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Orientational order parameters in the nematic and smectic A a binary mixture of smectogenic liquid crystals

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ABSTRACT

High resolution optical transmission data of a binary mixture of two smectogenic compounds of which one having NCS terminal group exhibiting smectic A phase and the other with CN terminal group showing Smectic Ad phase have been analyzed to determine the orientational order parameters as a function of temperature. The orientational order parameters (OOPs) value increases with decreases of temperature both the nematic and smectic A phases. Haller's extrapolation procedure has been used to determine the orientational order parameter <P2> from the birefringence data. The temperature dependence of birefringence were measured from the transmitted intensity data for wavelength λ=632.8 nm and λ=532 nm. The modified four parameter model consistent with the mean-field theory for weakly first order transition have been used. This result has also been successfully fitted with those calculated from the Maier-Saupe theory for the nematic and McMillan's theory for the Sm A phase.

1. Introduction

Liquid crystalline compounds can exhibit one or more mesophases with symmetry intermediate between that of an isotropic liquid and three dimensionally ordered solid crystal [1]. Study of the physical properties of various mixtures of liquid crystalline compounds has been a subject of considerable interest in order to produce room temperature mesophases for application in display technologies [2]. The order parameter is one of the very important parameter of the nematic phase. Orientational order parameter determines all of its anisotropic properties and relation between macroscopic and microscopic properties. Several techniques for measurement of the orientational order parameter were proposed since it has great importance for investigation of physical properties of liquid crystals. About thirty years ago, the discussion concerning orientational order parameter has been carried out but no suitable conclusion taken until today. Nevertheless it is widely accepted that any of the bulk tensorial properties like magnetic and electric susceptibilities elastic constants, refractive indices etc. can be used to determine the order parameter in liquid crystals. There are different methods are developed to study the order parameter from the birefringence study. One such method to evaluate orientational order parameter is the molecular polarizibility, and the anisotropy of this is one of the important properties of liquid crystals because the intermolecular interaction energies are based on them according to several theoretical models. Any physical properties of nematic liquid crystal are closely connected with orientational order parameter. Further de Gennes [1] suggested that the anisotropy of any physical quantity can be a measure of OOP. Latter , de Jeu [3] and Kuczynski et al.[4,5] proposed a simple method for the determination of the OOP from birefringence measurements without considering any local field experienced by the molecule in a liquid crystal phase. The transition observed between the isotropic liquid phase (I) and the nematic phase (N) exists only orientational order but no positional order. This transition is weakly first order transition . The smectic-A (SmA) phase exhibits Orientational order as well as one-dimensional positional order which can be described in terms of a two-component complex order parameter. In general terms the *N*-Sm*A* transition should belong to the three-dimensional *XY* universality class. The first-order and second-order character of the transitions of mesophases and the universality class of the critical exponents β have been investigated extensively by means of several experimental techniques. Nearly about thirty years ago McMillan [6], Kobayashi [7], de Gennes and Prost [1] suggested that the coupling between the nematic - smectic A (N-SmA) order parameter should belon to the 3D-XY universality class, giving rise to the first order N-SmA tricritical point (TCP).

In this work, we report a optical procedure for the determination of the orientational order parameter <P2> of a binary mixture of two smectogenic compounds 5-trans-n-pentyl-2-(4- isothiocyanatophenyl)-1,3-dioxane (5DBT) and 1, cyano-biphenyldecyl- ether (10OCB) showing an induced nematic phase in a certain concentration range 0.10 < x5DBT < 0.88. In addition, the order parameter critical exponent (β) is also obtained from a four parameter expression. We have been successful in calculating the OOP directly from the birefringence measurements using the well known Haller's extrapolation technique [8] and compared with those obtained from maier-Saupe theory [9] for nematogenic and McMillan's theory [10] for smectogenic mixtures.

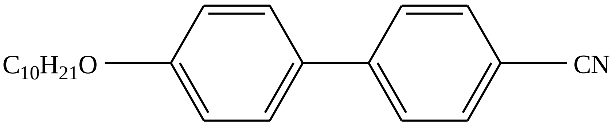
2. Experimental Details

2.1 Materials

The compounds 5DBT and 10OCB were purchased from AWAT Co. Ltd., Warsaw, Poland and Merck, U.K. respectively and were used without further purification. The structural formulae of pure smectogenic liquid crystal compounds (10OCB) and chemical names of the two pure smectogenic liquid crystal compounds are as follows:

Component 1: 5-trans-n-pentyl-2-(4-isothiocyanatophenyl)-1,3-dioxane (5DBT)

Component 2: 4-cyano-40-n-decyloxy-biphenyl (10OCB)



Cr 59.5°C SmA 84°C I

Twelve mixtures having molar concentration of 5DBT equal to 0.10, 0.16, 0.20, 0.25, 0.30, 0.40, 0.50, 0.60, 0.69, 0.74, 0.80 and 0.88 were prepared.

