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Phase Transitions and Order Parameter Studies from Polarizabilities in 3.Om and 3O.Om Liquid Crystalline Compounds

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As a part of our systematic studies on liquid crystals of nO.m, n.Om, nO.Om and n.m homologous series, n-(p-n-alkoxy/alkylbenzylidene)-p-n-alkyl/alkoxy anilines, we present in this article the nature of phase transitions across isotropic–nematic exhibited by all the compounds mentioned below. Further, the orientational order parameter in the nematic phase of N-(p-n-propyl/propyloxy benzylidene)-p-n-alkoxy anilines, 3.Om and 3O.Om with m = 6–8 are estimated from the molecular polarizabilities calculated using the experimental refractive indices and density results. The molecular polarizabilities α_e and α_o are obtained for all the compounds using the above results for both Vuks and Neugebauer local field models applicable to nematic liquid crystal. α_e and α_o calculated in this way are used to obtain $\Delta\alpha$. The polarizability anisotropy in the perfect order (absolute K) is calculated theoretically using the δ-function model developed by Lippincott et al. and molecular vibration method. These enabled the calculation of the orientational order parameter S. The values of polarizability anisotropy for both local electric field models differ significantly. No criterion is known to decide which value is correct. To avoid the determination of uncertain α and $\Delta\alpha$ values considering different local field models, a simple procedure developed by Kuczynski et al. was used for evaluation of S, based solely on birefringence measurement and this value of S is compared with those obtained from field models.

Keywords density; differential scanning caloriemetry; dilatometry; molecular polarizabilities; n.Om and nO.Om compounds; order parameter; refractive indices

1. Introduction

Different groups belonging to physics, chemistry and technology have shown interest on liquid crystals (LC) due to their multifaceted applications. LCs exhibits anisotropy in their mechanical, electrical, and optical properties, behaving like solid crystals. Nevertheless, they have no ability to support shearing, and thus they flow like ordinary isotropic solutions (liquids) [1]. This dual property nature made these materials important in technological applications such as displays and optical switches [2]. Furthermore, to understand the

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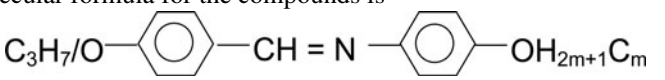
fundamental aspects and the usage of liquid crystalline compounds (LCs) in technological applications, the study of physical properties such as density, viscosity, refractive indices, specific heat, etc. will provide more information.

The LCs are of two different types, viz., thermotropic and lyotropic. The thermo tropic nature depends on temperature, where the liquid crystalline phases exhibit temperature dependence, while in lyotropics the phases are solvent dependent. This particular nature (temperature dependence) has great significance in a wide range of applications in modern technology [1]. The LC display technology is the major area which requires enormous data on the liquid crystalline materials, their response to electrical fields and the study regarding optical anisotropies. Hence, it is very important to gain the knowledge of the temperature dependence of the density, refractive indices, optical anisotropies, molecular polarizabilities, and the order parameter of the liquid crystalline materials. Systematic studies on LC compounds and the literature data [2–4] on the nO.Om compounds reveal that these exhibit 13 different phase variants starting from mono variant (N, A, or C) to penta variant (NACIG). Further, it has been observed from the systematic studies on the Schiff's base compounds that the position of the oxygen atom in the molecular moiety plays an important role in deciding the clearing temperature, the richness of the nematic phase and the phase variant a compound exhibits. Several workers [5–10] have done birefringence investigations of different thermotropic LCs.

The present manuscript determines the density, birefringence of the above materials with temperature. These data are utilized to calculate the molecular polarizabilities and in turn the orientational order parameter, S in the nematic phase of the LCs of two homologous series, *N*-(*p*-*n*-propylbenzylidene)-*p*-*n*-alkoxy anilines, 3.Om and *N*-(*p*-*n*-propyloxybenzylidene)-*p*-*n*-alkoxy anilines 3O.Om with $m = 6$–8. The molecular polarizability anisotropies are estimated from the semi empirical calculations from Lippincott et al. [11] and molecular vibration [12] methods. The results are compared with the value of S obtained directly from the birefringence by Zywucki et al [13, 14].

2. Experimental

The compounds of *N*-(*p*-*n*-propylbenzylidene)-*p*-*n*-alkoxy anilines, (3.Om) and *N*-(*p*-*n*-propyloxybenzylidene)-*p*-*n*-alkoxy anilines, 3O.Om are synthesized [15, 16] following the standard procedure. The respective *p*-*n* propyl/propyloxy benzaldehyde and the corresponding alkoxy anilines are taken in equimolar proportions in absolute ethanol and refluxed for 3–4 hr in the presence of few drops of glacial acetic acid. After refluxing the reactions for 3–4 hr, the solvent is removed by distillation under reduced pressure. The crude sample is subjected to repeated recrystallization from absolute ethanol in cold to give the pure compound, until the transition temperatures are constant. The compounds with the nematic range are only considered for the synthesis as the field models are applicable to nematics only. The molecular formula for the compounds is



where $m = 6$–8.

