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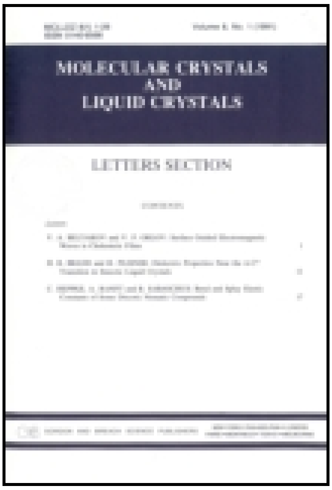

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Comparative Study of the Thermal Dependence of the Birefringence and Order Parameter of Two nOCB Compounds

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Comparative Study of the Thermal Dependence of the Birefringence and Order Parameter of Two *n*OCB Compounds

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The optical properties, birefringence and order parameter of two alkoxycyanobiphenyls (nOCBs, where n = *5 or 8) have been studied as a function of temperature. The variation of orientational order parameter has been determined experimentally. Theoretical order parameter values have also been computed in the smectic range using McMillan potential and in the nematic range using Maier–Saupe potential and compared with the experimentally obtained values. The variations of polarizabilities with temperature have also been evaluated from density variation and birefringence studies.*

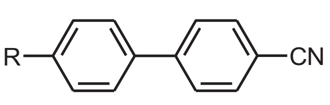
Comparison has been drawn between the physical behavior of 5OCB and 8OCB.

Keywords Birefringence; order parameter; polarizability; thermotropic liquid crystals

1. Introduction

Birefringence, polarizability, dielectric anisotropy, viscosity, order parameter, and phase transition temperatures are the most important properties of liquid crystalline materials since they determine their quality and practical applications. The order parameter is one of the fundamental physical parameters, which characterizes the physical properties of the nematic state. The knowledge of the order parameter and its dependence on temperature is essential for testing any model for its liquid crystalline behavior.

The alkoxycyanobiphenyls with general formula (Structure 1) are known for a long time for their liquid crystalline properties [1].



Structure 1

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The molecules have rigid cores with, the alkoxy tail at one end and at the other end a strongly polar-cyano (CN) group which gives a predominant longitudinal dipole moment. Cyano and isothiocyanato (NCS) groups are two commonly employed polar groups for elongating the molecular conjugation. The -CN group has a larger dipole moment than -NCS group, because of its linear structure. Polar nematic liquid crystal compounds having relatively high birefringence, low viscosity, and good photochemical stability are needed for display and photonic applications [2,3]. In previous works a number of physical parameters for the homologs series of *n*OCB's have been determined, particularly for pentyloxycyanobiphenyl (5OCB) and octyloxycyanobiphenyl (8OCB). The adiabatic compressibility based on ultrasonic velocity measurements, van der Waal's constant, molecular terahertz polarizability of 5OCB (leading to indirect determination of refractive index), the photorefractive properties of PVK-based polymeric composite doped with 8OCB have been experimentally measured and determined [4–6].

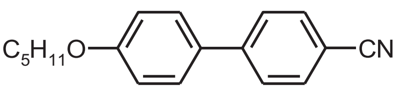
Monolayers of *n*OCB, ($n = 5$–8) at the air-water interface have been investigated using Maxwell displacement current and second harmonic generation measurements by monolayer compression [7]. Different polymorphic forms of nOCBs have been studied by slow or delayed cooling giving rise to a lower melting crystalline polymorphic form which slowly converted to a higher melting stable crystalline structure [8]. The effect of confinement on molecular processes in liquid crystalline 8OCB has been investigated by studying the dispersion of proton spin – lattice relaxation rates in nematic and smectic phase of 8OCB embedded in nano – porous medium [9].

The dielectric measurements near the isotropic – nematic transitions have been carried out for a number of strongly polar compounds, including 8OCB, to study the effect of pretransitional behavior in the vicinity of phase transition [10].

In this work the birefringence and density variations of 5OCB and 8OCB with temperature have been carried out directly. The polarizability anisotropies and their thermal variations have been evaluated from the data obtained and the information obtained has been applied for the determination of the order parameters and their thermal dependence. Theoretical values of order parameters based on Maier–Saupe [11] (for nematic phase) and McMillan [12] (for smectic phase) theories have been computed and compared with experimentally obtained values.

