4.1 Introduction:

Liquid crystals are important for fundamental research and for their applicability in display technology. Liquid crystals are best known for their application in displays; besides it they are widely used in liquid crystal thermometers [1], tunable microlenses [2], light modulators [3], switchable devices [4], light shutters [5], and many more. The liquid crystal display technology is a major area which requires complete knowledge on the liquid crystalline materials, their response to electric fields and the optical anisotropies. The refractive indices of a liquid crystal are mainly determined by molecular structure, operating wavelength, and temperature. Various theoretical models [6-9] have been developed to establish the wavelength and temperature dependence of LC refractive indices.

In liquid crystals, the molecular polarizabilities and their anisotropy are considered to be important characteristic inherent molecular properties because the intermolecular interaction energies, according to different theoretical models are dependent on them. Hence, it is important to gain knowledge of the temperature dependence of refractive indices, optical anisotropies, molecular polarizabilities and the order parameter of the liquid crystalline materials. An essential requirement for mesomorphism to occur in liquid crystal sample is that the molecule must be highly geometrically anisotropic in shape. When a light of frequency $\nu$, is incident upon a liquid crystal molecule, the electrons oscillate with the same frequency due to the electric field vector $E = E_0 \sin (2\pi vt)$. The dipole moment $P$ is induced in the molecule. The induced dipole moment $P$ of an atom or molecule is related to the electrical field by the equation

$$P \propto E$$

or $P = \alpha E \Rightarrow \alpha = P/E$, 


Here $\alpha$ is called the Polarizability and is defined as the dipole moment $P$ per unit electric field $E$. It is useful in the study of molecular structure and properties of organic compounds [10] and is important in determining the electro-optical behaviour of liquid crystals. The orientational order parameter $S$ [11-13] of a liquid crystal is one of the important parameters, which govern the physical properties. The simplest way of defining the orientational order parameter $S$ is

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

where $\theta$ is the angle which the long molecular axis makes with the director and the angular brackets denote a statistical average. The order parameter can be estimated from the polarizability values of liquid crystal materials. The molecular polarizabilities cannot be measured directly but can be calculated by the use of different theoretical approaches.

For the last four decades a number of workers followed different theoretical models to calculate molecular polarizability of liquid crystal molecules viz., Vuks [14], Neugebauer [15], Lippincott $\delta$-function model [16], Haller’s extrapolation method to explain the molecular polarizability and order parameter results in liquid crystals.

Recently Ramakrishna Nanchara Rao et al [17] has measured birefringence, polarizability and order parameter of p-n-alkoxy benzoic acids using various internal field models. A modified four-parameter model [18] which describes the temperature dependence of ordinary refractive index ($n_o$) and extraordinary refractive index ($n_e$) was developed by Kumar [19]. The validation of this model is made by fitting the theoretical values with experimental data of refractive indices. He used refractive indices ($n_e$, $n_o$) data of two liquid crystal samples MLC-9200-000 and MLC-6608. Refractive indices measurements of these liquid crystal samples were carried out in the temperature range of 288-328 K by Li et al [20] at a wavelength of $\lambda = 589$ nm.

Fakruddin et al [21] carried out birefringence, polarizability studies on 2O.O5 and 3O.O5. They calculated the mean polarizability using Lippincott $\delta$-function model and observed that the result is reasonably in good agreement with
the mean polarizability obtained from birefringence data using Vuks and Neugebauer models. The order parameter was determined using Vuks and Neugebauer approaches by Srivastava et al [22]. They measured the refractive indices \((n_e, n_o)\) and birefringence \((\Delta n)\) in solid, cholesteric and isotropic phases of cholesteryl carbonate, cholesteryl stearate and their three homogeneous mixtures of various concentrations. Subbaiah and Zareena [23] estimated the molecular polarizabilities of Adenosine and few of its nucleotides by the quantum mechanical \(\delta\)-function model and molecular dynamic methods. They found that the results obtained were in good agreement for both the methods.

The temperature variation of the refractive indices \((n_o, n_e)\) and density are reported for two liquid crystals HBT and OBT by Sarna and Bhide [24]. The order parameter is evaluated by both Vuks’ and Neugebauer’s approaches. The possible source of error was discussed in evaluating the order parameter from refractive indices measurements. Paul et al [25-27] investigated the temperature variation of density and refractive index for a number of compounds. They calculated the molecular polarisabilities from refractive indices using Vuks’ formula and evaluated orientational order parameters from polarisabilitity values. Sarkar et al [28] also studied the temperature dependence of density, refractive indices for 11CHBT and calculated the orientational order parameter. It was also proved that order parameter do not depend on wavelength.

Datta Prasad et al [29] calculated the birefringence and orientational order parameter of LC compounds and reported that the S value evaluated from different methods agree near the IN interface while it shows divergence when the nematic phase stabilizes. Pardhasaradhi et al [30] estimated the order parameter of liquid crystal compounds of 5O.5, 5.05 and 6O.05. Chizu Sekine et al [31] synthesized and investigated new three ring phenyl acetylene liquid crystals and their refractive indices and order parameter with temperature. They studied the effect of position of methyl group as lateral substituent on the refractive index and order parameter of liquid crystals and found that the most effective methyl position for improving nematic temperature range was on the central ring and this is also best position for obtaining high \(\delta n\) values.
The orientational order parameter and distribution function using refractive index and density data for the nematogenic mixtures octyl benzoic acid (OBA) and nonyl benzoic acid (NBA) was determined by Divya et al [32]. From this they found that with the increase of temperature, $<P_2>$ and $<P_4>$ decrease showing that there is decrease in ordering of molecules in the nematic phase. Murthy et al [33] employed a new theoretical method of evaluating polarizabilities of liquid crystalline compounds, namely n-alkyl-p-(4-ethoxy benzyldiene amino)-α-methyl cinnamates, which exhibit smecticA and nematic phases where the vibrational frequencies are used to evaluate the force constants, mean amplitude of vibration and hence bond polarizabilities. A sound consonance is found between the values estimated from this method and reported data which confirms the applicability of this method to smecticA and nematic phases. The variation of order parameter with temperature is also studied.

