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X-ray diffraction and optical studies of an oriented Schiff's base liquid crystal

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In this paper we have reported results of X-ray diffraction studies and refractive index measurements of the compound *p-n*-butoxybenzylidene-*p'-n*-butylaniline (BBBA). The compound BBBA possesses three smectic phases, cybotactic nematic phase and ordinary nematic phase. Orientational order parameters of the aligned sample have been determined using the X-ray data and refractive indices values. $\langle P_2 \rangle$ values determined from optical measurements agree with the Maier-Saupe theoretical values but $\langle P_2 \rangle$, $\langle P_4 \rangle$ determined from X-ray intensity measurements differ from the theoretical values.

1. Introduction

p-n-Butoxybenzylidene-*p'-n*-butylaniline (BBBA), a polymorphic Schiff's base, is a compound of much interest and a number of studies have been made on this compound by different workers. Orientational order parameters of EBBA, BBBA and PBBA were determined by Kirov *et al.* [1] from an infrared dichroism study. Fujimura *et al.* [2] measured the degree of orientational order of these three compounds by studying the N.M.R. spectra. Ultrasonic studies on this compound were undertaken by Rao and Murty [3]. Goodby *et al.* [4] studied the compound by optical microscopy and a miscibility method. So far no X-ray study or refractive index measurements have been reported. We therefore investigated the title compound using these techniques.

2. Theoretical backgrounds

2.1. Calculation of the distribution function and the order parameter from X-ray diffraction photographs

The orientational distribution functions, according to the rules of statistical mechanics, are given in terms of the potential function by the following relation

$$f(\beta) = Z^{-1} \left[\exp \left(- \frac{v(\beta)}{kT} \right) \right],$$

where Z is the single molecule partition function and is given by

$$Z = \int_0^{\pi/2} \exp \left[- \frac{v(\beta)}{kT} \right] \sin \beta \, d\beta.$$

For a system of rigid rods the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are defined by

$$\langle P_L \rangle = \int_0^{\pi/2} P_L(\cos \beta) f(\beta) \sin \beta \, d\beta,$$

with $L = 2, 4$. Leadbetter and Norris [5] related the intensity $I(\psi)$ around the diffuse equatorial arc with the orientational distribution function, by the following equation

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

where $f_d(\beta)$ now describes the distribution function of the cluster in which the molecules are perfectly aligned, rather than the true singlet orientational distribution function. It has been shown [5] that $f_d(\beta)$ may be approximated by the singlet orientational distribution function. We have fitted our $f(\beta)$ values to the form

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

where Z has been treated as a constant within the small temperature range considered. The detailed discussions of all the calculations are given in our previous work [6].

2.2. Calculation of the order parameter from the refractive index measurement

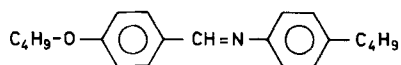
The birefringence of liquid crystals is the visible result of their long range order and is defined only for a uniformly ordered domain. Nematic liquid crystals are optically uniaxial and strongly birefringent. Their refractive indices are very sensitive to temperature. Therefore by studying the birefringence we can easily determine the order parameters and their variation with temperature. We make use of Vuk's formula [7] to calculate principal molecular polarizabilities (α_e, α_o) from refractive indices (n_e, n_o) and the order parameter (S) was calculated using the relation [8]

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}},$$

where α_{\parallel} and α_{\perp} are the polarizabilities parallel and perpendicular to the long axis.

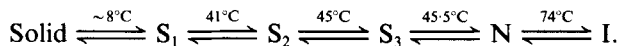
3. Experimental method

A purified (by vacuum distillation) and recrystallized sample of BBBA (I) was supplied by the late Professor M. Wada of Tohoku University, Japan [9].



(I)

The transition temperatures are



The melting behaviour was examined using a polarizing microscope (Towa, India) with a hot stage attachment designed by the authors. Observations were performed under crossed polarizers with a magnification $150\times$. A sample was taken between two cover slips. Since Schiff's bases are very sensitive to atmospheric moisture care was taken to minimize the exposure to the atmosphere.