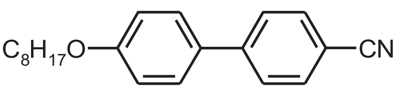
The investigated 5OCB and 8OCB samples have been synthesized and provided by the group of K. Czupyński (MUT Warsaw). The compounds exhibit the following phase sequences and transition temperatures.

5OCB



Cr 48 N 68 Iso

8OCB



Cr 54.5 SmAd 67.5 N 81 Iso

2. Experimental Methods

2.1. Optical Microscopy

Prior to birefringence studies, optical microscopy was performed on each of the samples to confirm the nature of the phase and phase transition temperatures. Each sample taken on a clean glass slide and covered with a cover slip was introduced into a hot stage (Mettler FP 82 HT) whose temperature was raised at the rate of 1°C min^{-1} during heating. Each sample was heated from the room temperatures and then allowed to cool at an average rate of 1°C min^{-1}. Optical microscopy studies confirmed the phase transition temperatures of 5OCB and 8OCB with an accuracy of 0.5°C.

2.2. Birefringence Studies

Birefringence studies were conducted using a He-Ne source (wave length $\lambda = 633$ nm) on the basis of the Chatelain–Wedge principle. Each sample was introduced into a glass prism of angle between 1° and 2°. The prisms were formed with glass slides whose inner surfaces were treated with polyvinyl alcohol for planar surface alignment. The liquid crystal sample was introduced into the prism at room temperature through the open edge of the prism which was then sealed. The prism encapsulated in a sample holder was placed in an aligning magnetic field of 8 KGauss such that the direction of rubbing (along the prism edge) is along the magnetic field.

The temperature of sample holder could be regulated with an accuracy of ± 0.5°C up to a temperature of 150°C. The laser beam from the source was made incident on the sample through a hole in the sample holder and the emerging beams (ordinary and extraordinary) emerging through the opposite side of the hole were projected on a screen held several meters (5.0 m) away. The sample was taken through a number of temperature cycles in the presence of the magnetic field to ensure an aligned monodomain sample.

Each sample was heated at the rate of 1°C per min to a temperature beyond its isotropic temperature and was allowed to cool at the same average rate. From the changes in the patterns observed on the screen, the transition temperatures could be confirmed. They were found to be in agreement with the findings from the optical microscopic study. From angular deflection measurements on the screen, the refractive indices n_e and n_0 of the extraordinary and ordinary rays could be determined with the knowledge of the prism angle. The prism angle for each prism was determined prior to the introduction of the sample by measuring the angular deviations of the laser beam reflected from the front and back surfaces of the prism. The measurements of both the top and bottom ends of each of the circular spots (of $\cong$ 0.6 cm in diameter) were taken and the mean of these was used for calculation. The birefringence as a function of temperature was thereby determined for both the samples 5OCB and 8OCB. Details of procedure are given in [13].

To obtain the polarizabilities α_e and α_o and thereby the order parameters from birefringence studies, the densities have to be determined as a function of temperature. The densities of each sample at various temperatures were obtained by introducing the weighed sample in the molten form in a dilatometer, which was then placed in a heat bath. The length of the sample column in the dilatometer tube was measured with a traveling microscope at temperature intervals of 2°C and the density of the sample was calculated. The polarizabilities were determined using Vuks formula [14]

$$\left(n_\Upsilon^2 - 1\right)/\left(n_{\text{avg}}^2 + 2\right) = \left(4\prod\right)/3N\alpha_\Upsilon$$

($\Upsilon = e$ or o, $n = n_{\text{avg}} = [n^2{}_e + 2n^2{}_o]/3$, N is the number of molecules per cubic centimeter and is given by $N = N_A d/M$ where N_A is the Avogadro number, and d is the density of the sample and M the molecular weight).