Ranga Reddy et al [34] tested the viability in the application of the modified Lippincott $\delta$-function potential method for binary mesophase mixtures. The values of polarizabilities, polarizability anisotropies and order parameters of binary mesophase mixtures containing N-(p–propoxy benzylidene)-p-pentyl aniline, when evaluated through this method and compared with the reported values and found to be in good agreement with each other. The mean polarizabilities of phenyl benzoate liquid crystals by using modified Lippincott $\delta$-function potential method was determined by Ranga Reddy and Rama [35]. They also evaluated mean polarizabilities of a few liquid crystalline schiff bases MBBA, HBT, OBT, PBPA and BBPA using Lippincott $\delta$ function potential model and compared these with the values obtained by Adamski et al [36] using refractivity method.

Fernandez et al [37] calculated the temperature variation of density and refractive index and had determined the principal polarizabilities using Vuk’s model in the liquid crystalline 8O.1. Shashidhara Prasad et al [38] provided the information about the density, heat of transition and refractive index variation with temperature in isotropic and re-entrant isotropic phases and estimated the molecular polarizabilities using the Lippincott-$\delta$-function method. Hauser et al[39] reported the density, heat of transition and refractive index results in liquid
crystalline compounds of 5-n-hexyl-2-(4-alkoxy phenyl) pyrimidine homologues series and premeditated the pressure dependence of IN transition temperature, packing fractions, order parameter and the local field anisotropy.

Kali et al studied [40] density and refractive index variation with temperature in the nematic phase of homologues of alkyl and alkoxy phenyl cyclohexane carboxylates and order parameters and effective polarizibilities were calculated using Vuks and Neugebauer models. Palffy-Muhoray, Balzarini and Dunmur reported [41] a first order IN transition using temperature variation of density and refractive index for the compounds EBBA, and butyl p-(p’-ehoxyphenoxy carbonyl) phenyl. Susmitas et al [42] calculated the effective polarizabilities of alkyl cyanobiphenyls, alkoxy cyanobiphenyls and one more mixture of two alkyl cyanobiphenyls in the nematic phase using the methods of Neugebauer [15], Vuks [14] and Sauge-Maier [13] and infered that they are appreciably different though the order parameter S evaluated with those values are in good agreement. Lockhart et al [43] reported the measurement of refractive indices and their relation to orientational order at smectic A to smectic C transition. Their interpretation of the data was on the basis of Neugebauer model.

Rama Murthy and Ranga Reddy [44] evaluated the mean polarizabilities of a homologues series of nematic liquid crystal of p,p’-di-n-alkyl azoxy benzenes by using a modified Lippincott δ-function potential model and these values were found to be in good agreement with the values calculated from refractive indices. They [45] calculated the mean polarizabilities of homologues series of nematogenic trans-4-ethoxy-4’-n-alkonylazobenzenes by using modified Lippincott δ-function potential model which were compared to the results obtained from refractivity method and found to be in good agreement with them. They [46] also evaluated the mean polarizabilities of nematic phase using Lippincott δ-function potential model and the results were compared with the values obtained from Born’s relation and were found to be in good agreement. Rama Murthy et al [47] evaluated the parallel, perpendicular and mean polarizabilities for two series of nematogenic homologous series p, p-- di-n-alkoxy-azoxy benzenes and p- (p-alkoxy phenyl) azo phenyl ester using modified
Lippincott-δ function potential model and found that the values were in agreement with the other reported values of α, providing a basis of the applicability of Lippincott δ function potential model to liquid crystals.

Madhusudhana[48] argued that the order parameters calculated using Neugebauer and Vuks models agree reasonably well in the nematic phase (Sarna et al[49]) of HBT and OBT which is due to the error in the density or in the alignment of the sample while measuring the refractive indices. He pointed out that if the density is increased by 1% in the nematic phase the calculated values of S increases by about 11.5% in the case of Neugebauer approach and decreased about only 1% in the case of Vuks approach. Also he pointed out that if the density measurements are correct in the results reported by Sarna et al [49] one is forced to the conclusion that the alignment of the sample is poor. Because as shown by Madhusudhana [48] if the director is not strictly parallel to the glass surface but tilted at an angle 10° to it, one would measure an effectively lower value of extraordinary refractive index nₑ hence the Neugebauer method leads to an effective S value which is about 3.4% higher than the value measured for the truly homogeneous sample whereas Vuks method gives a value of S which is 4.4% lower for the misaligned sample. Sarna et al [50] argued that their previous results [49] were corrected and they contradicted the conclusions and corrections suggested by Madhusudhana.

The optical anisotropies, when calculated by Somasekhar et al [51] from the Vuks formulae are found to be too high and are difficult to account for, especially in the case of substances with large birefringence. On the other hand, the polarizabilities calculated through the Neugebauer approach agree reasonably well with the estimates of polarizabilities made from bond polarizability data. The order parameter for PAA and PAP calculated by Subrahmanyam et al[52] yeild the conclusion that the use of the Neugebauer relations led to results which are consistent and that the calculated internal field constants confirm the anisotropic nature of molecular distribution in nematic liquid crystals. They also calculated the principle polarizabilities of nematic compounds using Vuks and Neugebauer approaches which supported the validity of the Neugebauer relations rather than the Vuks formulae.
Haller et al [53] reported the measurement of ordinary refractive index, birefringence, density and diamagnetic susceptibility as a function of temperature for three materials that exhibit nematic liquid crystalline phases in the vicinity of room temperature. They opined that the temperature dependence of the nematic order parameter is essentially identical for the three materials. They also evaluated the applicability of models used in the computation of polarization fields of anisotropic molecules.

