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DETERMINATION OF OPTICAL BIREFRINGENCE AND ORIENTATIONAL ORDER PARAMETER OF FOUR MEMBERS OF ALKYL CYANOBIPHENYLS USING HIGH RESOLUTION TEMPERATURE SCANNING TECHNIQUE

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ABSTRACT

We report the measurements of birefringence as a function of temperature of a homologous series of alkyl cyanobiphenyls (nCB) liquid crystalline compounds by means of high resolution optical transmission method. The temperature dependence of the birefringence (Δn) were determined from the transmitted intensity data for wavelength λ= 532nm. From the birefringence data, orientational order parameters ($<P_2>$) were determined using three parameter Haller's extrapolation technique. The order parameter critical exponents β obtained in this way have values <0.2, which do not match any of the predicted theoretical values. However, the critical exponent (β) obtained from Haller's extrapolation technique can be improved by using four-parameter fitting procedure, which yielded a higher value of β(~0.24), consistent with the mean-field theory for a weakly first order transition. Moreover, we have fitted our experimental order parameter values with those calculated from the Maier-Saupe theory for the nematic and McMillan's theory for the Sm A phase.

KEYWORDS: Critical Exponent, Cyanobiphenyls, Optical Birefringence, Orientational Order Parameter

INTRODUCTION

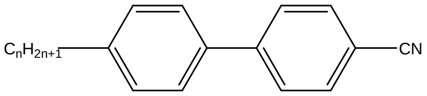
Liquid crystals are partially ordered anisotropic fluids, thermodynamically located between the three dimensionally ordered solid state crystal and the isotropic liquid [1]. They have many interesting properties from the phase transition and application point of view. The application of liquid crystal materials in different types of devices depends upon several properties like optical birefringence, dielectric anisotropy, magnetic susceptibility, orientational order parameter etc. For the display devices the knowledge of optical anisotropy and its temperature variation is important. Due to their room temperature nematic (N) range, stability over a large temperature region, simple molecular configuration homologous series 4-cyano-4′-n-alkylbiphenyls (*n*CB) have been studied extensively [2] and mixtures of these compounds have been used in display devices. Their versatile usefulness from the experimental to several theoretical proposals made them such a good candidates to study. The first four members are either non liquid crystal or shows monotropic transitions, for small n ≤7 the members of this series exhibit only nematic phase, for n = 8, 9 both the nematic and smectic A (SmA) phase are present while for n>9, the compounds exhibit only smectic A phase. Several reports on the optical birefringence (Δn) of these members have been reported so far. But most of the cases the resolutions in the measurements of refractive index and birefringence are insufficient to extract the critical exponent β, since refractive index and birefringence measurements are generally obtained on the visual inspection by means of an Abbe refractometer or wedge method. Thus in order to extract the critical behavior near the phase transition region it should be emphasized that high-resolution (in both temperature and birefringence) measurements are essential. In this work optical transmission method have been used to determine the temperature dependences of high-resolution (both birefringence and temperature) optical birefringence, Δn, which provides a macroscopic measure of the anisotropy of the liquid crystalline phase and can also be considered as a measure of the orientational order parameter $<P_2>$. The critical behavior of the orientational order parameter at the nematic-isotropic transition has been studied in detail and compares our results with the latest report in the literature. Four members of a homologous series of alkyl cyanobiphenyls (nCB) were studied.

Several methods have been developed to calculate the orientational order parameter ($<P_2>$). But the most commonly used method is the optical method due to its simplicity as well as accuracy. The typical procedure for the evaluation of the long range order parameter from optical method requires the measurement of both the ordinary and extraordinary refractive indices as well as the density data. In such cases, using these three measured quantities, either the standard Vuk's isotropic model [3] or the Neugebauer's relations based on the anisotropy of the internal field [4] are adopted to determine the principal polarizabilities parallel and perpendicular to the molecular long axes and hence, the anisotropy of the molecular polarizabilities ($\Delta\alpha$) can be calculated. The normalized polarizability ($\Delta\alpha_o$) for perfectly order crystal is determined from the well-known Haller's extrapolation procedure [5] and the order parameter is calculated from the ratio $\Delta\alpha/\Delta\alpha_0$. According to de Jue [6], the variation of density (ρ) over the nematic range is usually small and the temperature dependence of Δn gives a good indication of the variation of order parameter with temperature. Kuczynski et. al. [7] have also shown that the order parameter determined directly from birefringence measurements are consistent with the $<P_2>$ values calculated from the polarizability data. In this work we calculated the order parameter ($<P_2>$) directly from the birefringence value using the well known Haller's extrapolation method [5] and compared with those obtained from Maier-Saupe theory [8] for three nematogens and McMillan's model [9] for one smectogen.