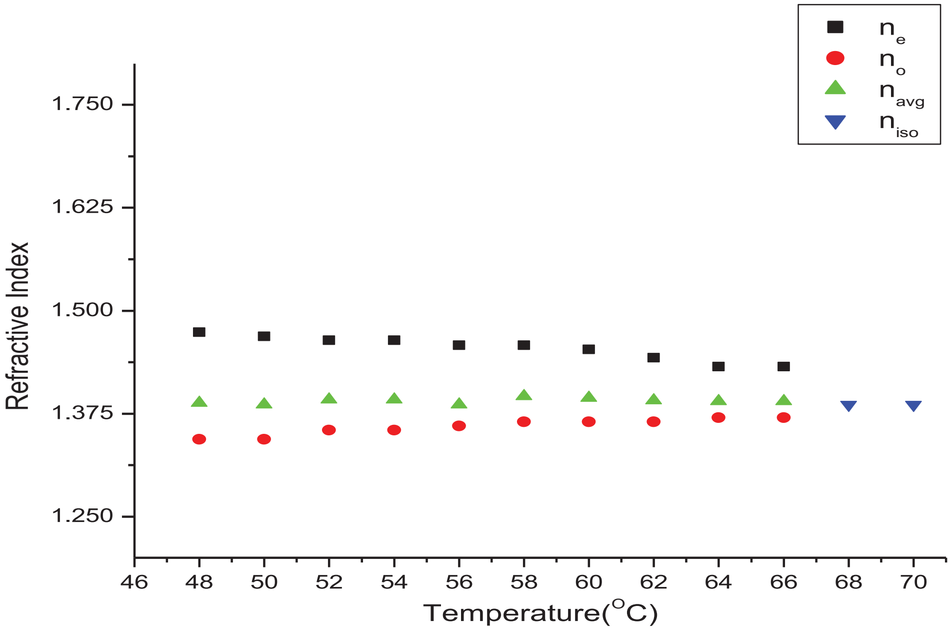


Figure 1. Variation of refractive index with temperature of 5OCB.

The order parameters $<P_2>$ was calculated using deGennes expressions [15] in the form.

$$<P_2> = (\alpha_e - \alpha_o)/(\alpha_{\Pi} - \alpha_{\perp})$$

where (α_{Π}-$\alpha_{\perp}$) refer to the parallel and perpendicular polarizabilities in the perfectly ordered crystalline state of the sample.

In the present case since data on (α_{Π}-$\alpha_{\perp}$) is not available (α_{Π}-$\alpha_{\perp}$) was determined by Haller's extrapolation [16] procedure by plotting In (α_e-α_o) versus In (T_C–T) and extrapolating the straight line thus obtained to $T = 0$ that is, to In T_C to obtain (α_{Π}-$\alpha_{\perp}$) from the intercept.

3. Results and Discussion

Figures 1 and 2 show the variations of refractive indices n_e and n_o with temperature for 5OCB and 8OCB, respectively. In both cases $n_{avg} = (n_e + 2n_o)/3$, shows a smooth transition to the n_{iso} value at the nematic-isotropic transition temperature without suffering any discontinuity. Average refractive index n_{avg} is found to be greater for 5OCB ($n_{avg} = 1.3907$ at 64°C) than for 8OCB ($n_{avg} = 1.3038$ at 64°C). However an increase in the optical anisotropy is observed on comparing the Δn values of investigated compounds 5OCB and 8OCB, the experimental values being 0.062 (64°C) and 0.0918 (64°C) for 5OCB and 8OCB, respectively. The estimated error in the determination of refractive index is about 1%.

The thermal variations of polarizabilities α_e and α_o of the two compounds have been presented in Figs. 3 and 4, respectively. The transition from α_{avg} to α_{iso} is smooth without any discontinuity for both 5OCB and 8OCB samples as it was observed for refractive index