3.1. X-ray study

A detailed description of the experimental set-up used for the X-ray diffraction study is given elsewhere [10]. Diffraction photographs were taken from room temperature

to the isotropic phase at 5°C intervals and also for both aligned and unaligned samples. Photographs of unaligned samples were taken using a flat plate camera. To align the sample we heated it to the isotropic liquid state and cooled it very slowly to the desired temperatures in the presence of a magnetic field of 6.1 kG . Photographs were taken with X-rays perpendicular to the field direction with the magnetic field being used throughout the exposure time. The specimen was enclosed in a glass capillary of 1 mm diameter. The temperatures were measured and regulated with an accuracy of $\pm 0.5^{\circ}\text{C}$ with the help of a thermocouple inserted in the block containing the sample.

In order to determine the various parameters, the photographs were scanned, both linearly and circularly, by an optical micro densitometer (VEB Carl Zeiss Jena, Model MD 100) equipped with an auto recording facility. The measured optical densities were converted to X-ray intensities with the help of a calibration curve following Klug and Alexander [11].

3.2. Refractive index measurement

Refractive indices were measured with the help of hollow glass prisms with a refracting angle of about 1° . The prisms were made up of optically flat glass plates. The plates were rubbed parallel to one of their edges, they were then treated with 1 per cent polyvinyl alcohol solution and then dried. Again they were rubbed along the same direction as before. The prisms were formed keeping the treated surface inside and the rubbing directions parallel to the edge of the prism. The prisms were precalibrated by measuring the refractive indices of distilled water and glycerine at different temperatures. The liquid crystal sample was allowed to flow in by melting a few crystals at the top. The combination of rubbing and flow, together with the magnetic field of strength $\sim 5\text{ kG}$ in the direction of rubbing, produced a homogeneous nematic specimen with the optic axis parallel to the edge of the prism. The experimental details of this procedure are given in the paper of Zeminder *et al.* [12]. The prism was placed inside a brass thermostat heated electrically. The refractive indices were measured for different wavelengths from a mercury lamp. The densities of the samples were determined by putting the weighted samples inside a glass capillary tube which was then placed in a thermostat. The length of the column was measured by a travelling microscope. The densities were calculated after correcting for the expansion of glass.

4. Results and discussion

4.1. Identification of phases

The samples were heated slowly and the textures were observed both during heating and cooling. From room temperature to 41°C a mosaic texture was found, this phase may be a S_G phase. From 41°C to 45°C the variant mosaic texture was obtained indicating the phase to be a smectic B phase. Bâtonnets were observed within a very small temperature range (0.5°C), so the S_A phase is present. From 45.5°C to 74°C schlieren texture was found which is characteristic of the nematic phase.

Aligned diffraction photographs at 50°C and 70°C are shown in figure 1. The intensity of the inner diffraction ring of the photograph at 50°C (figure 1 (a)) is greater than that of the outer ring which is generally found in the orthogonal or skewed cybotactic nematic phase (N_{OC} or N_{SC}) [13]. After 59°C the diffraction patterns correspond to the ordinary nematic phase (figure 1 (b)). So BBBA possesses both the cybotactic nematic phase and the ordinary nematic phase. Rao and Murty [3] also reported the presence of both types of nematic phase in this sample. The inner