2.2 Optical Transmission (OT) Method

The high resolution optical transmission method (accuracy $\pm 10^{-5}$) enables us to carry out to measure the intensity of a laser beam transmitted through a homogeneously aligned LC cell of thickness 5.1 µm. A solid state green laser (λ = 532 nm) and a He-Ne laser (λ = 632.8 nm) were used to explore its phase retardation. The temperature of the cell was controlled and measured with a temperature controller (Eurotherm PID 2404) with an accuracy of ± 0.1°C by placing the LC cell in a heater made of brass. The heater temperature was varied at a rate of 0.5°C $\min^{-1}$, this translates into a temperature difference of 0.025°C between two successive readings. Intensity of the transmitted light was measured by a photo diode at an interval of 3 seconds. The stability of the intensity of laser was monitored by another identical photo diode. The photo diode outputs were precise by precession multimeters (Keithely model 2000). The experimental details for the birefringence measurement from optical transmission method in the nematic and SmA phases have been illustrated in earlier publications [11,12].

3. Results and Discussions

3.1 Determination of orientational order prameter

The temperature variation of the order parameter <P2> values obtained from the optical transmission method for all the mixtures and pure compounds are shown in the figure 3. It is seen that near the nematic-smectic A phase transition temperature the order parameter values as determined from optical birefringence measurements are observed to decrease very slowly. Orientational order parameter was determined frequently for nematic liquid crystal but it is very hard for smectic and cholesteric liquid crystals. Therefore the physical properties of a nematic liquid crystal and the orientational order parameter ($<P_2>$) are associated very much to one another. de Gennes [1] proposed that the anisotropy of any physical quantity can be a measure of orientational order parameter for nematic liquid crystal. A precise and very simple method used for the determination of the optical order parameter based on Birefringence Measurements for all phases of liquid crystal. The procedure for determination of the order parameter ($<P_2>$) can be defined by following equation [1]

$$\langle P_2 \rangle = \frac{\Delta n}{\Delta n_0} \qquad [1]$$

Where Δn_0 is the birefringence in the completely ordered state and was obtained from the temperature dependence of Δn. According to de Jeu [3] birefringence data (Δn) used for the determination of ($<P_2>$) is good approximation for nematogens as well as some smectogens considering local field applied for the liquid-crystal molecule. Zywucki and Kuczynski [5] have been predicted that the result of order parameter may be differ for different procedures.Later Kuczynski et al. [4] provide evidence that birefringence data (Δn) can be used to determine order parameter ($<P_2>$) without considering the local field experienced by the molecule in a liquid-crystal phase for nematogens as well as some smectogens. In case of uniaxial liquid crystalline phase the temperature dependence of optical birefringence (Δn) was fitted according to the following Haller's type equation [2]:

$$\Delta n = \Delta n_0 \left(1 - \frac{T}{T^*}\right)^{\beta} \qquad (2)$$

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 temperature variation of birefringence data (Δn) is different for different phases for which birefringence data (Δn) value solely calculated from higher temperature nematic phase applying equation (2). So for all the mixtures the Δn data can be well represented by the Haller's type equation in nematic and smectic phases. The birefringence data changes very well represented by Equation (2) only in the nematic phase but in the entire range of the smectic A phase the agreement is very poor. Therefore the extrapolation technique used for the birefringence data (Δn) obtained in smectic phase gives inaccurate values of the fitted parameters Δn_0, T^* and β for the mixture are listed in Table 1 for both green and red laser. Hence our procedure is safe only nematic range for wide temperature nematic region. The critical exponents β, obtained from Haller's extrapolation lies within the range from 0. 085 to 0.204 for geen laser and from 0.136 to 0.199 for red laser, which are quite less compare to the predicted tricritical value (β=0.25). The Haller's extrapolation technique used to determined order parameter ($<P_2>$) without consideration of the internal field for which the value of critical exponent β lies at the critical region inside the NI region where the fluctuation is large.