The validity of the Vuks model in an isotropic internal field in a molecule and was first applied to nematic liquid crystals by Chandrasekhar and Madhusudana [54] and the Neugebauer model first applied to uniaxial liquid crystals by Saupe and Maier and later on by Subramhaniyam and Krishnamurthi [55] based on the internal field to be anisotropic through the introduction of a depolarization tensor. Madhusudana et al [56] applied the Vuks theory to calculate the order parameter in anisaldazine and the excellent agreement between the values of S obtained at different wavelengths confirmed the reliability of the vuks method. An alternative way of calculating the polarizability anisotropy in the crystal phase can also be the Haller’s extrapolation method [57].

In recent years, liquid crystal dimers, which are prepared by joining two mesogenic units through a flexible alkyl spacer, are attracting much interest because of their unusual properties compared with monomeric liquid crystals as well as their capability to act as model compounds for semi-flexible main chain liquid crystal polymers [58-61]. The author presents here an optical study of the two nematogenic symmetric liquid crystal dimers 6.O12O.6 and 7.O12O.7. The compounds are in the homologues series of schiff base symmetric liquid crystal dimers viz., α, ω–bis-(4-n-alkylaniline benzylidene – 4’ –oxy) alkanes (m.OnO.m). By measuring the extraordinary and ordinary refractive indices, the molecular polarizability anisotropies are evaluated using Lippincott δ – function model, the molecular vibration method, Haller’s extrapolation method and scaling factor method. The molecular polarizabilities $\alpha_e$ and $\alpha_o$ are calculated using Vuks’ isotropic field model and Neugebauer’s anisotropic field model. The orientational order parameter, S, is estimated by using the molecular
polarizability values calculated from refractive index and density data as well as polarizability anisotropy values calculated as a function of temperature in the nematic phase of both of the dimers. These values are discussed with reference to the order parameter values obtained directly from the optical birefringence, Δn, data without assuming any internal field. A comparison of the order parameter values from all of these methods was carried out in the light of available literature data.

4.2 Result and discussion

4.2.1 Evaluation of mean polarizability using δ-function model

The electrical polarizability is one of the fundamental properties of a molecule. The polarizability and refractive index are linked by the well-known Lorentz - Lorentz equation.

\[
\frac{4}{3} \pi N \alpha = \frac{n^2 - 1}{n^2 + 2} \left( \frac{M}{d} \right)
\]  

(4.1)

Where \( \alpha \) is the mean polarizability, \( N \) is Avogadro’s number, \( n \) is the refractive index, \( d \) is the density and \( M \) is the molecular weight.

Lippincott and Stutman [16] have calculated the molecular polarizabilities of diatomic and polyatomic molecules from semi-empirical δ–function electronic wave functions. Before them many workers attempted to obtain the atomic and molecular polarizabilities from quantum mechanical models. The δ-function potential model, by Frost [62] and later modified by Lipincott has shown encouraging results in obtaining the polarizability values for different diatomic and polyatomic molecules. A deviation of about 10% is found between Lippincott and Stutman results and experimental results. This method can be used for easy calculations of the polarizabilities of big molecules without much computational difficulties.
4.2.1.1 The Lippincott δ function potential model:

The Lippincott δ-function potential model [16] is based on the quantum mechanical approach. To measure the potential variation about the nucleus a mathematical function called δ-function is used. The properties of δ function are,

a) \( \delta(x) = 0 \) when \( x \neq 0 \)
   \( \delta(x) = \infty \) when \( x = 0 \)

b) \( \delta(x-a) = 0 \) when \( x \neq a \)
   \( \delta(x-a) = \infty \) when \( x = 0 \)

c) The area under δ function curve = 1

d) \( \int \delta(x) \, dx = 1 \)

In order to explain the potential of an atom δ function is more appropriate i.e., at the centre of the atom (at the nucleus) the potential rises sharply and decays rapidly when move just away from the nucleus (i.e., potential function vanishes sharply).

In the case of diatomic molecule, the potential value is very high at the nuclei position and zero elsewhere. For a diatomic molecule the single electron potential has the form

\[
V(x) = -\left[A_1 g \delta(x - a/2) + A_2 g \delta(x + a/2)\right]
\]

(4.2)

Where ‘a’ is the δ-function spacing, \( A_1, A_2 \) are δ-function strengths or the reduced electro negativities (REN’s) for the two nuclei, \( g \) is the unit δ-function strength (the value for the hydrogen atom).

The A values can be obtained from separated atom energies by the equation

\[
A = (2E_i)^{1/2}
\]

(4.3)

Lippincott and Stutman [16] used the following empirical relation for obtaining A value for atoms other than hydrogen atom.

\[
A = \left[X/(2.6n - 1.7p - 0.8D + 3F)\right]^{1/2}
\]

(4.4)
where X is the electro negativity of the atom taken from Pauling, n is the principle quantum number, p is 1 for atoms with p electrons in valance shell, 0 for atoms with no p electrons in the valance shell, D is the total number of completed p and d shells in atom. F is the total number of ‘f’ shells in atom.