The purity of the compounds measured through differential scanning calorimetry (DSC) is given in Table 1. The yield of the compounds is about 70–80%. The characterization is carried out using polarizing optical microscope with the hot stage attached (SD Technical specialties, Machilipatnam) and DSC (Perkin Elmer Diamond). An indigenous U-shaped bicapillary pyckometer in conjunction with the cathetometer was used for the

Table 1. Purity of the compounds from DSC

Compound	Melting temperature/°C	Purity
3.O6	63.45	99.45±0.14%
3.O7	64.71	99.49±0.26%
3.O8	68.04	99.09±0.30%
3O.O6	99.50	99.22±0.41%
3O.O7	102.94	98.61±1.04%
3O.O8	101.87	98.01±0.87%

density measurements. The absolute error in the measurement of density is $\pm 10^{-4}$ g cm^{-3}. The cooling rate during the measurement was 0.5 K hr^{-1} and the temperature accuracy is ±0.1°C. The transition temperatures and the enthalpy values obtained from DSC along with those from thermal microscope are presented in Table 2.

The refractive indices of six 3.Om and 3O.Om (with $m = 6$–8 in both the cases) LCs are measured using the modified spectrometer [5] and a wedge shaped cell. The temperature accuracy is ± 0.1°C. The refractive indices n_e and n_o are measured at wavelength 589.3 nm. The refractive index in the isotropic phase (n_{iso}) shows very nominal increment with the decrease of temperature. At the IN phase transformation, the isotropic ray splits into two rays which indicates the onset of birefringence, one value higher and another lower than isotropic value corresponding to extraordinary (n_e) and ordinary refractive (n_o) indices, respectively. This is clearly observed in the telescope of the modified spectrometer at the angle of minimum deviation. In the nematic region, the n_e increases while the n_o decreases with the decrease of temperature. Figures 1–6 will show the variation of refractive index with temperature in all the six LC materials.

3. Results and Discussion

All the compounds exhibit only nematic liquid crystalline phase in between solid and isotropic phase. The methods used, the expressions employed and the procedures adopted are described below in each case for a ready reference

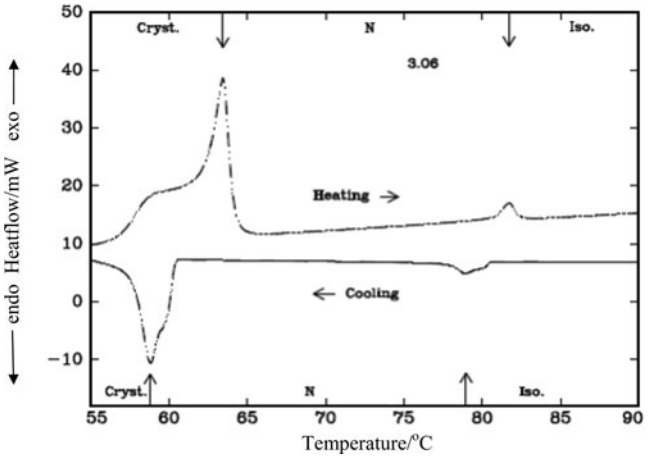


Figure 1. DSC thermo gram of the compound 3.O6.

Table 2. The transition temperatures in °C and heats of transition across different phases

Compound	Phase variant	Method	Melting temp. (°C)	Solidification	NI
3.O6		Heating	63.45		
		ΔH/j/g	37.63		
	N	Cooling		58.80	78.96
		ΔH/j/g		31.03	2.70
		TM	64.0	58.5	79.0
3.O7		Heating	64.71		77.54
		ΔH/j/g	88.02		2.07
	N	Cooling		59.12	76.00
		ΔH/j/g		38.42	2.39
		TM	65.00	60.00	76.00
3.O8		*Heating*	68.04		79.56
		ΔH/j/g	49.35		1.33
	N	Cooling		61.97	78.07
		ΔH/j/g		28.81	1.75
		TM	68.00	61.00	78.00
3O.O6		Heating	99.50		110.33
		ΔH/j/g	69.65		1.93
	N	Cooling		91.27	108.55
		ΔH/j/g		71.98	2.79
		TM	100.00	92.00	108.4
3O.O7		Heating	102.94		105.90
		ΔH/j/g	101.68		3.18
	N	Cooling		94.86	104.56
		ΔH/j/g		78.70	2.97
		TM	103.00	95.00	104.50
3O.O8		Heating	101.87		105.88
		ΔH/j/g	56.12		1.50
	N	Cooling		92.23	104.23
		ΔH/j/g		61.35	1.72
		TM	102.00	62.00	104.00

3.1. Density Measurements in N-(p-n-propyl/propyloxy benzylidene)-p-n-alkoxy Ailines, 3.Om and 3O.Om Compounds, (m = 6–8)

The *N*-(*p*-*n*-propyl benzylidene)-*p*-*n*-alkyloxy anilines, 3.Om *N*-(*p*-*n*-propyloxy benzylidene)-*p*-*n*-alkyloxy anilines, 3O.Om with m = 6–8 in both the series exhibit only nematic phase apart from isotropic and solid crystalline phases and this is identified by the characteristic texture, viz., the threaded marble which is shown in plate 1 for the case of 3.O8 material. The DSC curves are shown in Figs. 1 and 2 for the compounds 3.O6 and 3O.O6.