Table 1a. Values of the fitting parameters Δn_0, T^* and β obtained from Haller's extrapolation. From equation (2) using red laser beam:

Mixture	Δn_o	T(K)	β
0.1	0.288±0.066	351.67 ±0.12	0.146±0.035
0.16	0.301±0.012	350.025±0.076	0.186±0.008

0.2	0.292±0.032	347.884±0.077	0.193±0.020
0.25	0.302±0.005	346.62 ±0.075	0.192±0.005
0.3	0.282±0.001	344.64±0.024	0.171±0.001
0.4	0.297±0.009	342.15 ±0.023	0.199±0.001
0.5	0.278±0.011	341.56 ±0.115	0.190±0.009
0.6	0.266± 0.001	340.64 ±0.051	0.192±0.005
0.7	0.253±0.001	340.86 ±0.040	0.156±0.003
0.74	0.268±0.001	341.11 ±0.039	0.1791±0.03
0.8	0.321±0.007	341.60 ±0.044	0.1981±0.03
0.9	0.236±0.006	343.15±0.0271	0.1369±0.05

Table 1b. Values of the fitting parameters Δn_0, T^* and β obtained from Haller's extrapolation. From equation (2) using green laser beam:

Mixture	Δn_o	T(K)	β
.1	0.198±0.019	351.61 ±0.29	0.085±0.01
.16	0.277±0.012	349.80 ±0.10	0.156±0.09
2	0.286±0.008	347.70 ±0.05	0.173±0.06
.25	0.305±0.002	347.80±0.02	0.182±0.02
.3	0.311±0.001	344.67 ±0.03	0.184± 0.01
.4	0.288±0.003	342.41 ±0.01	0.182±0.04
.5	0.311±0.005	341.43 ±0.01	0.198±0.06
.6	0.286±0.004	340.47 ±0.02	0.198± 0.06
.7	0.302±0.002	341.17 ±0.07	0.204±0.02
.74	0.302±0.001	340.64 ±0.01	0.178±0.01
.8	0.278±0.005	341.33 ±0.04	0.146±0.04
.9	0.186±0.004	343.08 ±0.03	0.124±0.04

To overcome this discrepancy for the improvement the value of critical exponent a four parameter power-law expression [13] for order parameter $<P_2>$ has been introduce completely free at the entire region of NI transition for which T approaches to T_{NI}, at the same time the value of critical exponents β would approach the mean field predicted value. The mean field theory for critical exponent β as well as tricritical behaviour for a weakly first order transition has been performed using the following expression

$$D = A[B + (1-B)(1-\frac{T}{T^*})^{\beta}] \qquad (3)$$

Where D is the physical parameter under consideration (birefringence in this case), A and B are constants, is the critical exponent and T* is slightly greater than the clearing temperature. The fitting were done by considering the nematic phase only and the curves are extrapolated to the smectic phase. The temperature variation order parameter depicted in figure 1 and the solid lines represent the four parameter fit using equation 3. The different parameters obtained by fitting the experimental data to Equation (3) are displayed in Table 2. Our observed order parameter critical exponent values represent the nearly the to the theoretically predicted value of 0.25 strongly supporting the nature of nematic-isotropic phase transition.

Table 2a. Values of the fitting parameters obtained from four parameter fit to Equation (3) using red laser beam:

Mixture	A	B	T	β
0.1	0.293±0.128	0.227± 0.022	351.67±0.027	0.250± 0.165
0.16	0.346± 0.014	0.079± 0.007	350.02±0.026	0.251± 0.012
0.2	0.356± 0.028	-0.008±0.038	348.00±0.092	0.231± 0.030
0.25	0.352± 0.006	0.057± 0.009	346.61±0.026	0.250± 0.009
0.3	0.356± 0.017	0.038± 0.114	344.75±0.620	0.243± 0.056
0.4	0.309± 0.002	0.101± 0.008	342.05±0.019	0.249± 0.006
0.5	0.327± 0.001	0.064± 0.004	341.55±0.018	0.250± 0.003
0.6	0.311± 0.004	0.008± 0.044	340.76±0.243	0.245± 0.020
0.7	0.287± 0.011	0.116± 0.116	341.25±0.695	0.239± 0.059
0.74	0.282± 0.008	0.109± 0.083	341.007±0.433	0.230± 0.042
0.8	0.371± 0.007	0.046± 0.010	341.60±0.039	0.249± 0.009