EXPERIMENTAL

Materials

The nCB (n=5-8) compounds were obtained from British Drug House (at present E. Merck), Poole U.K. and used without further purification. The structural formula and the transition temperatures of the four compounds are:



(nCB) (n=5-8)

- **Pentyl-cyanobiphenyl(5CB):** Cr 24°C N 35.3°C I
- **Hexyl-cyanobiphenyl(6CB):** Cr 14.5°C N 28.3°C I
- **Heptyl-cyanobiphenyl(7CB):** Cr 30°C N 42.3°C I
- **Octyl-cyanobiphenyl(8CB):** Cr 21.5°C SmA 33.5 °C N 40.2°C I

Optical Birefringence Measurements

A solid state green laser (λ = 532 nm) beam was directed onto a homogeneously aligned (planar) liquid crystal cell of thickness 5.1 μm(purchased from AWAT Co. Ltd., Warsaw, Poland) , placed between two crossed linear polarizers. The temperature of the cell was regulated and measured with a temperature controller (Eurotherm PID 2404) with an accuracy of ± 0.1 °C by placing the cell in a custom built heater made of brass. The transmitted light intensity was measured by a photo diode at an interval of 3 seconds. When the heater temperature is varied at a rate of 0.5°C min-1, this translates into a temperature difference of 0.025°C between two readings. The transmitted light experiences a phase difference $\Delta\varphi$ between its extraordinary and ordinary component of refractive indices. The optical birefringence (Δn) of the liquid crystal medium can be measured by measuring that phase difference. The phase difference ($\Delta\varphi$) is calculated from the transmitted laser light intensity (I) by using the relation [10]:

$$\Delta\varphi = \cos^{-1}\left(1-\frac{2I}{\sin^2 2\theta}\right) \tag{1}$$

where θ, which is set to 45^o, is the angle made by the polarizer with the optic axis. The phase difference is calculated from the measured transmitted intensity [10, 11]. Using equation (1) we calculate the temperature variation of the optical birefringence by the relation

$$\Delta n = \left(\Delta\varphi.\frac{\lambda}{2\pi d}\right) \tag{2}$$

where d is the cell thickness. The optical birefringence measurements were performed for several cooling and heating runs and reproducible results were obtained.

RESULTS AND DISCUSSIONS

Optical Birefringence Measurements

In Figure 1 the optical birefringence Δn vs temperature data at a wavelength of λ = 532 nm of the four compounds upon cooling from the isotropic liquid to the room temperature is displayed. In the isotropic phase the birefringence is zero and increases with decreasing temperature as expected. However, an enhancement in Δn takes place upon lowering the temperature towards the Sm A phase for 8CB. The Δn is enhanced as the smectic like short-range order builds up, reflecting the enhancement in the nematic (orientational) order parameter. Within a range about 1-3°C above and below the N-Sm A transition the pretransitional behavior was clearly observed. Our high resolution birefringence values were also compared with the values obtained from Chirtoc et. al. [2] for λ=589.3nm. It was observed that for 5CB, 6CB and 8CB the two sets of data agree quite well. Only for 7CB our data is higher than the reported data [2].