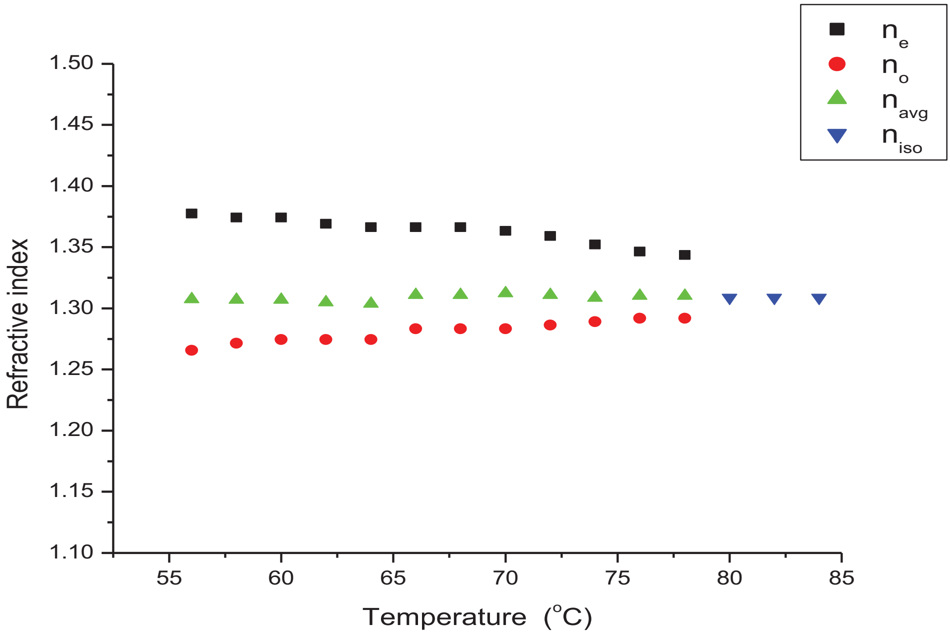


Figure 2. Variation of refractive index with temperature of 8OCB.

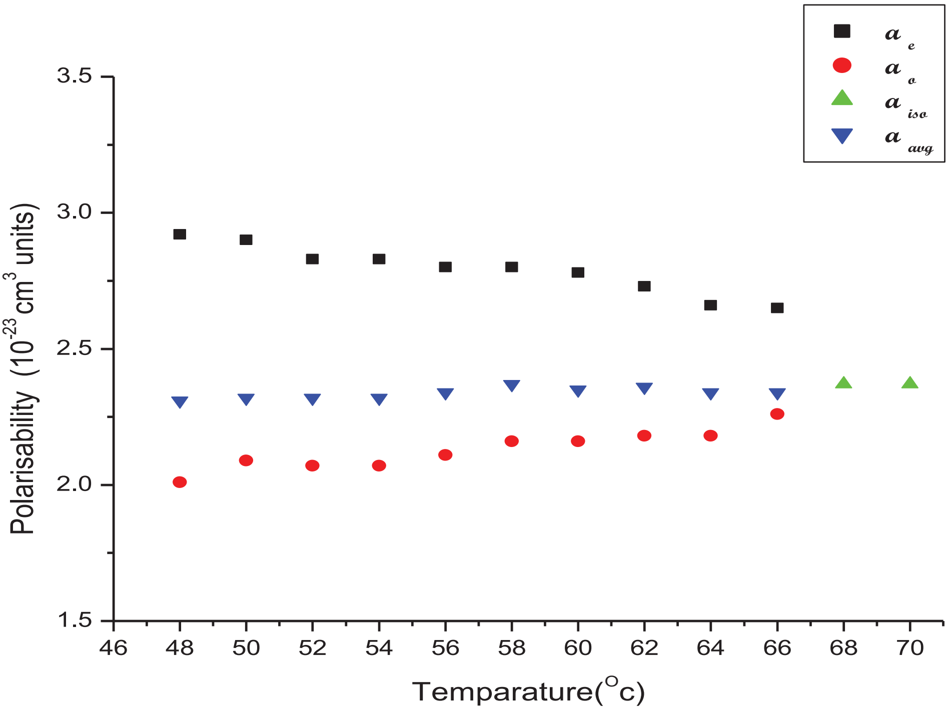


Figure 3. Variation of polarizability with temperature of 5OCB.