0.9	0.328±0.043	0.086± 0.017	343.15±0.046	0.231± 0.029

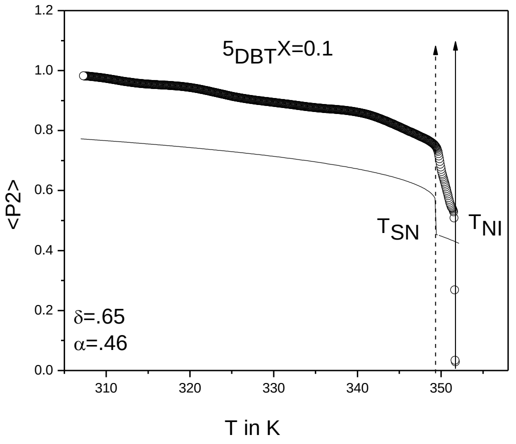
Table 2b. Values of the fitting parameters obtained from four parameter fit to Equation (3) using green laser beam:

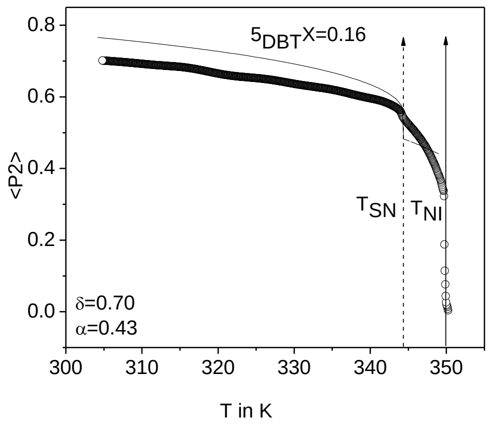
Mixture	A	B	T	β
.1	0.287±0.106	0.236±0.083	351.61±0.059	0.250± 0.079
.16	0.367± 0.024	0.082± 0.012	349.80±0.025	0.248± 0.021
2	0.364± 0.051	0.052± 0.028	347.70±0.046	0.240± 0.043
.25	0.342± 0.004	0.098± 0.030	347.80±0.210	0.250± 0.016
.3	0.330± 0.001	0.112± 0.005	344.67±0.029	0.243± 0.003
.4	0.308± 0.0008	0.126± 0.003	342.36±0.013	0.249± 0.002
.5	0.327± 0.0009	0.092± 0.003	341.43±0.011	0.250± 0.002
.6	0.298± 0.0008	0.097± 0.003	340.32 ±0.007	0.245± 0.002
.7	0.313± 0.013	0.082± 0.102	341.03±0.5863	0.245± 0.054
.74	0.319± 0.002	0.090± 0.007	340.61±0.011	0.223± 0.004
.8	0.317± 0.013	0.192± 0.012	341.29±0.038	0.251± 0.020
.9	0.259± 0.03	0.126± 0.016	343.08±0.040	0.237± 0.037

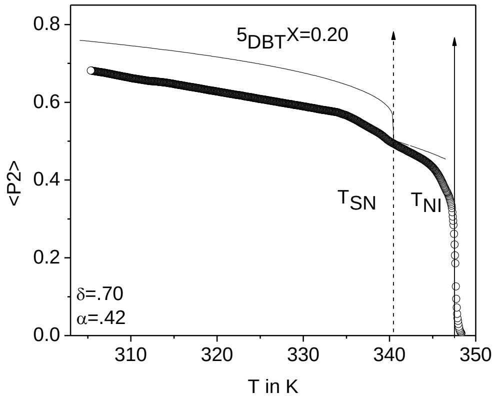
Our order parameter values for the temperature variations of order parameter ($<P_2>$) for the all mixtures are shown in Figure 1. It is clear that order parameter $<P_2>$ increases when mixture enters from higher temperature (isotropic) region to lower temperature (nematic) region. The order parameter value do not agree well with maier-Saupe theory [9] for $X_{5DBT}=0.3$. However, for mixtures $X_{5DBT}=0.4$, $X_{5DBT}=0.5$, $X_{5DBT}=0.6$, only nematic phase exists, the agreement is quite good. The order parameters have been fitted to those calculated from McMillan's theory [6]. Now the single particle McMillan potential is given by

$$\varepsilon(\cos\theta, z) = -\varepsilon_0\left[\delta\alpha\tau\cos(2\pi z/d) + \{\eta + \alpha\sigma\cos(2\pi z/d)\}P_2(\cos\theta)\right] \tag{4}$$

where α and δ are two adjustable parameters, d is the layer thickness, z is the displacement along the layer normal, $\eta = <P_2(\cos\theta)>$, 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 values of η, τ and σ are calculated using the self-consistency relationships as a function of temperature. In the calculation using McMillan's theory, the parameter α, which varies with the chain length, has been varied keeping the parameter δ fixed. The agreement between the experimental <P2> values from birefringec measurements with those calculated from McMillan's theory is poor for all mixtures. The best fitted theoretical curves were obtained by changing the values of α and δ is shown in Figure 1 (a-l). In order to improve this disagreement, we have compared our <P2> values from birefringencec measurements with those calculated from the modified McMillan theory as proposed by Luckhurst and Timimi [14]. The agreement between the experimental <P2> values from birefringence measurements with those calculated from the modified McMillan theory is very good for all the mixtures.