Furthermore, it has been observed from the systematic studies on these Schiff's base compounds that the position of the oxygen atom in the molecular moiety plays an important

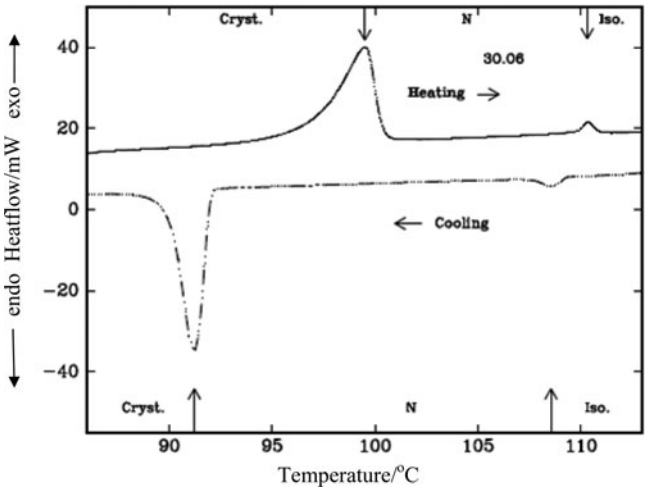


Figure 2. DSC thermo gram of the compound 3O.O6.

role in deciding the clearing temperature, the richness of the nematic phase, and the phase variant a compound exhibits. The following observations are made [17–21].

1. When the oxygen atom is on the left side of the rigid core (nO.m) compounds, generally, the clearing temperatures are below 100°C, no compound exhibits smectic-I phase, only few compounds show smectic-A to smectic-C (AC) transition.
2. When the oxygen atom is on the right side of the rigid core (n.Om), the situation is more or less same as the case of nO.m compounds except in the exhibition of phase variants.
3. When the oxygen atom is on both sides of the rigid core (nO.Om), the clearing temperatures are elevated to >100°C, the presence of nematic phase even in compounds with high alkoxy chain number, and the exhibition of rare phases like smectic-I and the phase transitions like smectic-A to smectic-C (AC), smectic-C to smectic-I (CI).
4. When the oxygen atom is quenched from the molecular moiety (n.m), the clearing temperatures are lowered to around 50°C, the liquid crystalline nature in some cases

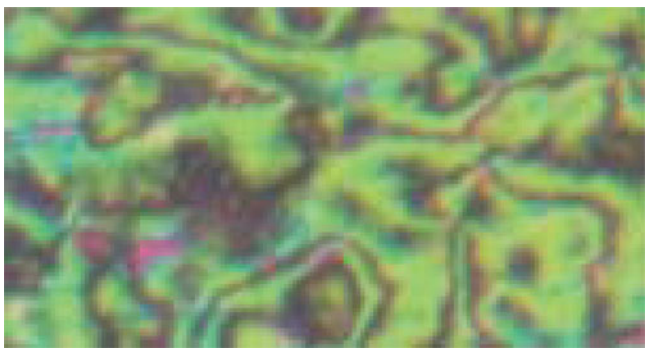


Plate 1. Nematic threaded marble texture of 3.O8 compound at 75.2°C.

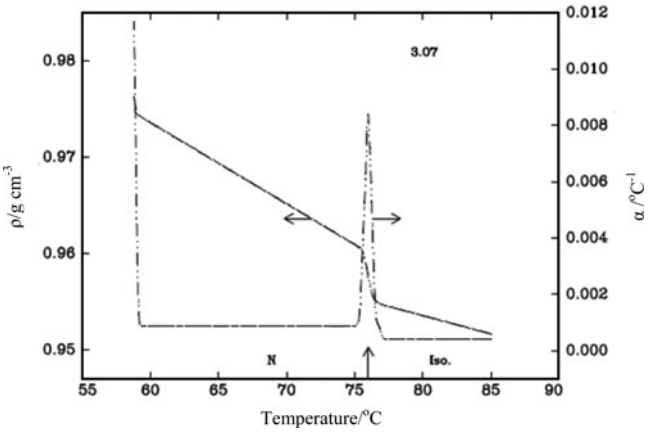


Figure 3. Variation of ρ (gm/cm^3) and α ($10^{-4}\,^{\circ}C^{-1}$) with temperature in 3.O7.

goes below room temperature and as a result the thermal range of nematic phase is reduced.

The compounds studied show the above properties, viz., in the 3O.Om compounds the clearing temperature is high compared to 3.Om compounds as well as the nematic thermal range is high.

The density ($\rho = m/V$) of a substance is defined as the mass per volume and is generally determined by measuring the volume (V) of a known mass (m) of a substance. Several scientists [21] had done dilatometric investigations of various thermotropic LCs in order to obtain relations between the molecular structure and mesomorphic properties. Parameters such as specific volume ($v = 1/\rho$), and molar volume (M_v = molecular weight/density (ρ)), which are closely related to density are also measured in a number of compounds. The thermal expansion coefficient [$\alpha = (1/M_v)\ (dM_v/dT)$] of the material can also be obtained from the dilatometric studies. The density measurement is useful in determining the order of phase transition, pretransition behavior, and critical exponent. Fundamentally, the density is related to the derivatives of Gibb's free energy (G). The first-order transition

