos\beta) + (3900 + 1500)\langle P_4\rangle P_4(\cos\beta)$; —·—·—from pseudopotential, $V(\beta)/k = -2460\langle P_2\rangle P_2(\cos\beta) + (3900 - 1500)\langle P_4\rangle P_4(\cos\beta)$.

ranges concerned. Taking the six temperature data the angular part of the pseudopotential upto $P_4(\cos\beta)$ term for 5OCB can be written as:

$$\begin{aligned} V(\beta)/k = &-(2460 \pm 350)\langle P_2\rangle P_2(\cos\beta) \\ &+(3900 \pm 1500)\langle P_4\rangle P_4(\cos\beta) \end{aligned} \qquad (5)$$

Equation (5) has the form proposed by Humphries *et al.*[11] It is seen that the standard deviation for b_4 is quite large which suggests the breakdown of the assumptions inherent in the mean field theory. In Figure 4 we have also shown calculated normalized $f(\beta)$ values at 49°C as obtained from several pseudopotentials.

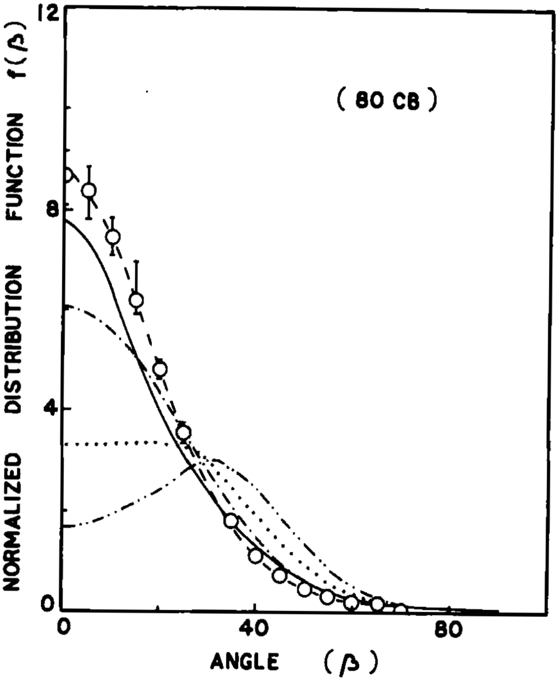

FIGURE 5 Normalized orientational distribution function $f(\beta)$ against orientation angle β for 8OCB at 74°C. Calculated $f(\beta)$ values: ——from X-ray data; ------from pseudopotential, $V(\beta)/k = -(2300 \pm 130)\langle P_2\rangle P_2(\cos\beta)$; ········from pseudopotential, $V(\beta)/k = -2300\langle P_2\rangle P_2(\cos\beta) + 4400\langle P_4\rangle P_4(\cos\beta)$; —··—··—from pseudopotential, $V(\beta)/k = -2300\langle P_2\rangle P_2(\cos\beta) + (4400 + 2700)\langle P_4\rangle P_4(\cos\beta)$; —·—·—from pseudopotential, $V(\beta)/k = -2300\langle P_2\rangle P_2(\cos\beta) + (4400 - 2700)\langle P_4\rangle P_4(\cos\beta)$.

In the case of 8OCB in the nematic phase we have only two X-ray diffraction photographs in the narrow temperature range of 12.5°C. Taking data from these two temperatures the angular part of the mean field potential can be written as

$$V(\beta)/k = -(2300 \pm 130)\langle P_2\rangle P_2(\cos\beta) + (4400 \pm 2700)\langle P_4\rangle P_4(\cos\beta) \tag{6}$$

In Figure 5 we have included the calculated $f(\beta)$ values at 74°C obtained from several pseudopotential. A study of Figure 4 and Figure 5 indicates that the inclusion of the $P_4(\cos\beta)$ term in the pseudopotential results in worse agreement with the experimental $f(\beta)$ values. This is