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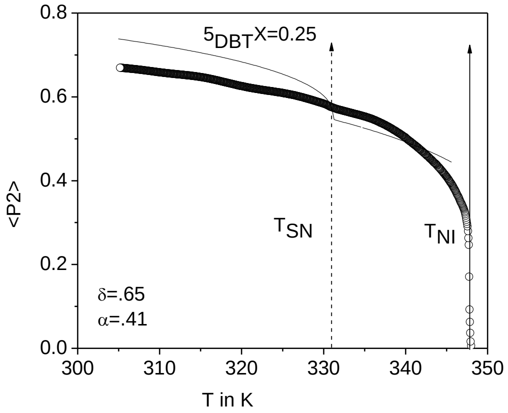
T in K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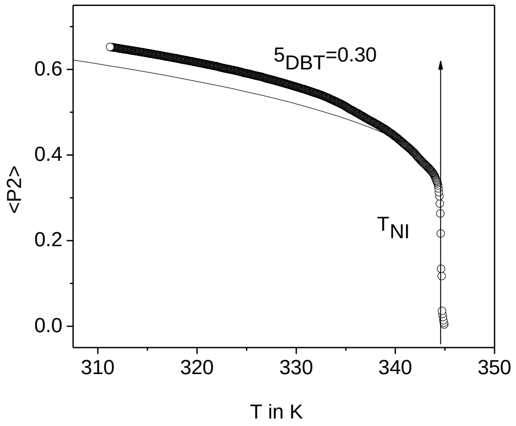
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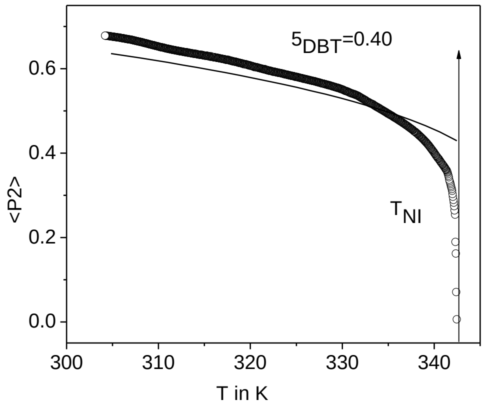
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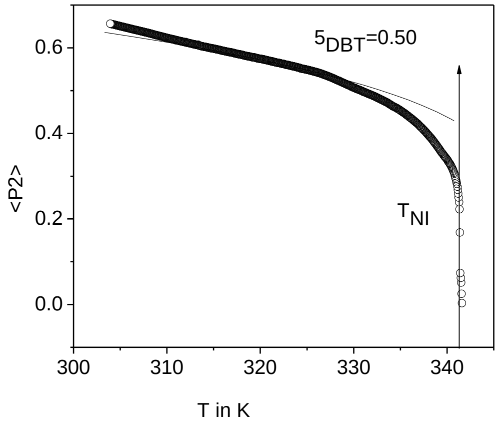
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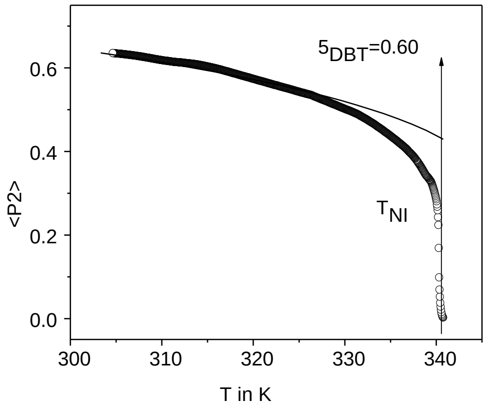
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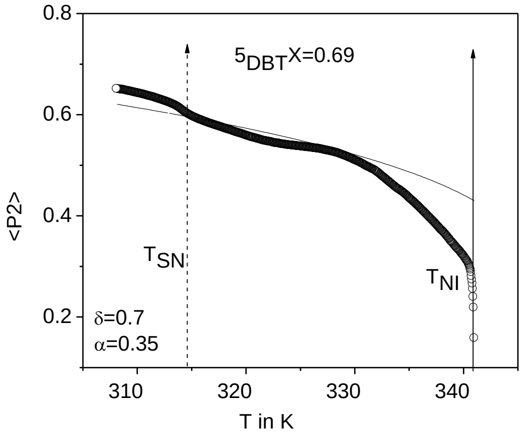
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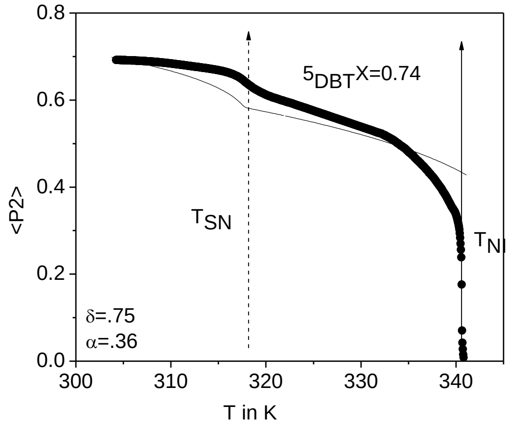
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T in K