The electron in this potential behaves as matter wave, so corresponding wave equations are called Eigen states which are the solutions of Schrödinger’s differential equation. For n energy levels n wave functions being possible, the ith bound wave function has the form,

\[ \Psi_i = N \left [ e^{-c_{i} |x_1 + a/2|} + e^{-c_{i} |x_1 - a/2|} \right ] \]

(4.5)

Where \( c_i = (-2E_i)^{1/2} \), \( E_i \) is the separated atom energy for the ith particle (when the atom is individual or isolated).

Lippincott and Dayhoff [63] eliminated the problem of obtaining the ri for each individual electron by generating a super one-electron situation from the corresponding n-electron situation. A resultant c is obtained (written \( c_R \)) and is assumed to account for an electron pair. For homonuclear situation,

\[ C_R = A (nN)^{1/2} \]

(4.6)

Where A is the one-electron \( \delta \)-function strength for the atom, n is the principle quantum number and N is the two times the column number in the periodic table.

For the case of heteronuclear diatomics are readily treated by forming a geometric mean molecular \( \delta \)-function strength \( C_{R12} \).

\[ C_{R12} = (C_{R1}C_{R2})^{1/2} = [(n_1n_2N_1N_2)^{1/2} A_1A_2]^{1/2} \]

(4.7)

and solving the wave equation as if the molecule were homo-nuclear. Lippincott et al [63] extended the same principle to the polyatomic molecules by forming the linear combination of atomic \( \delta \)-function wave functions. Lippincott et al [16] calculated the molecular polarizabilities for a number of diatomic and polyatomic molecules. The principle and the formulae involved in brief are given below.

- Evaluating the parallel bond components from the \( \delta \)-function model.
• Corrections are to be made to the parallel component from the non-bonding regions.

• Obtaining the perpendicular bond components from the \( \delta \)-function strengths.

• Finally evaluating the mean polarizabilities from the parallel and perpendicular components.

4.2.1.2 The parallel component of polarizability

The parallel component of polarizability is mainly due to contribution of electrons in the bond region and non bond region.

a) Bond region parallel component, \((\alpha_{11b})\)

\[
\alpha_{11b} = \frac{4na}{\alpha_0} \left( \langle x^2 \rangle \right)^2
\]

\[(\langle x^2 \rangle)^2 = \left( \frac{R^2}{4} + \frac{1}{2C_R^2} \right)^2 \quad (4.9)\]

\[
\alpha_{11b} = \frac{4na}{\alpha_0} \left( \frac{R^2}{4} + \frac{1}{2C_R^2} \right)^2 \quad (4.10)
\]

\((\langle x^2 \rangle)^2\) is the square of the average of the expectation value of the position of the electron.

Where \( n = \) bond order, \( A \) is the geometric mean \( \delta \) function strength of nuclei 1 and 2, \( \alpha_0 \) is radius of Bohr orbit, \( R= \) bond length.

\[
C_R^2 = [A_1A_2(n_1N_1n_2N_2)^{1/2}]
\]
$A_1, A_2$ are the Pauling electro negativities of two atoms, $n_1, n_2$ are principle quantum numbers of first and second atoms, $N_1, N_2$ are twice the column no. in the periodic table of the two atoms respectively.

In the case that the bond is of hetero nuclear type, a polarity correction is necessary to produce ionic character believed to exist in reality. Hence,

$$\alpha_{11p} = \alpha_{11b}\sigma$$

(4.11)

where

$$\sigma = \exp \left[ \frac{-(x_1 - x_2)^2}{4} \right]$$

(4.12)

For hetero nuclear type, a polarity correction is required and in such a case,

$$\alpha_{11b} = \frac{4nA}{a_0} \left( \frac{R^2}{4} + \frac{1}{2C_R^2} \right)^2 \exp \left[ -\left( \frac{x_1 - x_2}{2} \right)^2 \right]$$

(4.13)

b) Non bond region parallel component, ($\alpha_{11n}$)

The parallel component of polarizability due to non bond region is given by

$$\alpha_{11n} = \sum f_i \alpha_i$$

(4.14)

Here $f_i$ is the fraction of electrons of the $i^{th}$ atom which are not in the bond regions and $\alpha_i$ is the atomic polarizability.

For a poly-atomic molecule, the parallel component of polarizability is

$$\sum \alpha_{11} = \sum \alpha_{11p} + \sum \alpha_{11n}$$

(4.15)

$$\sum \alpha_{11} = \frac{4nA}{a_0} \left( \frac{R^2}{4} + \frac{1}{2C_R^2} \right)^2 \exp \left[ -\left( \frac{x_1 - x_2}{2} \right)^2 \right] + \sum f_i \alpha_i$$

(4.16)

4.2.1.3 The Perpendicular component of polarizability

It is well known that the $\delta$ function model is one dimensional. Hence it was necessary to obtain the perpendicular component by a contrived but justifiable approach. This is discussed in detail by Lippincott and Stutmann [16]. For this purpose, Lippincott assumed that every isolated atom is allowed to possess three degrees of polarizability degrees of freedom, and every bond which
is formed between the two atoms removes two of these degrees of freedom with the exception that (1) if the two bonds are formed from the same atom and exists in a linear configuration, then only three atomic degrees of freedom are lost and (2) if three bonds are formed from the same atom and lies in a plane, then only five atomic degrees of freedom are lost. Using these rules the sum of all of the perpendicular components of the molecule is given as

\[ 2\alpha_{\perp} = (3N - 2n) \left[ \sum \frac{x_i^2 \alpha_{ii}}{\sum x_i^2} \right] \] (4.17)

\( N \) = number of atoms in the molecule, \( n \) = number of bonds in the molecule, \( \alpha_i \) is the polarizability of \( i^{th} \) atom. \((3N-2n)\) number of residual atomic polarizability degrees of freedom, this is obtained by knowledge of symmetry of the geometry of the molecular system.