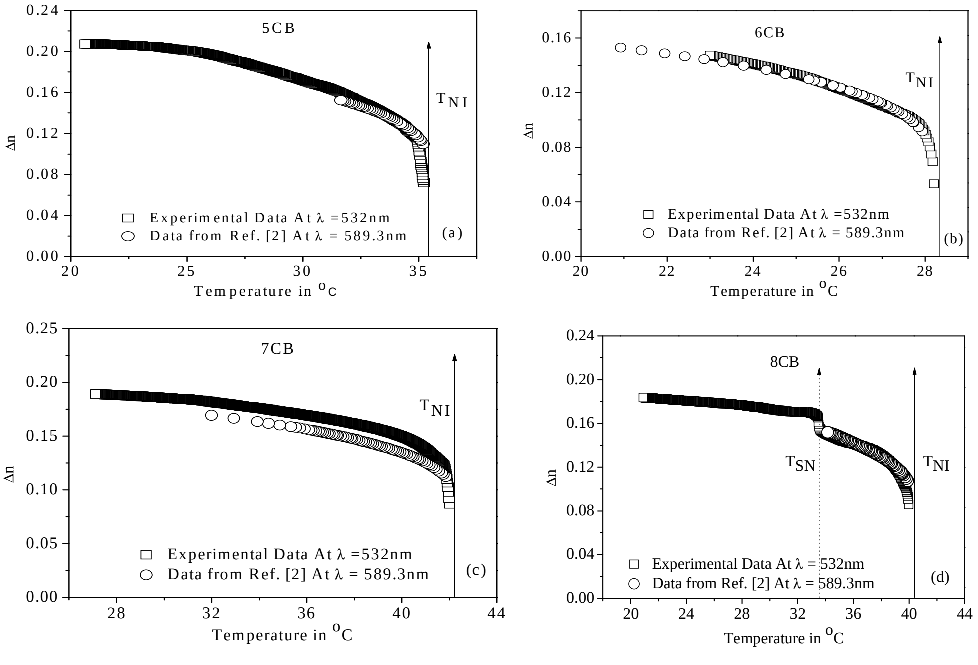


Figure 1: Temperature Dependence of Birefringence (Δn) for (a) 5CB, (b) 6CB, (c) 7CB, (d) 8CB. □ - Data Obtained from Optical Transmission Method with λ =532 nm and o - Data from Ref. [2] for λ =589.3 nm. Solid Arrow and Dotted Arrow Indicates the Nematic-Isotropic Transition Temperature (T_{NI}) and Smectic A –Nematic Transition Temperature (T_{SN}) Respectively

Determination of Orientational Order Parameter

In this work we used a simple technique to determine the orientational order parameter (<P_2>) for the four compounds under study. The temperature dependence of birefringence was fitted to the following Haller’s type equation [5]:

$$\Delta n = \Delta n_0 \left(1 - \frac{T}{T^*}\right)^{\beta} \tag{3}$$

where T* and β are two adjustable parameters, T* is 0.01-4K higher than the clearing temperature and the critical exponent β depends on the molecular structure and its value is close to 0.2. Δn_0 is the extrapolated birefringence in the perfectly ordered state (i.e. at T=0K). The order parameter <P_2> can be determined by the following equation

$$\langle P_2 \rangle = \frac{\Delta n}{\Delta n_0} \tag{4}$$

Employing equation (3) to the birefringence data and using the equation (4) we have determined the orientational order parameter values for all the compounds under study. For 8CB where both the N and Sm A phases are present, temperature dependence of birefringence have been fitted only in the N phase. The temperature variations of order parameter (<P_2>) for the four compounds are shown in the Figure 2. It is seen that the order parameter increases rapidly as the compounds enters into the nematic phase from the disordered isotropic phase and nearly saturates far away from N-I transition temperature. The value of the fitted parameters Δn_0, T* and β for all the compounds are shown in Table 1. The experimental order parameters so obtained are compared with Haller’s fit and Maier-Saupe values [8] for 5CB, 6CB and 7CB. All the cases, agreement is fairly good except near the nematic–isotropic transition temperature.