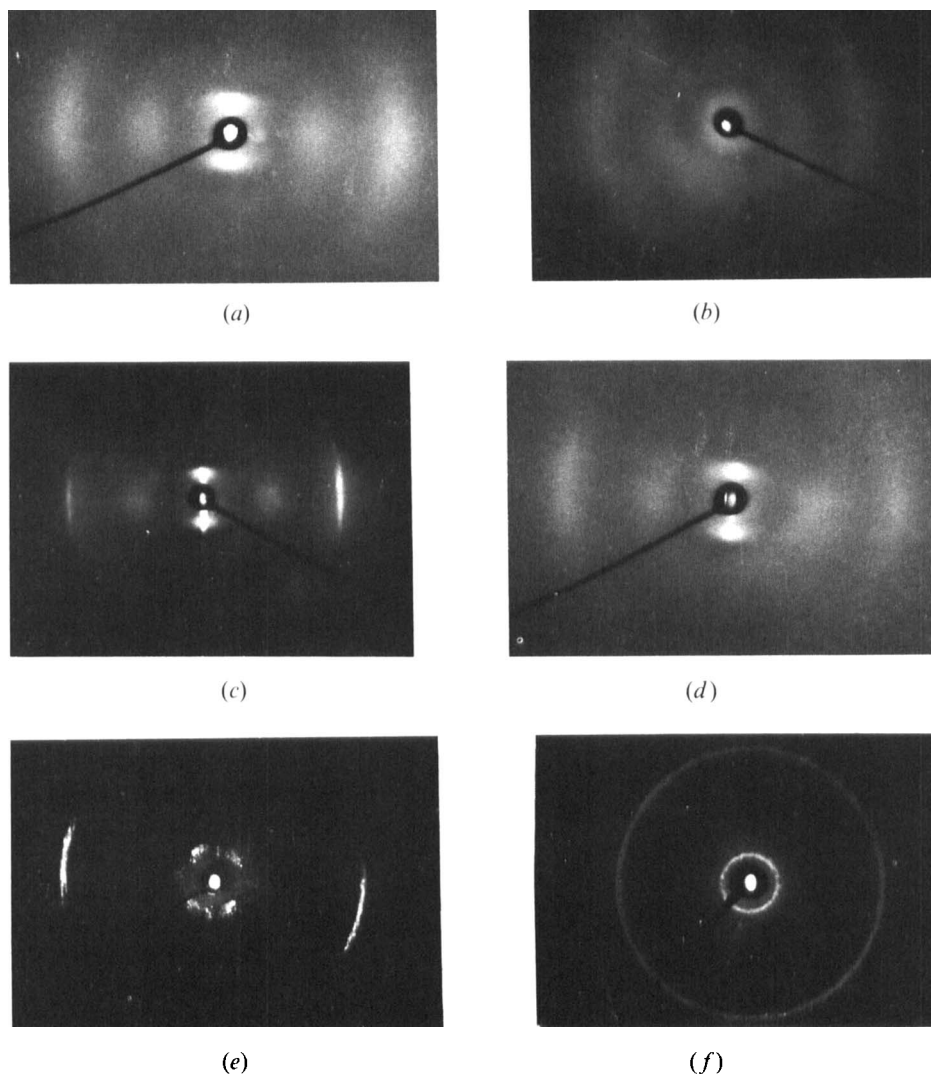
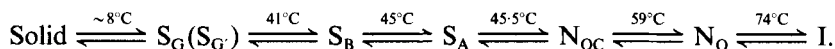


Figure 1. Aligned X-ray diffraction photograph at: (a) 50°C; (b) 70°C; (c) 43°C; (d) 45°C; (e) 19°C; and (f) 19°C (non-aligned).

diffraction ring splits up into four discrete spots in the aligned N_{SC} phase which is not observed in our photographs. Moreover the next two phases (S_A and S_B) are orthogonal (see later). So we identified the cybotactic phase as orthogonal (N_{OC}). Figure 1(c) is the aligned photograph at 43°C, this shows one sharp inner maxima in the form of a bar and one sharp outer ring, the angle between the maxima of the two rings being 90°. The S_2 phase is unequivocally a smectic B phase. Figure 1(d) is the diffraction photograph at 45°C, it shows the characteristics of both the N_{OC} and S_A phases. In our set-up we cannot take photographs within the range of 0.5°C. But from the texture result and from the nature of this photograph we presume that there is an S_A phase with a very small temperature range near 45°C, so S_3 is an S_A phase. Figures 1(e) and 1(f) are, respectively, the aligned and non-aligned photographs in the S_1 phase. The non-aligned photograph shows several hkl reflections, very closely

spaced of which two are strong and others are weak reflections. The aligned photograph is taken with the X-ray beam parallel to the smectic planes, so the outer ring does not break up into six diffraction maxima. The inner ring is split and second order spots are also present. So this phase is a long range three-dimensional ordered tilted phase with pseudo-hexagonal packing within the layers [14]. From the photographs it was not possible to ascertain the nature of the tilt, so S_t may be S_G or S_C . X-ray diffraction patterns of the solid phase could not be taken as we did not have facilities for taking photographs below room temperature.