**4.2.1.4 Mean polarizability of the molecule**

\[ \alpha_M = \frac{1}{3} \left[ \sum \alpha_{11p} + \sum \alpha_{11n} + \sum 2\alpha_{\perp} \right] \] (4.18)

\[ \alpha_M = \frac{1}{3} \left[ \frac{4nA}{a_0} \left( \frac{R^2}{4} + \frac{1}{2C_R^2} \right)^2 e^{-\frac{(x_a - x_b)^2}{4}} + \sum f_i \alpha_i + n \sum \frac{x_i^2 \alpha_i^2}{\sum x_i^2} \right] \] (4.19)

The above equation was used by Lippincott et al. [64] to measure the polarizabilities for a number of organic compounds.

**4.2.1.5 Application of \( \delta \) function model to liquid crystals**

In crystalline state, there will be only the crystalline field acting on the system whereas in liquid phase, pure Brownian field alone acts on the system. However, in liquid crystalline state, both these fields will be acting as this state will have the flow property like a liquid and anisotropic property like pure crystal. The resultant effect is the increase in the potential of the electron (system). This behaviour can be expressed empirically as

\[ A_{LC} = A \exp \left( \frac{T - T_C}{T_C} \right) \] (4.20)
where $T$ is the temperature pertinent to the study of the liquid crystal property and $T_C$ is the liquid crystalline transition temperature (clearing temperature). $A$ and $A_{LC}$ are the reduced electro negativities (REN) values in isotropic and LC phases.

$$
\sum \alpha_{\parallel p} = \frac{4nA}{a_0} \left[ \exp \left( \frac{T - T_C}{T_C} \right) \right] \frac{R^2}{4} \left[ 1 - \frac{1}{2C_R^2} \right] \exp \left[ \frac{(x_1 - x_2)^2}{4} \right]
$$

(4.21)

Using the above equations (4.21), (4.14) and (4.18); $\sum \alpha_{\parallel p}$, $\sum \alpha_{\parallel n}$ and $\sum 2\alpha_{\perp}$ can be calculated. Now the mean polarizability

$$
\alpha = \left[ \frac{\sum \alpha_{\parallel p} + \sum \alpha_{\parallel n} + \sum 2\alpha_{\perp}}{3} \right]
$$

(4.22)

The mean polarizability determined from the above equation refers to the isotropic state and the calculation of mean polarizability for the LC state needs the following considerations. If $N_L$ and $N_{LC}$ are the number of molecules per unit volume in the isotropic and LC phases and $\alpha_L$ and $\alpha_{LC}$ are the respective polarizabilities, they can be related by the following equation.

$$
\frac{4\pi N_L}{3} \alpha_L = \frac{4\pi N_{LC}}{3} \alpha_{LC}
$$

or

$$
\frac{N_L}{N_{LC}} = \frac{\alpha_L}{\alpha_{LC}}
$$

(4.23)

Again $N_L$, $N_{LC}$ are related to the density of isotropic phase ($\rho_L$) and density of liquid crystalline phase ($\rho_{LC}$) by the relation

$$
\frac{N}{N_{LC}} = \rho_L/\rho_{LC}
$$

(4.24)

From the density measurements $\rho_{LC}$ is related to $\rho_L$ by

$$
\rho_{LC}/\rho_L = 1 + [(m/\rho_L)(T - T_C)]
$$

(4.25)

Here $m$ is the slope of the temperature Vs density graph. Thus mean polarizability of the LC compound is
\[
\tilde{\alpha} = \alpha_L \left[ 1 - \frac{m}{\rho_L} (T_C - T) \right]
\]  \hspace{1cm} (4.26)

where \( \alpha_L \) is the mean polarizability in the isotropic state obtained from Lippincott \( \delta \)-function model. Using above equation \( \tilde{\alpha} \) can be obtained.

**4.3 Evaluation of molecular polarizabilities using molecular vibration method**

**4.3.1 Evaluation of mean polarizability of LC compounds by Molecular vibration method.**

A more superior method over the Lippincott \( \delta \)-function model is the molecular vibration method. This method records even the small deviation in intermolecular forces due to changes in chemical environment which affect their force constants and vibrational frequencies. Further the conformational changes in vibrational frequencies are more sensitive than the bond lengths and reduced electro negativity values used in the Lippincott-\( \delta \) function model. Let \( b_L \) and \( b_T \) are longitudinal and transverse coefficients and \( n_i \) be the number of bonds in a molecule. Then the molecular polarizability \( \alpha_M \), estimated by the molecular vibration method is

\[
\alpha_M = \left[ \frac{1}{3} \sum n_i (b_{Li} + 2b_{Ti}) \right]
\]  \hspace{1cm} (4.27)

Let \( b_L \) and \( b_T \) are longitudinal and transverse coefficients. Let \( n_i \) be the number of bonds in a molecule. The empirical relation between mean polarizability of a bond and its mean amplitude of vibration is [33],

\[
b_L + 2b_T = C P^j \sigma^{nr} \sigma^{1/2}
\]  \hspace{1cm} (4.28)