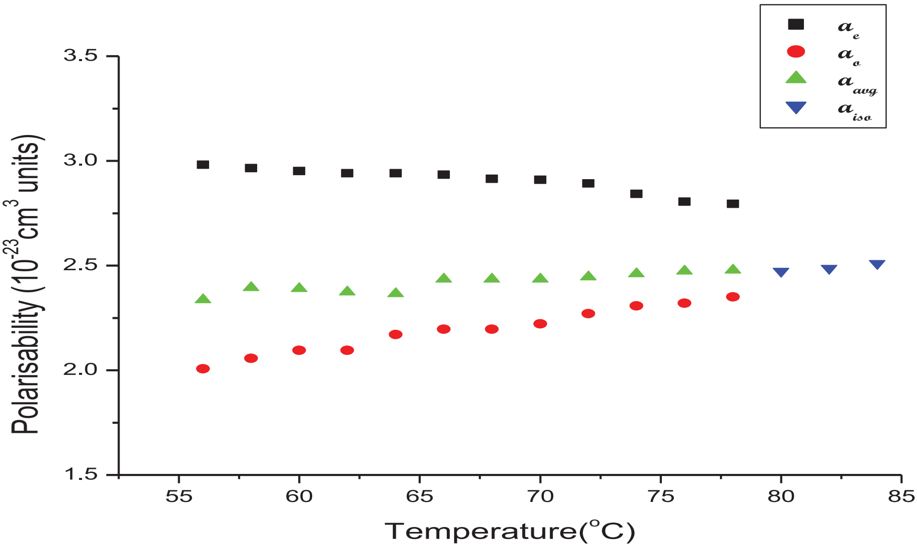


Figure 4. Variation of polarizability with temperature of 8OCB.

variation. The average polarizability α_{avg} is greater for 8OCB (2.366×10^{-23} at 64°C) than for 5OCB (2.34×10^{-23} at 64°C).The estimated error in the determination of polarizability is about 2–3%.

Figures 5 and 6 show the variations of order parameters with temperature for the two compounds. The experimental values of the orientational order parameter have been

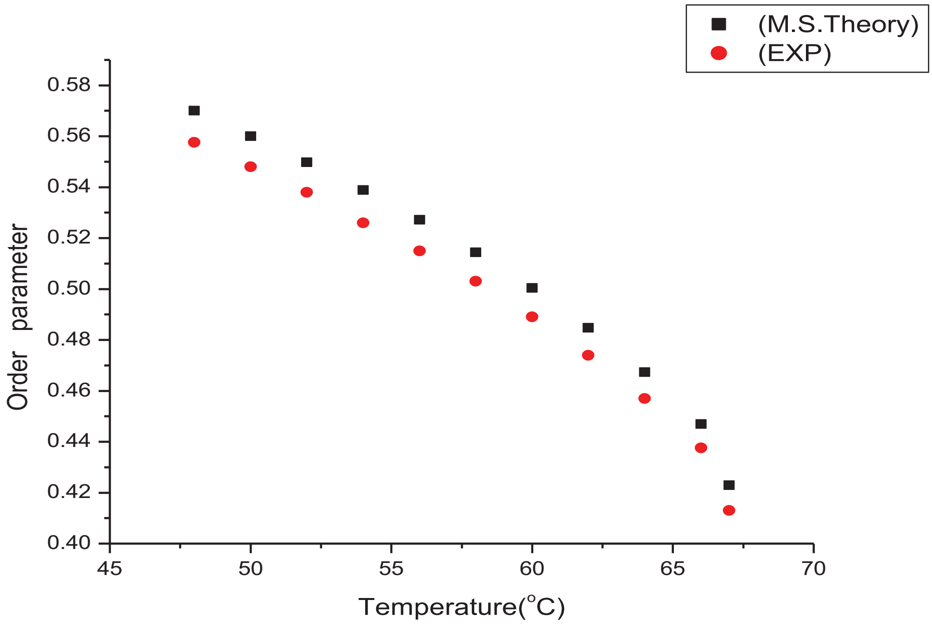


Figure 5. Variation of order parameter with temperature of 5OCB.