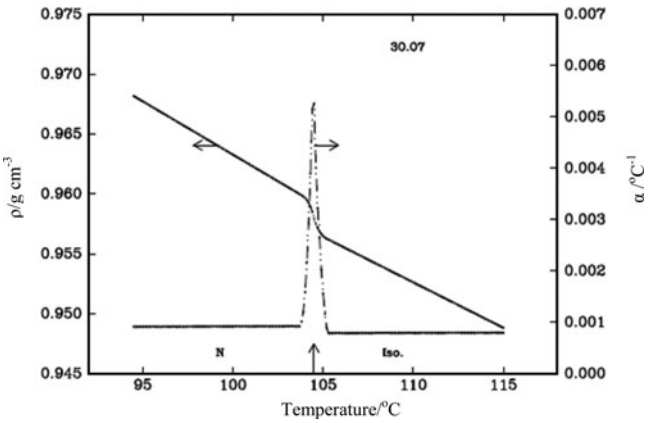


Figure 4. Variation of ρ (gm/cm^3) and α ($10^{-4}\,^{\circ}C^{-1}$) with temperature in 3O.O7.

Table 3. % of density jumps in nematic phase of 3.Om and 3O.Om compounds

Compound	Phase variant	% of density jumps $\Delta\rho/\rho$ across NI phase transition
3.O6	*N*	0.39
3.O7	*N*	0.54
3.O8	*N*	0.33
3O.O6	*N*	0.38
3O.O7	*N*	0.27
3O.O8	*N*	0.38

is characterized by a discontinuity or a steep change in specific volume associated with a thermal expansion coefficient. The dilatometric technique gives complementary results to calorimetric techniques such as DSC and thermal microscopy TM.

It is found that density decreases with the increase of temperature in the liquid crystalline phases except in the vicinity of phase transformations where it shows a steep increase, before it attains equilibrium value of the next (lower temperature) phase. The density jump, $(\Delta\rho/\rho)$ is calculated as the vertical distance between the density values (ρ_1 and ρ_2) obtained by the linear extrapolation from either sides of the transitions, (which are in fact the average value of the above two extrapolated density values), i.e., $[\{(\rho_1 - \rho_2)\}/\{(\rho_1 + \rho_2)/2\}]$. The variation of density and the thermal expansion coefficient with temperature in the studied compounds with $m = 6$–8 are shown in Figs. 3 and 4 for the compounds 3.O7 and 3O.O7.

The variation of molar volume per methylene is found to be 16.02×10^{-6} m^3.mol^{-1} and agrees with the literature data available on nO.m compounds whose values vary between 15 and 17×10^{-6} m^3.mol^{-1}. The observed density jump $(\Delta\rho/\rho)$ and the thermal expansion coefficient maxima (α_{max}) across nematic phase transitions are presented in Tables 3 and 4.

3.2. Isotropic-Nematic Transition

The slope of the density variation with temperature $(d\rho/dT)_{iso}$ in the equilibrium isotropic phase for these compounds is 3.61, 3.79, 4.00, 7.29, 7.59, and 7.94 g.cm^{-3} °C^{-4}, respectively. The values are found to be smaller in the case of 3.Om compounds and in 3O.Om,

Table 4. Thermal expansion coefficient maxima at Iso-N phase in 3.Om and 3O.Om compounds

Compound	Phase variant	Thermal expansion coefficient maxima $\alpha/10^{-4}$ °C^{-1} at NI
3.O6	*N*	73.96
3.O7	*N*	84.13
3.O8	*N*	74.80
3O.O6	*N*	62.99
3O.O7	*N*	59.39
3O.O8	*N*	53.70

Table 5. Slopes of density in different phases of 3.Om and 3O.Om compounds

Compound	$(d\rho/dT)_{Iso} \times 10^{-4}\,^{\circ}C^{-1}$	$(d\rho/dT)_{N} \times 10^{-4}\,^{\circ}C^{-1}$
3.O6	3.61	8.20
3.O7	3.79	8.43
3.O8	4.00	8.64
3O.O6	7.29	9.11
3O.O7	7.59	8.89
3O.O8	7.94	9.83

Table 6. The density jumps, thermal expansion coefficient maxima, across IN phase transition in different LC compounds

Compound	% of density jumps $\Delta\rho/\rho$ across NI phase transition	Thermal expansion coefficient maxima $\alpha/10^{-4}\,^{\circ}C^{-1}$ at NI	Ref.
3.O6	0.39	73.96	PW
3.O7	0.54	84.13	
3.O8	0.33	74.80	
3O.O6	0.38	62.99	
3O.O7	0.27	59.39	
3O.O8	0.38	53.70	
7O.O3	0.48	65.92	6
7O.O5	0.52	69.56	
7O.O6	0.46	70.40	
7O.O7	0.51	60.19	
7O.O9	0.54	76.11	
1O.O4	0.46	71.75	12
3O.O4	0.47	73.12	
6O.O4	0.17	42.86	
7O.O4	0.51	85.19	
10O.O4	0.51	72.96	
7O.1	0.20	133.0	17-20
7O.2	0.27	96.00	
7O.3	0.32	119.0	
7O.4	0.28	58.00	
7O.5	0.34	140..0	
7O.7	0.51	182.0	

they are in agreement with the dilatometric measurements on nO.m compounds [22, 23], PBnA [24] and nO.O4 [21] compounds. The IN transition observed in these six compounds are accompanied by distinct jumps $(\Delta\rho/\rho) \times 100$ and the thermal expansion coefficient maxima, α_{max} values are given in the Table 6. The values of density jumps vary around 0.35 ± 0.05 which are on the higher side compared to those values observed in other LC compounds which exhibit IN transition but of comparable magnitude with those of nO.O4