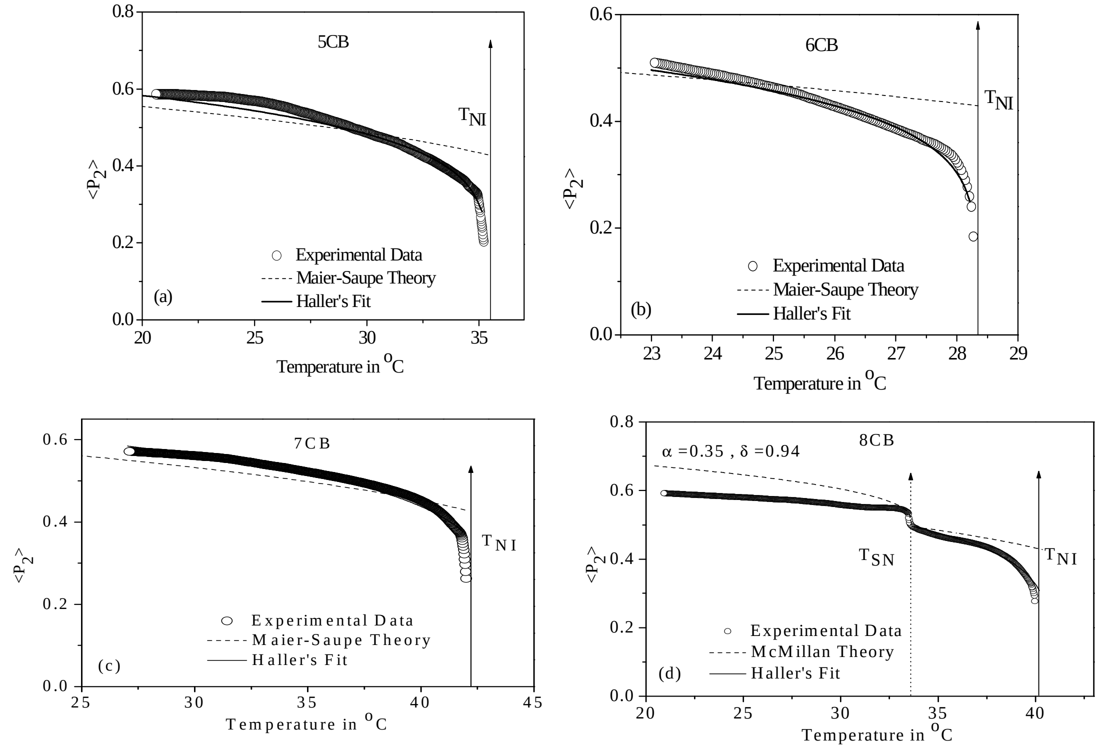


Figure 2: Temperature Variation of <P_2> for (a) 5CB, (b) 6CB (c) 7CB, (d) 8CB. o - <P_2> from Birefringence Measurement; – <P_2> from Haller’s Fit to Equation (3); ----- <P_2> from Maier-Saupe Theory ((a), (b) and (c)), from McMillan’s Theory ((d)). T_{NI} = Nematic – Isotropic, T_{SN} = Smectic A– Nematic Phase Transition Temperatures. For (d), the α and δ Values Required to Fit Experimental Data is Shown in the Respective Figures

We have also fitted the theoretical McMillan order parameter values with our experimental values by varying the α and δ parameters of the McMillan potential [9] for 8CB. According to McMillan the single particle potential is given by

$$\varepsilon(\cos\theta, z) = -\varepsilon_0\left[\delta\alpha\tau\cos(2\pi z/d) + \{\eta + \alpha\sigma\cos(2\pi z/d)\}P_2(\cos\theta)\right] \tag{5}$$

where α and δ are two adjustable parameters, d is the layer thickness, z is the displacement along the layer normal, η = $<P_2 (\cos\theta)>$, the orientational order parameter, while $\tau = <\cos(2\pi z/d)>$ is the translational order parameter and $\sigma = <P_2(\cos\theta)\cos(2\pi z/d)>$ is the mixed translational and orientational order parameter. The parameter ε_0 is obtained from the nematic-isotropic phase transition temperature, assuming the simple mean field theory result (kT_{NI}/ε_0=0.22019).

Table 1: Values of Fitting Parameters Δn_0, T* and β Obtained from Haller's Extrapolation

Compound	**Δn_0**	**T^*(K)**	**β**
5CB	0.398±0.0028	308.55±0.04	0.180±0.002
6CB	0.307±0.0067	301.7±0.05	0.184±0.003
7CB	0.331±0.0041	315.80±0.16	0.181±0.004
8CB	0.310±0.0129	314.04±0.23	0.185±0.003

The values of η, τ and σ are calculated using the self-consistency relationships as a function of temperature for several values of α and δ. The best fitted theoretical curve which was done by changing the α and δ value is shown in Figure 2(d). The agreement between the experimental $<P_2>$ values from the birefringence measurements with those calculated from McMillan's theory is poor except near the SmA –N transition. It has been found that the extrapolated birefringence Δn_0 and β exhibit an odd-even effect when plotted against the alkyl chain length as shown in the Figure 3(a) and 3(b) respectively.