Thus from texture and X-ray diffraction studies the phases observed in BBBA, which are in good agreement with earlier reports [3, 4], are as follows:



4.2. Intermolecular distance, layer spacing and tilt angle

The outer equatorial arc arises essentially from the intermolecular spacings perpendicular to the long axes of the molecules. We obtain the average intermolecular spacings using the formula, $2D \sin \theta = 1.117\lambda$ based on the arguments of cylindrical symmetry [13]. However, in the S_B phase we used Bragg's relation and in the S_G phase we could not calculate D since we did not get well-aligned diffraction photographs which could be indexed. The variation of D with temperature is shown in figure 2. In the nematic phase D first increases with temperature then, at high temperatures it remains constant. The discontinuous change in the D value near 59°C is presumably due to transformation of a cybotactic nematic group of molecules into an ordinary state.

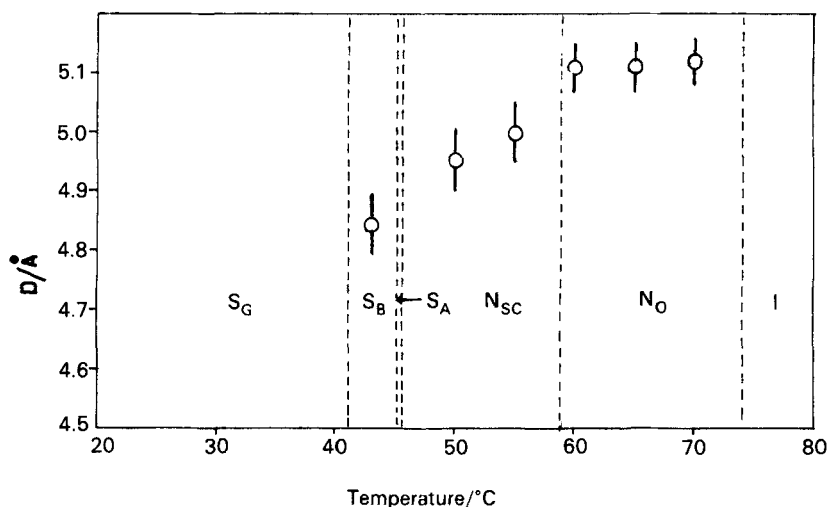


Figure 2. Variation of average intermolecular distance (D) with temperature.

The scattering about the meridional direction differs qualitatively between different types of materials. The positions of these reflections are expressed as Bragg spacings ($2X \sin \theta = n\lambda$) and are compared with the maximum molecular length measured on molecular models. X is taken to be the apparent molecular length l in the case of nematic and the layer spacing d in the case of the smectic phase. Variation

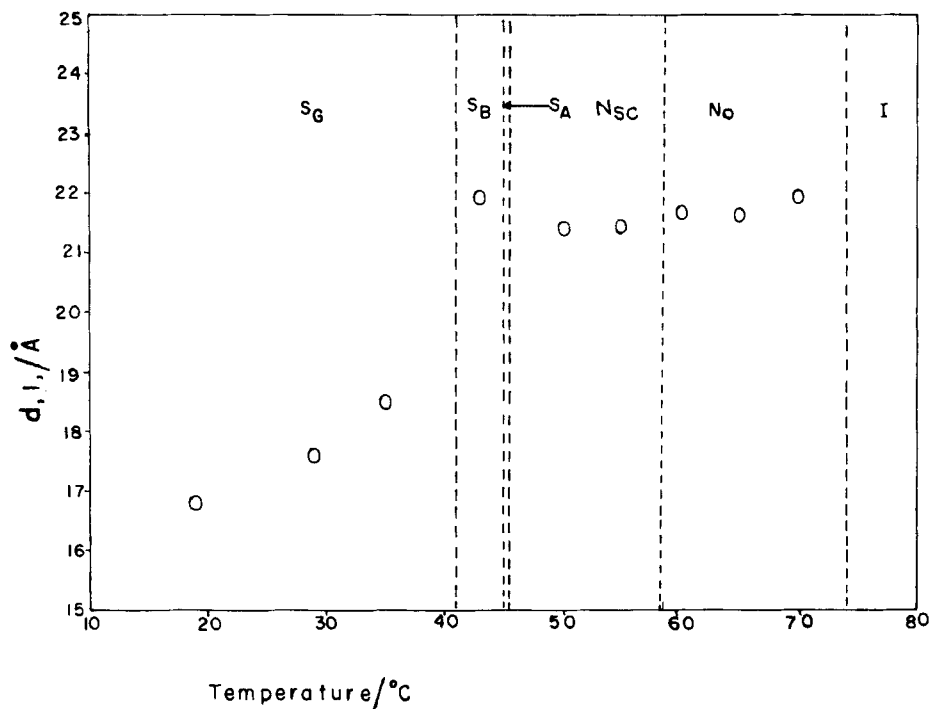


Figure 3. Variation of layer spacings (d) and apparent molecular length (l) with temperature.