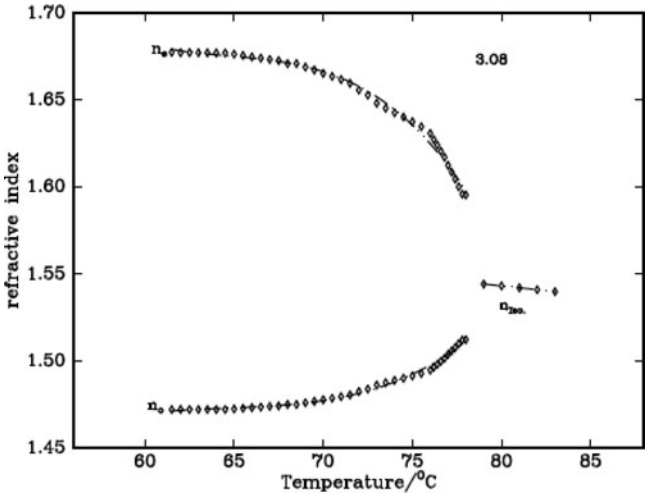


Figure 5. Variation of n_e and n_o with temperature in 3.O8.

[21] compounds except in the case of 3.O7 which is on the higher side. The distinct density jumps and the thermal expansion coefficient maxima suggest the IN transition nature is first order and are found to be in agreement with the body of the data available in other compounds [22–29]. For the sake of comparison the density jumps data of other LC compounds along with these compounds are presented in Table 6. The smaller jump in the case of 6O.O4 like in other compounds is not uncommon. The higher values of slopes of density variation with temperature in equilibrium nematic phase in these compounds (Table 5) than in the isotropic region indicate in the molecular packing in the nematic phase and the accompanying growth of long range orientational order from a completely disordered molecular arrangement in the isotropic phase

3.3. Refractive Index Measurements

The refractive indices of six 3.Om and 3O.Om (with $m = 6$–8 in both the cases) LCs are measured using the modified spectrometer and a wedge shaped cell. The temperature accuracy is $\pm 0.1^{\circ}$C. The refractive indices n_e and n_o are measured at wavelength 589.3 nm. The refractive index in the isotropic phase (n_{iso}) shows very nominal increment with the decrease of temperature. At the IN phase transformation, the isotropic ray splits into two rays which indicates the onset of birefringence, one value higher and another lower than isotropic value corresponding to extraordinary (n_e) and ordinary refractive (n_o) indices, respectively. This is clearly observed in the telescope of the modified spectrometer at the angle of minimum deviation. In the nematic region, the n_e increases while the n_o decreases with the decrease of temperature. Figures 5 and 6 will show the variation of refractive index with temperature in 3.O8 and 3O.O8 LC materials as representative cases.

3.3.1. Estimation of Molecular Polarizabilities from Refractive Indices and Density. The extraordinary (α_e) and ordinary (α_o) polarizabilities corresponding to the electric vector parallel and perpendicular to the optic axis are given as:

$$\alpha_e = \bar{\alpha} + 2\left(\alpha_{||} - \alpha_{\perp}\right) S/3 \tag{1}$$

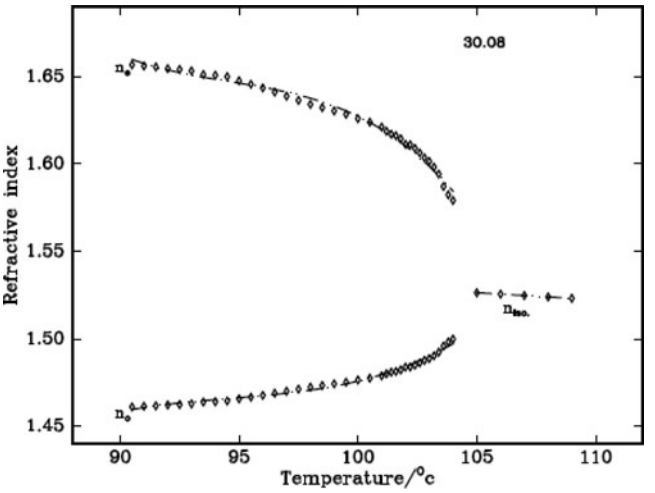


Figure 6. Variation of n_e and n_o with temperature in 3O.O8.

$$\alpha_o = \bar{\alpha} - \left(\alpha_{||} - \alpha_{\perp}\right) S/3 \tag{2}$$

Where S is the order parameter $\alpha_{\parallel}$ and $\alpha_{\perp}$are polarizabilities of the molecule parallel and perpendicular to the long molecular axis of the LC molecule. The average molecular polarizability $\bar{\alpha}$ is given as:

$$\bar{\alpha} = (\alpha_e + 2\alpha_o)/3 = \left(\alpha_{||} + 2\alpha_{\perp}\right)/3 \tag{3}$$