The critical exponents β obtained from Haller's extrapolation lies within the range 0.180 to 0.185 which are less compare to the predicted theoretical value. So, three parameter Haller's extrapolation results lower values of the critical exponent β<0.20. This is due to the fact that Haller's extrapolation does not always account for the weakly first order nature of nematic-isotropic phase transition. To improve the critical exponent, recently a four parameter power-law expression has been introduced [2] which is consistent with the mean-field theory for a critical as well as a tricritical behaviour for a weakly first-order transition and can be written as

$$D = A[B + (1-B)(1-\frac{T}{T^*})^{\beta}] \tag{6}$$

where D is the physical property under consideration (birefringence in this case), A and B are constants, β is the critical exponent and T* is slightly greater than the clearing temperature. In equation (6), B = 0 leads to the Haller's type equation (3). The value of the four parameters obtained by fitting the birefringence data to equation (6) has been shown in Table 2. So, four parameters fit results β values very close to the mean field predicted value. These β values when plotted against the alkyl chain length of nCB as shown in Figure 3(b), show odd-even effect and from the figure it is clear that four parameter fit yields higher values of β ≈0.24 than three parameters Haller's fit.

Table 2: Values of Fitting Parameters Obtained from Four Parameter Fit

Compound	**A**	**B**	**T*(K)**	**β**
5CB	0.415±0.039	0.097±0.001	308.70±0.23	0.235±0.002
6CB	0.331±0.010	0.102±0.010	302.10±0.75	0.242±0.004
7CB	0.326±0.025	0.200±0.004	315.90 ±0.85	0.232±0.006
8CB	0.293±0.009	0.223±0.008	314.10±0.97	0.245±0.008

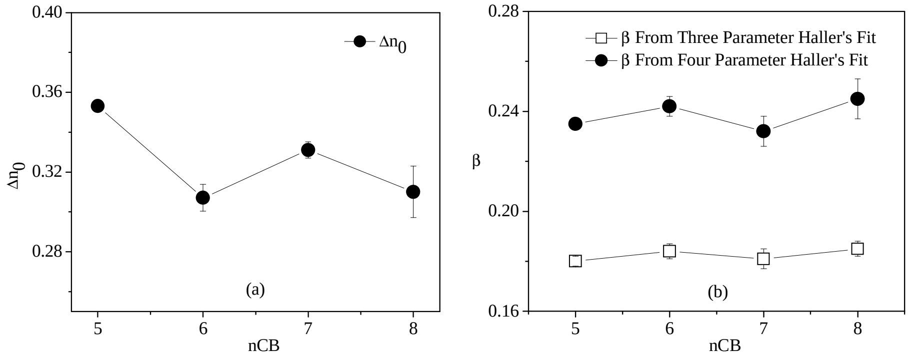


Figure 3: (a) Odd-Even Effect of Fit ParameterΔn_0 as a Function of Alkyl Chain Length of nCB Homologus Series. (b) Odd-Even Effect of β as a Function of Alkyl Chain Length of nCB Homologus Series. ( ) Represent β from Three Parameter Haller's Fit and (•) Represent β from Four Parameter Haller's Fit. The Vertical Bars are the Errors Associated with the Value

CONCLUSIONS

High resolution temperature scanning method, a simple and precise technique, has been carried out to measure the birefringence with reasonably good accuracy (better than $\pm 10^{-4}$) of four members of 4-cyano-4′-n-alkylbiphenyls (n=5-8). The measured birefringence agrees well with those reported by Chirtoc *et. al.* The compound 8CB which has smectic phase shows pretransitional behavior in the vicinity of N-Sm A transition owing to coupling between the nematic and smectic order parameters. The birefringence data was used to determine the order parameter by using Haller's extrapolation technique and were fitted with Maier-Saupe theory for nematogens (5CB-7CB) and McMillan theory for compound (8CB) with smectic phase. Three parameters Haller's fit yields systematically lower values of β but the four parameter fit produce some higher value which is close to the predicted mean field theoretical value. Both Δn_0 and β values show odd-even effect when plotted against the alkyl chain length of the compounds.

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