Where \( C \) is a constant equal to \( 5.24 \times 10^{-15} \), \( P \) is the characteristic of the atom and is equal to 1, 1.2, 1.3, 1.4 and 1.5 according as it belongs to 2\(^{nd}\), 3\(^{rd}\), 4\(^{th}\), 5\(^{th}\) and 6\(^{th}\) row in the periodic table, \( n \) is +1 or -1 according as the bond is non hydride or hydride. \( r \) is saturation factor, \( r = (\text{electrons in bonding} / \text{valence electrons}) \).
Mean amplitude of vibration \( \sigma^{1/2} = \left[ \frac{E \Delta K}{G^{-1}} \right] \) (4.29)

\[
\Delta K = \frac{\hbar}{8\pi^2 \nu_k} \left[ \cot \left( \frac{\hbar c \nu_k}{2KT} \right) \right]
\] (4.30)

where \( E \) is the energy constant, \( G^{-1} \) is reduced mass, \( \nu_k \) is the vibrational frequency and \( K \) is the boltzman constant. The values of vibrational frequencies and \( b_L + 2b_T \) values of various bonds are given in table 4.1

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Bond</th>
<th>Vibrational frequencies cm(^{-1})</th>
<th>( b_L + 2b_T ) ( \times 10^{24} ) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C – H</td>
<td>3000</td>
<td>2.04</td>
</tr>
<tr>
<td>2</td>
<td>C – C</td>
<td>1200</td>
<td>2.54</td>
</tr>
<tr>
<td>3</td>
<td>C = C</td>
<td>1650</td>
<td>2.16</td>
</tr>
<tr>
<td>4</td>
<td>C – O</td>
<td>1053</td>
<td>2.89</td>
</tr>
<tr>
<td>5</td>
<td>C = O</td>
<td>1715</td>
<td>2.50</td>
</tr>
<tr>
<td>6</td>
<td>C = N</td>
<td>1650</td>
<td>0.72</td>
</tr>
<tr>
<td>7</td>
<td>O – H</td>
<td>3620</td>
<td>4.65</td>
</tr>
</tbody>
</table>

**4.3.2 Determination of \( b_L \) and \( b_T \) values from vibrational method**

The polarizability of a molecule is associated with its vibration. When a molecule is displaced from its equilibrium position, the equilibrium is restored by restoring force, which per unit displacement is found to be proportional to the square of the frequency of vibration.

Rao and Murthy [65] have developed an equation relating longitudinal (\( b_L \)) and transversal (\( b_T \)) bond polarizabilities with stretching force constant (\( K \)).
\[ b_L - b_T = A \left( X_1 X_2 \right)^{1/2} \left( \frac{aN}{K-b} \right)^{3/2} \]

\[ S = \left( \frac{K}{3b-2K} \right) \]

(4.31)  
(4.32)

where \( X_1 \) and \( X_2 \) are electronegativities of atoms forming the bond of length of \( r \) and \( N \) is the bond order, \( a \) and \( b \) are Gordys constants [66].

The parameter \( A \) is characteristic of bond under consideration and is given by

\[ A = 0.1 \left( \frac{(i,j)}{(i,j)} \right) \]

(4.33)

where \((i,j)\) refers to the product of row and column numbers of atom in the periodic table. Values of \( \Sigma b_L \), \( \Sigma b_T \) and \( (\Sigma b_L - \Sigma b_T) \) for the compounds 6.O12O.6 and 7.O12O.7 using this method are shown in the table 4.2.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>( \Sigma b_L ) (_{10}^{24} ) cm(^3)</th>
<th>( \Sigma b_T ) (_{10}^{24} ) cm(^3)</th>
<th>( \Sigma b_L - \Sigma b_T ) (_{10}^{24} ) cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.O12O.6</td>
<td>139.07</td>
<td>73.93</td>
<td>65.13</td>
</tr>
<tr>
<td>2</td>
<td>7.O12O.7</td>
<td>145.11</td>
<td>77.58</td>
<td>67.53</td>
</tr>
</tbody>
</table>

Table 4.2 Values of \( \Sigma b_L \), \( \Sigma b_T \) and \( (\Sigma b_L - \Sigma b_T) \) of 6.O12O.6 and 7.O12O.7

The principal molecular polarizability anisotropy and the mean polarizability are evaluated for the compounds 6.O12O.6 and 7.O12O.7 using the Lippincott \( \delta \) – function model [63, 64] and the molecular vibration method [33]. The principal molecular polarizability components as well as mean polarizabilities for the compounds 6.O12O.6 and 7.O12O.7 using these two methods are given in Table 4.3.
Table 4.3 Principal Parallel, perpendicular components and mean Polarizabilities (x10^{-24} cm^3) of 6.O12O.6 and 7.O12O.7

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Polarizabilities by Lippincott δ– function model 10^{-24} cm^2</th>
<th>Vibrational method 10^{-24} cm^2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>αₚ</td>
<td>2αₚ</td>
</tr>
<tr>
<td>6.O12O.6</td>
<td>180.82</td>
<td>112.10</td>
</tr>
<tr>
<td>7.O12O.7</td>
<td>188.58</td>
<td>116.86</td>
</tr>
</tbody>
</table>

*The values given for αₚ are included in αₚ

4.4 Refractive indices nₑ and nₒ in 6.O12O.6 and 7.O12O.7

The refractive indices of the above liquid crystals are measured using the modified spectrometer and a wedge shaped cell (the details are described in the experimental section). The accuracy in the measurement of refractive indices was ±0.0005. The extraordinary and ordinary refractive indices, nₑ and nₒ, were measured using a source of wave length 589.3 nm. The variation of refractive index with temperature in 6.O12O.6 and 7.O12O.7 are shown in Figures 4.1 and 4.2. It can be observed that while cooling the sample from isotropic phase, the value of refractive index in isotropic phase (nᵢₜ) is constant in both of the compounds. At the I – N transition the isotropic refractive index value splits into two: extraordinary refractive index (nₑ > nᵢₜ) and ordinary refractive index (nₒ < nᵢₜ). This splitting is clearly observed in the telescope of the modified spectrometer at the position of angle of minimum deviation at the I – N transition. When the temperature is further decreased, the value of nₑ increases while the value of nₒ decreases slightly; and when the temperature is further decreased, deep in the nematic phase, the values of both components of refractive index saturates. The I - N temperatures observed in the birefringence measurements are
in good agreement with those observed in DSC and density measurements [67,68]. Also, the density data reported in these references was used for calculating the molecular polarizability values, $\alpha_e$ and $\alpha_o$.