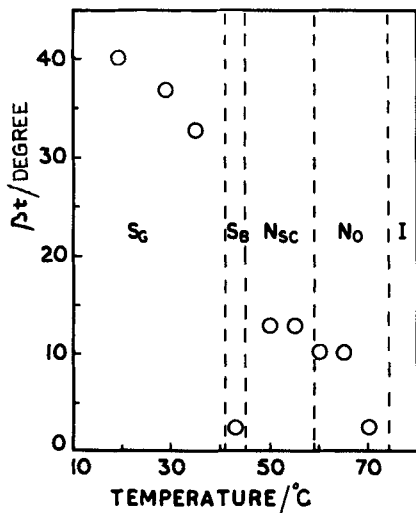


Figure 4. Variation of tilt angle β_t with temperature.

of this parameter with temperature is shown in figure 3 and discontinuous changes in X values are observed near the transitions. In the S_G phase d rises with temperature indicating a decrease in the tilt angle. We define a tilt angle β_t as $\beta_t = \cos^{-1}(X/L)$ where L is the length of the molecule in its most extended conformation. This definition of β_t is, of course, somewhat arbitrary in that it includes any change of internal conformation. Variation of β_t with temperature is shown in figure 4. In the

nematic phase the l values increase very slowly with the rise of temperature. The molecular length L determined from a stereo model unit (Prentice Hall, Inc, West Nyack, New York) was 22 \AA which agreed well with the experimentally determined values. (Note: In figures 2, 3 and 4 N_{SC} should be N_{OC} .)

4.3. Refractive indices

The experimental values of the refractive indices are shown in figure 5. Due to the absorptions of extraordinary rays in the smectic phases of BBBA n_e data could not be taken below 43°C . We could not calculate directly the values of α_{\parallel} and α_{\perp} since solid phase data were not available and we adopted Haller's [15] extrapolation procedure for this purpose. We plotted $\log(\alpha_e - \alpha_0)$ versus $\log(T_c - T)$ giving a straight line at lower temperatures which is extrapolated to $\log T_c$. The limiting value of $(\alpha_e - \alpha_0)$ is assumed to correspond to $(\alpha_{\parallel} - \alpha_{\perp})$. The values of principal polarizabilities and densities are given in the table. The refractive indices have been measured for green, yellow, red and blue light. The variation of Δn with wavelength is shown in figure 6. It is evident from the figure that Δn , for blue light, is much different from those of the other three colours. This type of variation of optical anisotropy with wavelengths was also found by Blinov *et al.* [16] for PAA and MBBA and by the authors for PBBA [17] which justifies our experimental technique. The presence of the S_A phase over a