Combining the above two equations S, the order parameter is

$$S = (\alpha_e - \alpha_o) / \left(\alpha_{||} - \alpha_{\perp}\right) \tag{4}$$

Table 7. Parallel, perpendicular components, and mean polarizabilities of (10^{-24} cm^3) 3O.Om and 3O.Om compounds

	Polarizabilities by Lippincott δ - function model				Vibrational** method
Compound	$\alpha_{\parallel}$ 10^{-24} cm^3	$2\alpha_{\perp}$ 10^{-24} cm^3	$^*\alpha_n$ 10^{-24} cm^3	α_M 10^{-24} cm^3	α_M 10^{-24} cm^3
3.O6	77.01	48.95	0.6918	41.98	40.28
3.O7	80.62	50.98	0.6918	43.87	42.51
3.O8	84.23	53.02	0.6918	45.75	44.73
3O.O6	79.89	48.56	1.0900	42.82	43.57
3O.O7	83.54	50.70	1.0900	44.75	45.54
3O.O8	87.19	52.84	1.0900	46.68	47.51

$^*\alpha_{\parallel n}$ value included in parallel component of polarizability.

Table 8. Values of Σb_L, Σb_T, and (Σb_L - Σb_T) of 3O.m and 3O.Om compounds

Compound	Σb_L	Σb_T	Σb_L-Σb_T
	10^{-24} cm^3	10^{-24} cm^3	10^{-24} cm^3
3.O6	58.70	31.08	27.61
3.O7	61.72	32.91	28.82
3.O8	64.75	34.72	30.02
3O.O6	64.80	32.96	31.84
3O.O7	67.66	34.48	33.18
3O.O8	70.52	36.00	34.52

Table 9. Percentage of deviations of order parameter, S estimated assuming the two field models from that obtained using Δn, the birefringence in perfect order

	Vuks		Neugebauer	
Compound	Lip.	Vib.	Lip.	Vib.
3.O6	−3.8	−1.1	+9.2	+11.0
3.O7	−2.1	−4.9	−3.1	0.4
3.O8	+48.0	+53.9	+43.0	+48.8
3O.O6	+10.7	+14.7	+10.5	+9.7
3O.O7	+8.5	+9.9	+13.7	+13.1
3O.O8	+11.7	+11.4	+11.3	+9.2

For the estimation of the molecular polarizabilities of LC molecules, the authors have considered both the models, one due to Vuks [30] which considers the local field of the molecule as isotropic and the other due to Neugebauer [31] which considers the local field

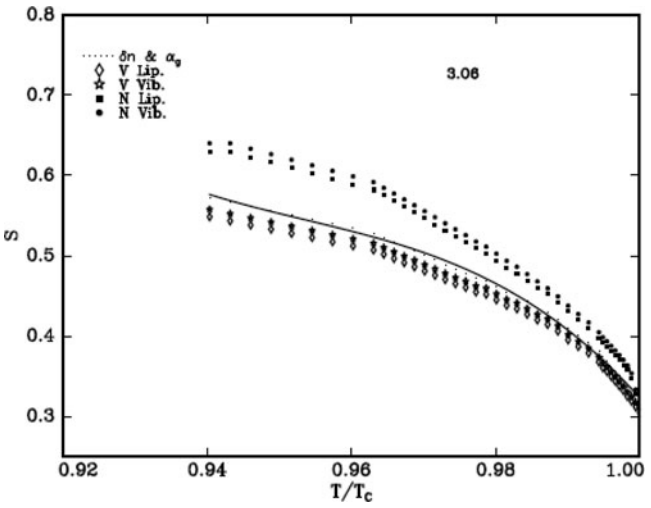


Figure 7. Variation of S with reduced temperature in 3.O6.

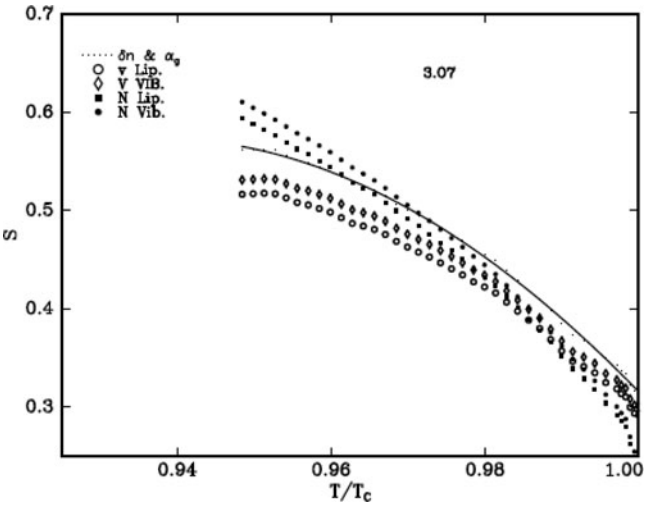


Figure 8. Variation of S with reduced temperature in 3.O7.

as anisotropic. The relevant equations of the two models for the calculation of molecular polarizabilities are given below.