### 4.5 Estimation of molecular polarizabilities from refractive indices and densities employing Vuks and Neugebaur methods

#### 4.5.1 Vuks Method

This model was first applied to liquid crystal molecules by Chandrasekhar et al [54] in which the internal field is assumed to be isotropic even in anisotropic crystal. These assumptions lead to the following equations

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

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

(4.34)

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.

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

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

#### 4.5.2 Neugebauer method

Saupe and Maier [13] and Subramanyam et al [55] applied this method to liquid crystal molecule in which the internal field is assumed to be anisotropic. According to this method the molecular polarizabilities are
\[ \alpha_e = \left( AB - 3 \pm \sqrt{(AB - 3)^2 - 4AB} \right) / 2A \] (4.35)

\[ \alpha_o = \left( AB + 3 \pm \sqrt{(AB + 3)^2 - 16AB} \right) / 4A \] (4.36)

where

\[ A = \frac{1}{\alpha_e} + \frac{2}{\alpha_o} \]

\[ = \frac{4\pi N}{3} \left[ \frac{n_e^2 + 2}{n_e^2 + 1} + \frac{2(n_o^2 + 2)}{n_o^2 - 1} \right] \] (4.37)

\[ B = (\alpha_e + \alpha_o) = (\alpha_e + 2\alpha_o) = 3\alpha \]

\[ = 9 \left( \frac{\alpha}{n - 1} \right) / \left( 4\pi N_i \left( \frac{\alpha}{n + 2} \right) \right) \] (4.38)

and \( N_i \) is the number of molecules per unit volume in the isotropic phase.

Using the two models the extraordinary \((\alpha_e)\) and ordinary \((\alpha_o)\) polarizabilities and the polarizability anisotropy \((\alpha_e - \alpha_o)\) in nematic phase of the compounds 6.O12O.6 and 7.O12O.7 were calculated at different temperatures and the values are presented in Table 4.4 and Table 4.5 respectively. From these two tables, following observations and conclusions can be made: the calculated values of \(\alpha_e\), \(\alpha_o\) and \((\alpha_e - \alpha_o)\) using both Vuks and Neugebaur methods are marginally larger for 7.O12O.7 than those for 6.O12O.6 and the values obtained for any single compound using these two methods are almost similar. This is rather surprising as it was assumed that the molecular distribution in the Vuks model to be isotropic even in the anisotropic crystal which was applied to anisotropic liquid crystals [33], whereas, the Neugebaur model assumes anisotropy of the internal field in a crystal [55] which was applied to liquid crystals [13,54]. However, the molecules are assumed as point polarizability distributed anisotropically in space. Also, if the small difference in the length of these two molecules is considered, the molecular polarizability values appears to be almost same in the nematic phase of both of these two compounds. The anisotropy in the molecular polarizabilities calculated using both Vuks and Neugebauer models increases with decrease of temperature in both 6.O12O.6 and 7.O12O.7. This could be explained as follows: at molecular level, if the motion of different parts of a molecule is considered viz., the possible free rotation about
the single bonds of the methylene units present in both spacer as well as end
groups, the hindered

Table 4.4 The molecular polarizabilities and polarizability anisotropy
($\alpha_e - \alpha_o$) in 6.O12O.6

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Vuks ($\times 10^{-24}$ cm)</th>
<th>Neugebauer ($\times 10^{-24}$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_e$</td>
<td>$\alpha_o$</td>
</tr>
<tr>
<td>132.0</td>
<td>108.14</td>
<td>89.55</td>
</tr>
<tr>
<td>131.9</td>
<td>108.66</td>
<td>88.93</td>
</tr>
<tr>
<td>131.8</td>
<td>109.22</td>
<td>88.35</td>
</tr>
<tr>
<td>131.7</td>
<td>109.87</td>
<td>87.84</td>
</tr>
<tr>
<td>131.6</td>
<td>110.53</td>
<td>87.34</td>
</tr>
<tr>
<td>131.5</td>
<td>111.21</td>
<td>86.86</td>
</tr>
<tr>
<td>131.4</td>
<td>112.31</td>
<td>86.21</td>
</tr>
<tr>
<td>131.3</td>
<td>113.09</td>
<td>85.73</td>
</tr>
<tr>
<td>131.2</td>
<td>113.74</td>
<td>85.34</td>
</tr>
<tr>
<td>131.1</td>
<td>114.25</td>
<td>85.04</td>
</tr>
<tr>
<td>131.0</td>
<td>114.88</td>
<td>84.69</td>
</tr>
<tr>
<td>130.9</td>
<td>115.01</td>
<td>84.57</td>
</tr>
<tr>
<td>130.8</td>
<td>115.26</td>
<td>84.40</td>
</tr>
<tr>
<td>130.7</td>
<td>115.74</td>
<td>84.11</td>
</tr>
<tr>
<td>130.6</td>
<td>116.20</td>
<td>83.85</td>
</tr>
<tr>
<td>130.5</td>
<td>116.80</td>
<td>83.51</td>
</tr>
<tr>
<td>130.4</td>
<td>117.35</td>
<td>83.20</td>
</tr>
<tr>
<td>130.3</td>
<td>118.09</td>
<td>82.80</td>
</tr>
</tbody>
</table>

rotation due to the presence of bulk groups or double bonds as well as non-
coplanarity of benzene rings reducing the conjugation effects are possible in
liquid crystalline phase. The number of molecules in which such motions take place and decrease of the amplitudes of such motions with decreasing temperature are possible leading to the increase of polarizability anisotropy as the temperature is decreased. Finally, the calculated values of $\alpha_e$ and $\alpha_o$ in the nematic phase of both 6.O12O.6 and 7.O12O.7 are nearly 2.5 times to those observed for the compounds of n.Om series viz., 6O.4, 6O.2 and 7O.1 [69] which