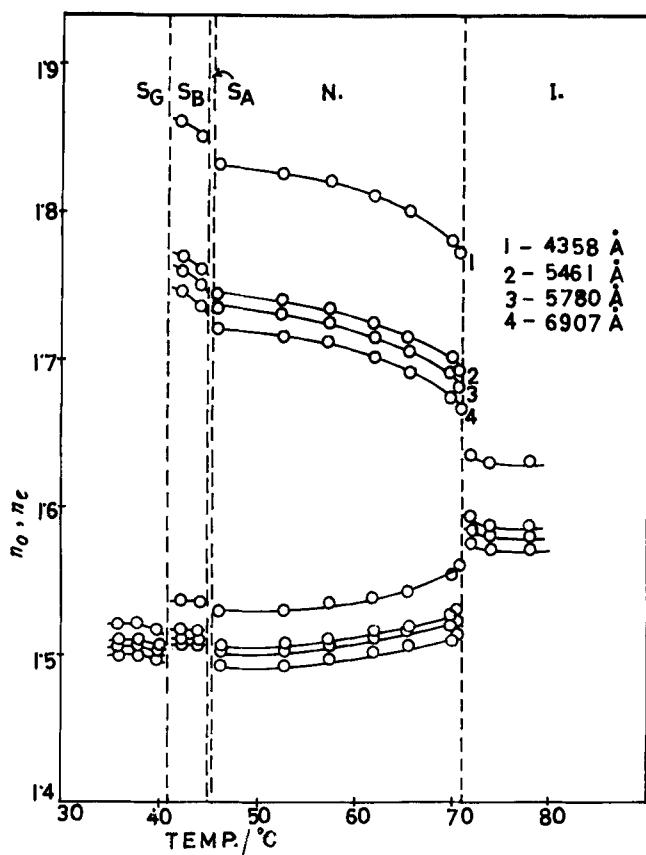


Figure 5. Values of refractive indices at different temperatures.

Density ($\rho/\text{g cc}^{-1}$), polarizability ($\alpha \times 10^{-24}/\text{cm}^3$) and orientational order parameter (S) of BBBA.

$T/^\circ\text{C}$	$\lambda/\text{\AA}$	6907			5780			5461			4358		
		α_0	α_c	S	α_0	α_c	S	α_0	α_c	S	α_0	α_c	S
42.3	1.0165	33.50	54.63	0.6345	34.02	55.57	0.6350	34.25	56.24	0.6341	34.74	62.71	0.6365
44.2	1.0160	33.60	53.87	0.6085	34.12	54.81	0.6095	34.36	55.48	0.6092	34.86	61.80	0.6129
46.0	1.0110	33.24	53.18	0.5987	33.77	54.14	0.6001	34.01	54.81	0.6000	34.56	60.95	0.6005
52.0	0.9960	33.78	53.58	0.5943	34.32	54.55	0.5959	34.56	55.23	0.5961	35.15	61.23	0.5933
57.3	0.9860	34.51	53.59	0.5730	35.05	54.57	0.5751	35.30	55.26	0.5759	35.91	61.07	0.5724
62.0	0.9750	35.33	53.25	0.5382	35.88	54.24	0.5411	36.13	54.94	0.5427	36.76	60.72	0.5453
65.5	0.9690	35.98	52.64	0.5001	36.53	53.64	0.5038	36.78	54.34	0.5028	37.51	59.81	0.5088
70.0	0.9600	36.81	51.77	0.4492	37.36	52.78	0.4540	37.62	53.48	0.4576	38.64	58.80	0.4586
72.5	0.9450	37.98	51.58	0.4083	38.55	52.61	0.4141	38.80	53.32	0.4188	40.05	58.55	0.4208

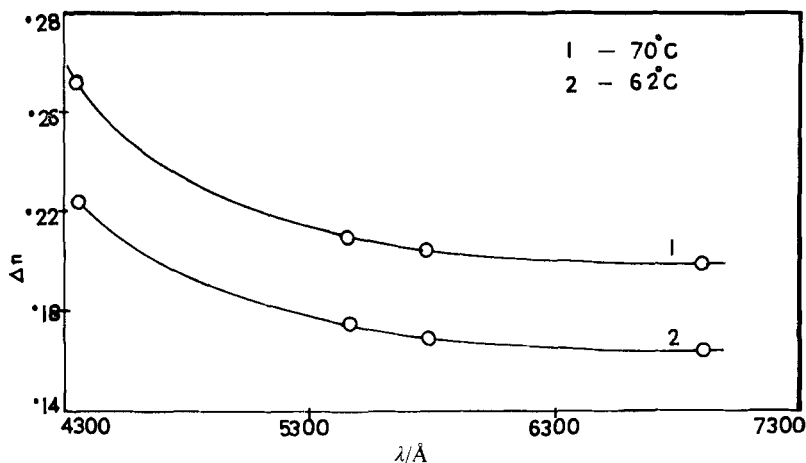


Figure 6. Variation of Δn with wavelengths.

very short range of temperature is also evident from our refractive index measurements (figure 5).

The orientational order parameters S at different temperatures were calculated using the method and formula given in § 2.2. Variation of S with temperature is shown in figure 8.