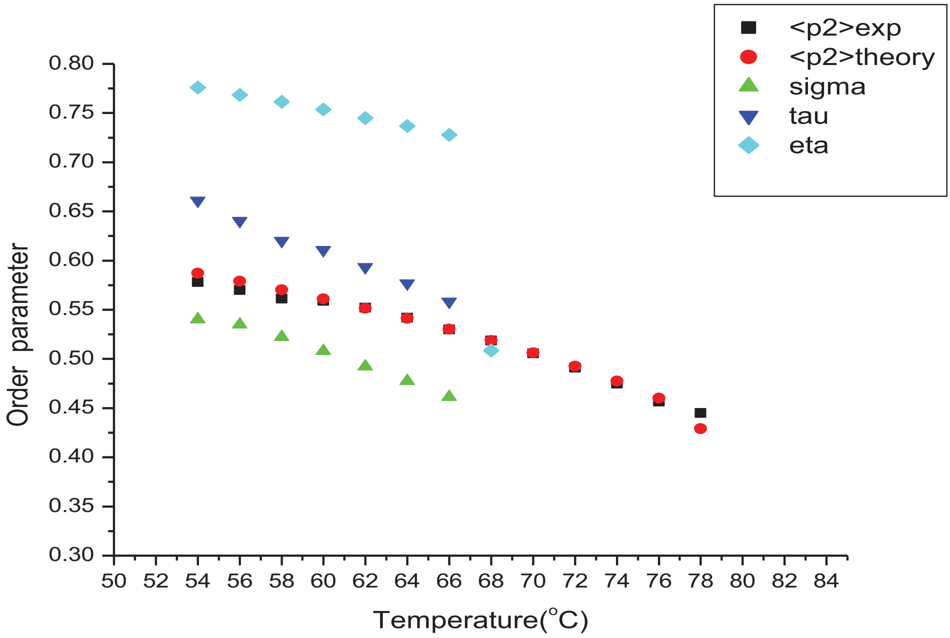


Figure 6. Variation of order parameter with temperature of 8OCB.

calculated and compared with that of the theoretical values from the Maier–Saupe (Nematic phase) and McMillan (SmA phase only) theories. In the case of 5OCB exhibiting only the nematic phase the agreement between the experimental and theoretical Maier–Saupe values is adequate, see Fig. 5. Although the Maier–Saupe values are relevant to the ordering in the nematic phase (orientational ordering), they have been depicted in the entire mesogenic range of 8OCB to enable the comparison of the orientational aspects of ordering in the presence/absence of any other type of ordering, namely€, translational. Theoretical values of order parameter for 8OCB exhibiting the SmAd phase have been calculated on the basis of Macmillan potential [12] for smectic A phase;

$$V(z, \cos\theta) = -v_o[\delta\alpha\tau \cos(2\pi z/d) + \{\eta + \alpha\sigma \cos((2\pi z/d)\} P_2(\cos\theta)]$$

where α and δ are two adjustable parameters, z is the displacement along the layer normal, d is the layer thickness, $\eta = <P_2\ (\cos\theta)>$ is the orientational order parameter, while $\tau = <\cos\ (\ 2\pi z/d)>$ is the translational order parameter and $\sigma = <P_2\ (\cos\theta)\ (2\pi z/d)>$ is the mixed translational and orientational order parameter, v_o determines the nematic to isotropic transition temperature and fixes the temperature scale of the model. Considering only η and σ Mcmillan has shown [17] that the nematic -isotropic transition temperature $T_{\mathrm{NI}} = 0.2202\mathrm{v}_0$ (given by Maier–Saupe theory) is valid for $\alpha < 0.98$ and that the SmeticA – Nematic transition temperature increases with α and reaches T_{NI} at $\alpha = 0.98$. For $\alpha >$ 0.98, SmA phase melts directly into the isotropic phase. For values of α below 0.98, there can be an Sm–N–I transition with an Sm–N transition of first order.

In case of lower values of α (<0.70) Sm–N–Iso transition occurs with an Sm–N transition of second order. In case of 8OCB which has an SmAd–N–Iso transition, the best reproducibility of transition temperatures were obtained with $\alpha = 0.85$ and $\delta = 0.45$, since this values of α falls below the 0.98 limit, we may expect SmAd–N transition to be of first order, though we note that in the present case not only η and σ but τ too have been considered in the potential. The order parameters both theoretical (Maier–Saupe and Mcmillan) and experimental for 8OCB have been presented in Fig. 6. The orientational order obtained experimentally however agrees excellently with the values predicted by Maier–Saupe [8]. In general, the order parameter of 8OCB is found to be greater than that obtained for 5OCB throughout the mesogenic range. The Mcmillan orientational order η is higher than that obtained experimentally in the smectic range but reduces to the Maier–Saupe values in the nematic range, thereby agreeing extremely well with the experimental values. The translational order parameter in the smectic range lies between the theoretical Mcmillan and experimentally obtained orientational order parameter values.

4. Conclusion

The present work investigates the nature of variations of order parameter with temperature for 5OCB and 8OCB based on data obtained from optical studies. In both cases, the variations are smooth and in the case of 8OCB there is no discernible discontinuity in order parameter at the transition from SmAd to Nematic phase. The orientational orders for both investigated samples are comparable. The experimental values show extremely good agreement with theoretical values computed from Maier–Saupe theory based on mean field theory. The fall in order parameter for 5OCB is more rapid than for 8OCB, which exhibits a slow and gradual variation indicating a greater functional stability of 8OCB in comparison to 5OCB.

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