(a) Vuks method

This model was first applied to LC molecules by Chandrasekhar et al. [32] assuming the internal field as isotropic even in anisotropic crystal. These assumptions lead to the following equations:

$$\alpha_e = \left[\frac{3}{4\pi N}\right]\left[\frac{n_e^2 - 1}{\bar{n}^2 + 2}\right] \tag{5}$$

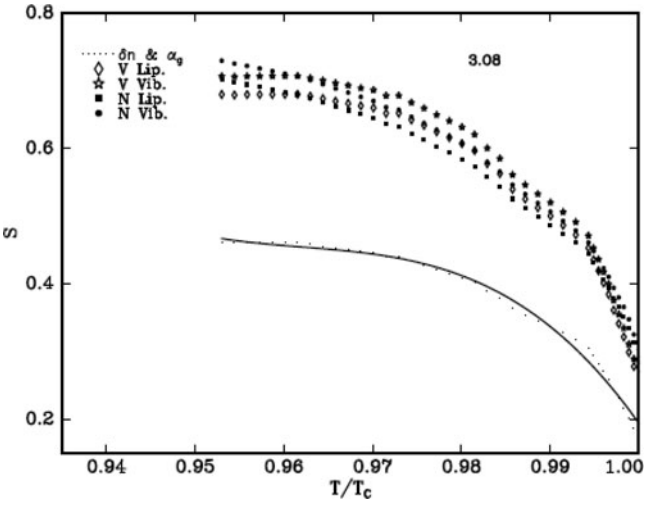


Figure 9. Variation of S with reduced temperature in 3.O8.

$$\alpha_o = \left[\frac{3}{4\pi N}\right]\left[\frac{n_o^2 - 1}{\bar{n}^2 + 2}\right] \tag{6}$$

where N is the number of molecules per unit volume, n_e and n_o are the extraordinary and ordinary refractive indices of the LC molecule.

$$\bar{n}^2 = \left[\frac{n_e^2 + 2n_o^2}{3}\right]$$

and $N = N_A\rho/M$, where N_A is the Avogadro number, ρ is the density, and M is the molecular weight.

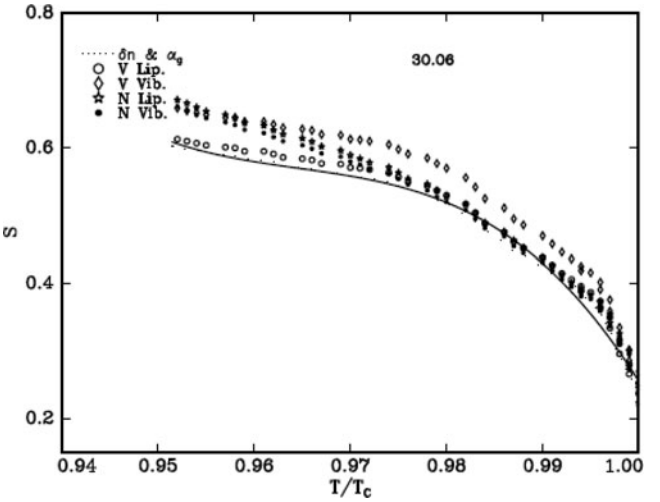


Figure 10. Variation of S with reduced temperature in 3O.O6.

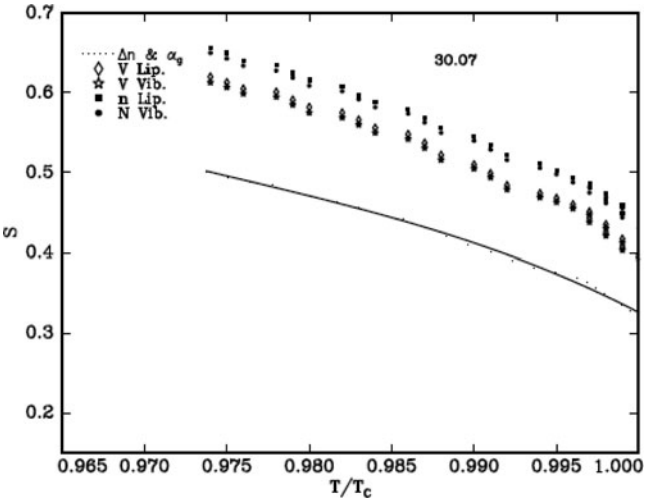


Figure 11. Variation of S with reduced temperature in 3O.O7.

(b) Neugebauer method

Subramanyam et al. [33] applied this method to LC molecule. According to this method the molecular polarizabilities are

$$\alpha_e = \left(AB - 3 \pm \sqrt{(AB-3)^2 - 4AB}\right)/2A \tag{7}$$

$$\alpha_o = \left(AB + 3 \pm \sqrt{(AB+3)^2 - 16AB}\right)/4A \tag{8}$$

where

$$A = \frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left[\frac{n_e^2+2}{n_e^2-1}\right] + \left[\frac{2(n_o^2+2)}{n_o^2-1}\right] \tag{9}$$

$$B = \left(\alpha_{||} + 2\alpha_{\perp}\right) = (\alpha_e + 2\alpha_o) = 3\alpha = 9\left(\bar{n}^{-2} - 1\right) \Big/ \left[(4\pi N_i)\left(\bar{n}^{-2} + 2\right)\right] \tag{10}$$

N_i is the number of molecules per unit volume in the isotropic phase.