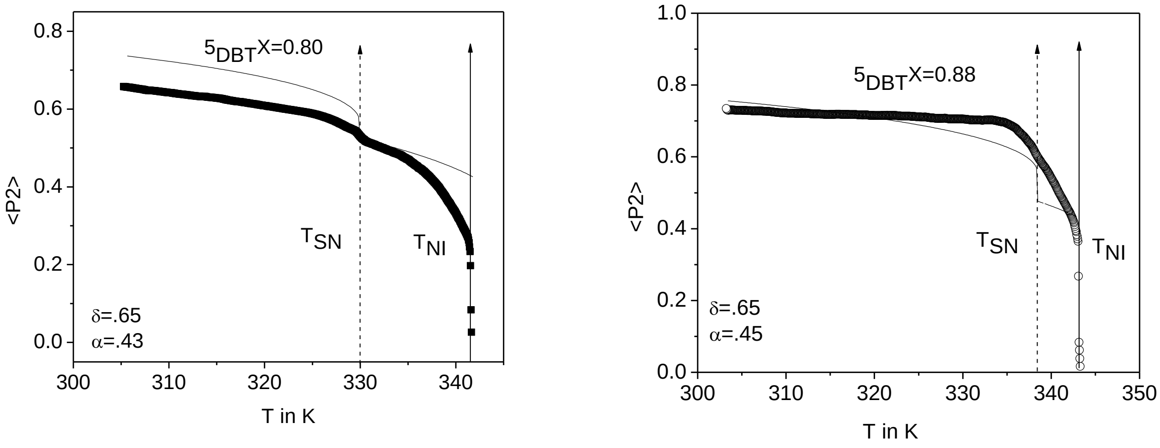

Figure 1. Temperature variation of $<P_2>$ for (a) x_{5DBT} = 0.10, (b) x_{5DBT} = 0.16, (c)) x_{5DBT} = 0.20, (d)) x_{5DBT} = 0.25, (e)) x_{5DBT} = 0.30, (f) x_{5DBT} = 0.40, (g) x_{5DBT} = 0.50, (h) x_{5DBT} = 0.60, (i) x_{5DBT} = 0.69, (j) x_{5DBT} = 0.74, (k) x_{5DBT} = 0.80, and (l) x_{5DBT} = 0.88, Solid arrow denotes nematic-isotropic transition (T_{NI}) and Dashed arrow represents nematic-smectic A transition (T_{NA}) temperatures respectively. ο- represent the experimental birefringence data and the solid lines are fit to Equation (3).

4. Summary and Conclusions

Optical transmission studies have been undertaken to measure the birefringence of a binary system of nematogenic compounds exhibiting induced smectic A*d* and re-entrant nematic phases. A simple and precise method for the determination of the optical birefringence as a function of temperature was used in this work. It was possible to measure the birefringence Δn with reasonably good accuracy (better than $\pm 10^{-4}$) in all the liquid crystalline phases. The agreement between the experimental $<P_2>$ values from the birefringence measurements with those calculated from McMillan's theory have been found to be poor in the smectic A*d* phase. This discrepancy has been removed by recalculating the orientational order parameter values according to a modified McMillan theory as proposed by Luckhurst and Timimi, taking into account slight temperature dependence.

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