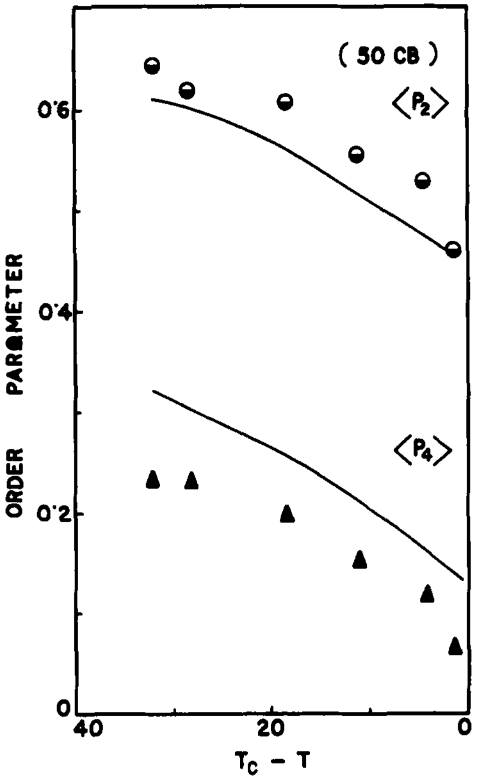

FIGURE 6 Variation of order parameters of 5OCB with temperature. Full line Maier-Saupe theoretical values. Half filled circles: experimental $\langle P_2 \rangle$ values; triangles: experimental $\langle P_4 \rangle$ values.

contrary to our previous work,[1] though nothing definite can be said in view of large uncertainty in b_4 values. Permanent dipole-permanent dipole interactions are present which may modify the pseudopotential to a form different from the form assumed by us (Eq. 4).[12]

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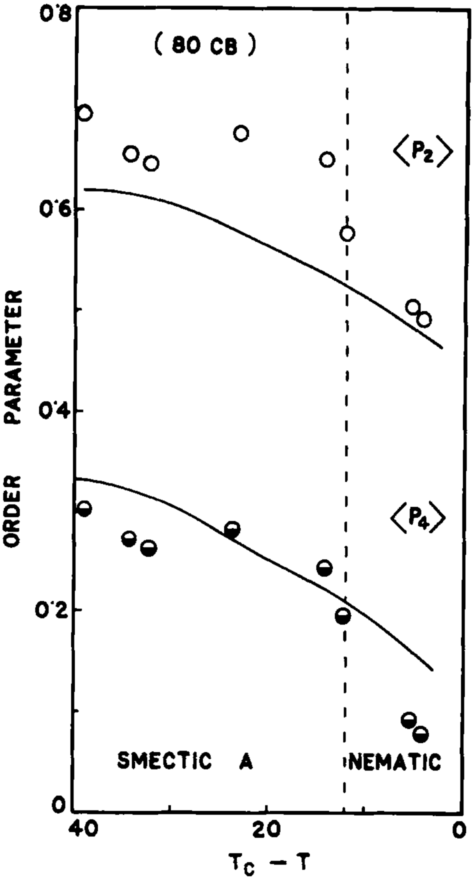

FIGURE 7 Variation of order parameters of 8OCB with temperature. Full line Maier-Saupe theoretical values. Open circles: experimental $\langle P_2 \rangle$ values; half closed circles: experimental $\langle P_4 \rangle$ values.

References

1. B. Bhattacharjee, S. Paul and R. Paul, *Molecular Physics*, **44**, 139 (1981).
2. A. J. Leadbetter and P. G. Wrighton, *J. Phys.*, Colleque, **40**, C3-234 (1979).
3. A. J. Leadbetter, J. C. Frost and J. P. Gaughan, *J. Phys.*, **40**, 375 (1979).
4. J. Alsniels, R. J. Birgenea, N. Kaplan, J. D. Litster and C. R. Safinya, *Bull. Am. Phys. Soc.*, **23**, 352 (1978).
5. B. Bhattacharjee, R. Paul and S. Paul; Communicated for Publication in *Mol. Cryst. Liq. Cryst.*

6. A. J. Leadbetter and E. K. Norris, *Mol. Phys.*, **38**, 669 (1979).
7. B. Jha and R. Paul, *Proc. Nucl. Phys. & Solid State Phys. Symp.*, (India) **19C**, 181 (1976).
8. D. Demus and L. Richter, *Texture of Liquid Crystals*, Verlag Chemie, Wienheim (1978).
9. A. deVries, *Mol. Cryst. Liq. Cryst.*, **10**, 219 (1970).
10. A. J. Leadbetter, R. M. Richardson and C. N. Colling, *J. Phys.*, (Paris) **36**, 1-37 (1975).
11. R. L. Humphries, P. G. James and G. R. Luckhurst, *J. Chem. Soc. Faraday Trans. II*, **68**, 1031 (1972).
12. N. V. Madhusudan and S. Chandrasekhar in *Pramana*, Suppl. **1**, pages 57–68, editor S. Chandrasekhar, Indian Academy of Science, Bangalore (1975).
13. J. W. Doane, R. S. Parker, B. Cvikl, J. L. Johnson and D. L. Fishel, *Phys. Rev. Letts.*, **28**, 1964 (1972).