The molecular polarizability anisotropy $\alpha_{\parallel}$ and $\alpha_{\perp}$ and the mean polarizability are estimated using the semi empirical models, viz., the Lippincott δ-function [11]and molecular vibration [12] whose particulars and the derivative particulars are given literature and they have been successfully used in many liquid crystalline compounds by Pisipati et al. [5–10]. Furthermore, the molecular anisotropy can be obtained from the Haller extrapolation technique using the experimentally evaluated molecular polarizabilities from refractive index and density data. The molecular polarizabilities α_e and α_o are evaluated assuming a local field that the nematic molecule experiences.

Using the Eq. (4) and the values from the Tables 7 and 8, the order parameter, S is estimated. The two models, viz., Vuks and Neugebauer, the molecular polarizabilities, α_e and α_o of all the LCs are evaluated from the refractive indices and density. The variation of S with the reduced temperature for the cases of δn, α_g (which are identical to one another), Vuks model (Lippincott and vibrational), and Neugebauer model (Lippincott and vibrational) are shown in Figs. 7–12 for all the compounds, respectively. The values are

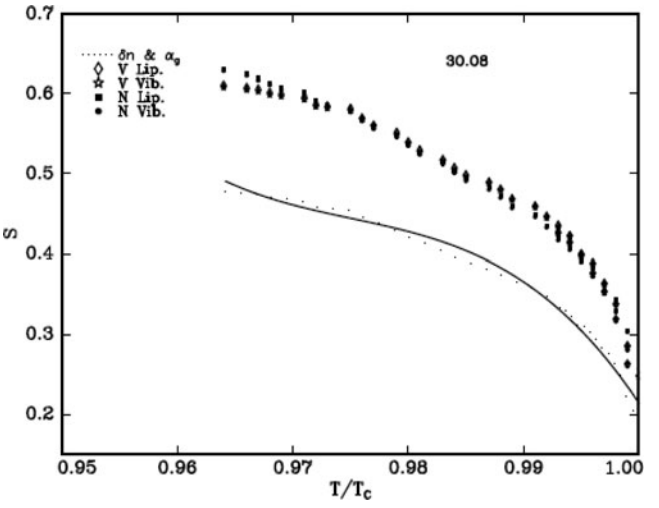


Figure 12. Variation of S with reduced temperature in 3O.O8.

Table 10. Parameters for the best fit through linear regression for the equation $\log \delta n = \log \Delta n + \beta . \log \left(\frac{T*-T}{T*}\right)$

Compounds	T_C	T_{C+}	$\beta \pm 0.002$	Δn	R
3.O6	352.0	353.000	0.202	0.286	0.9989
3.O7	349.0	349.700	0.202	0.278	0.9849
3.O8	351.*O*	351.001	0.236	0.445	0.9953
3O.O6	381.5	381.560	0.226	0.398	0.9972
3O.O7	377.4	378.600	0.201	0.392	0.9948
3O.O8	377.0	377.040	0.220	0.409	0.9989

compared with the S value evaluated from δn and α_g as the S value obtained from these methods, is independent of any internal field that the nematic LC molecule experiences.

In the cases of 3.O8, the variation (deviation) is very high and is more than the permissible value (Table 9). The authors feel the reason may be due to the small value obtained from δn and α_g. Furthermore, the reason for this may be due to the Δn (the birefringence at the perfect order) which is obtained from the linear fit by adjusting the three parameters, viz., the T_C, β, and the regression coefficient, R. The procedure adopted is due to Zywucki et al. [13, 14]. However, for the sake of continuity here the values of the fit parameters along with Δn values are given in Table 10. From the table, it can be seen that the Δn value is very high and is 0.445 and the value of β is as high as 0.226. The deviation errors in Table 9 will show that the values obtained from polarizability data are equal to one another with in the experimental data.

Conclusions

For the sake of comparison of S from different methods for two field models, with S from Δn, the percentage deviation of S value calculated for all methods to that calculated from Δn, the birefringence in perfect order. If the deviation is $\leq$15%, the values can be considered to be in agreement with the S from Δn with in the experimental error. From the tables, figures of density, and order parameter the following salient features are observed:

1. The isotropic to nematic transition is found to be first order as expected.
2. The density jumps observed across Iso.-N transition in the case of 3.O7 compound is found be on the higher side when compared with other 3.Om compounds as well as other nO.m compounds.
3. The slopes of the density in nematic phase are found to be higher suggesting the closer packing of the molecules.
4. It is found that the density slopes are smaller in 3.Om compounds compared to 3O.Om and other nO.m compounds. However, obtaining the smaller density slopes is not at all uncommon.
5. The S value obtained from the Lippincott δ-function, vibrational method in case of Vuks model agrees in all compounds.
6. If the values of percentage errors are compared, it is observed that all compounds exhibit more closeness with the order parameter evaluated from Δn.
7. Furthermore, the figures reveal that the compounds favour Vuks model than that of Neugebauer model. Even though the order parameter S is calculated using the

scaling factors of both Vuks and Neugebauer methods, the values are not included in figures. However, the values of S are always low compared to the above that are obtained using $f(B)$ parameter of Neugebauer method.

Finally, the overall observations from the all compounds suggest the Vuks isotropic model is somewhat favorable to that of Neugebauer model.

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