4.4. Normalized orientational distribution function and order parameters

In the nematic phase $f(\beta)$, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values were determined following the procedures described earlier [6]. The optical densities obtained from angular scanning of the outer diffraction ring are converted to intensity values from the calibration curve. The normalized distribution function $f(\beta)$ versus β at different temperatures is shown in figure 7. As expected the distribution curve broadens at high temperatures. The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at different temperatures are given in figure 8. The solid line gives the Maier-Saupe (MS) theoretical values, open circles correspond to the order parameter values obtained from X-ray data and half-filled circles are obtained from refractive index measurements. The $\langle P_2 \rangle$ values determined from refractive index measurements are found to be close to those obtained by Kirov *et al.* [1] from infrared dichroism and agree well with the MS theoretical values except near the clearing point. At this point $\langle P_2 \rangle$ values are lower than the theoretical values. Such observations in other compounds have been reported earlier [18, 19]. This is not unexpected since the thermal fluctuations of the director near the clearing temperature lower the values of the order parameter. In mean field approximation this fluctuation was not taken into consideration.

Orientalional order parameter values determined from X-ray diffraction measurements are slightly higher than the Maier-Saupe theoretical values. Such differences were found by Leadbetter and Norris [5] and also by the authors [6, 20]. It is well known that nematic phases may be distinguished by a long range order which can be studied by light scattering but it does not give rise to X-ray diffraction except for a small angle. Classical X-ray methods only allow us to obtain short range order. In most of the nematic liquid crystals for which X-ray diffraction study was performed there are antiparallel local ordering and short range dipole-dipole interactions. This short range interaction causes an increase in the orientational order parameter $\langle P_2 \rangle$.

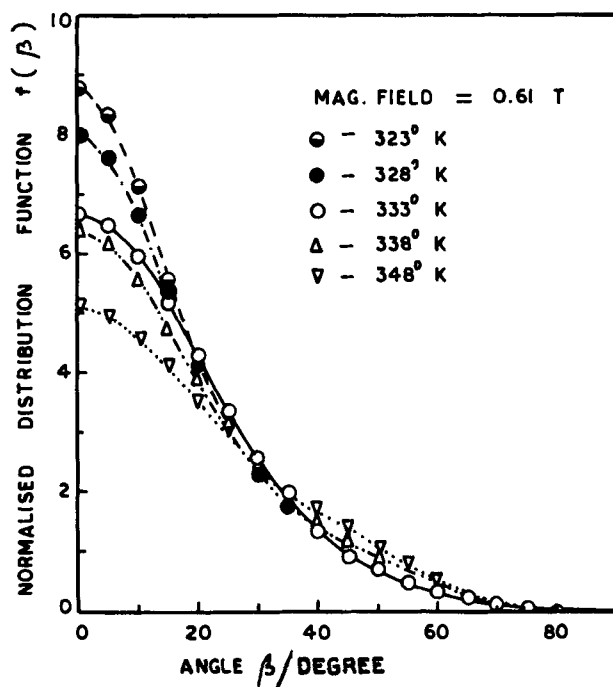
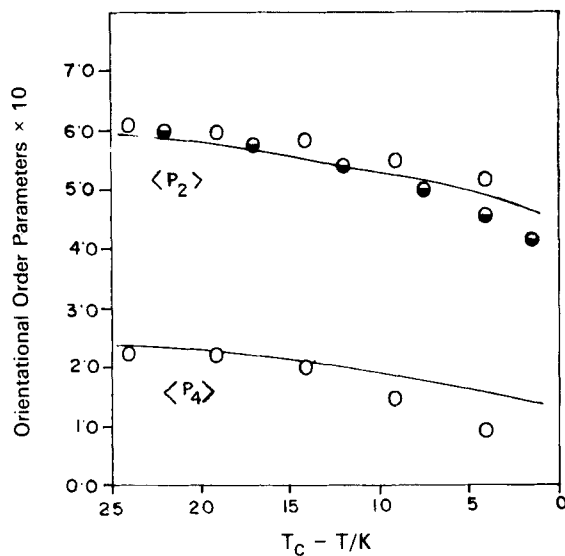
Figure 7. Variation of $f(\beta)$ with β .

Figure 8. Variation of order parameters with temperature. Solid line corresponds to Maier-Saupe values, open circles to X-ray data and half-filled circles to refractive index data.

The Maier-Saupe theory considers the mean field as continuous and long range. The $\langle P_4 \rangle$ values at higher temperatures are significantly lower than the theoretical predictions. Such behaviour of $\langle P_4 \rangle$ has been observed by others [6, 20–24]. This discrepancy remains unexplained.

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