Table 4.5 The molecular polarizabilities and the polarizability anisotropy ($\alpha_e$-$\alpha_o$) in 7.O12O.7

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Vuks ($\times10^{-24}$ cm)</th>
<th>Neugebauer ($\times10^{-24}$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_e$</td>
<td>$\alpha_o$</td>
</tr>
<tr>
<td>133.0</td>
<td>115.13</td>
<td>92.43</td>
</tr>
<tr>
<td>132.8</td>
<td>117.02</td>
<td>90.68</td>
</tr>
<tr>
<td>132.6</td>
<td>118.37</td>
<td>89.55</td>
</tr>
<tr>
<td>132.4</td>
<td>119.29</td>
<td>88.87</td>
</tr>
<tr>
<td>132.2</td>
<td>120.76</td>
<td>88.01</td>
</tr>
<tr>
<td>132.0</td>
<td>121.97</td>
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<td>131.2</td>
<td>127.51</td>
<td>84.32</td>
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<td>131.0</td>
<td>127.74</td>
<td>84.11</td>
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<tr>
<td>130.9</td>
<td>127.98</td>
<td>83.95</td>
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<td>130.8</td>
<td>128.00</td>
<td>83.89</td>
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<tr>
<td>130.6</td>
<td>128.47</td>
<td>83.57</td>
</tr>
<tr>
<td>130.4</td>
<td>128.82</td>
<td>83.30</td>
</tr>
<tr>
<td>130.2</td>
<td>129.18</td>
<td>83.03</td>
</tr>
<tr>
<td>130.0</td>
<td>129.54</td>
<td>82.76</td>
</tr>
<tr>
<td>129.8</td>
<td>130.89</td>
<td>82.50</td>
</tr>
<tr>
<td>129.6</td>
<td>130.25</td>
<td>82.23</td>
</tr>
<tr>
<td>129.4</td>
<td>130.60</td>
<td>81.96</td>
</tr>
<tr>
<td>129.2</td>
<td>130.96</td>
<td>81.70</td>
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<td>129.0</td>
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<td>132.02</td>
<td>81.00</td>
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<tr>
<td>128.6</td>
<td>132.38</td>
<td>80.74</td>
</tr>
<tr>
<td>128.4</td>
<td>132.71</td>
<td>80.46</td>
</tr>
<tr>
<td>128.2</td>
<td>132.97</td>
<td>80.13</td>
</tr>
<tr>
<td>128.0</td>
<td>133.16</td>
<td>79.76</td>
</tr>
<tr>
<td>127.9</td>
<td>133.00</td>
<td>79.44</td>
</tr>
</tbody>
</table>
are the precursors of these dimers with slightly different end chain lengths and those of other monomers (nO.Om) reported recently [30, 70].

4.6 Estimation of order parameter, S, from Molecular polarizability anisotropies and mean polarizabilities in different ways from different methods

In uniaxial liquid crystal phase the extraordinary ($\alpha_e$) and ordinary ($\alpha_o$) polarizabilities corresponding to the electric vector parallel and perpendicular to the optic axis are given as

\[ \alpha_e = \alpha + 2(\alpha_\parallel - \alpha_\perp)S/3 \]
\[ \alpha_o = \alpha - (\alpha_\parallel - \alpha_\perp)S/3 \]  

(4.39)

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

\[ \bar{\alpha} = (\alpha_e + 2\alpha_o)/3 = (\alpha_\parallel + 2\alpha_\perp)/3 \]  

(4.40)

Combining the above two equations S, the order parameter is

\[ S = (\alpha_e - \alpha_o) / (\alpha_\parallel - \alpha_\perp) \]  

(4.41)

The principal polarizabilities $\alpha_\parallel$ and $\alpha_\perp$ are estimated using different methods and the S is estimated for both cases viz., Vuks and Neugebauer. The methods used for obtaining principal polarizabilities are Lippincott $\delta$-function method [63, 64], molecular vibrational method [33], Haller [53] extrapolation method and scaling factor method. Therefore, the order parameter, S, using Vuks and Neugebauer methods is obtained in different ways employing the four different principle polarizabilities for both of the compounds, 6.O12O.6 and 7.O12O.7.

In the Vuks method the order parameter is given by [53, 71]
\[ S = \left[ \frac{\alpha}{\alpha_{\parallel} - \alpha_{\perp}} \right] \left[ \frac{n_e^2 - n_o^2}{n + 2} \right] \]  
(4.42)

where
\[ n = \left( \frac{n_e^2 + 2n_o^2}{3} \right) \]

In the Neugebauer method the order parameter \( S \) \([53, 72]\) is given by

\[ S = \left[ \frac{\alpha}{\alpha_{\parallel} - \alpha_{\perp}} \right] f(B) \]  
(4.43)

where
\[ f(B) = \left( \frac{9}{4B} \right) \left[ \left( B^2 - \left( \frac{10}{3} \right) B + 1 \right)^{\frac{1}{2}} + \frac{B}{3} - 1 \right] \]

and
\[ B = \frac{n^2 - 1}{n^2 + 1} \left( \frac{n_e^2 + 2}{n_e^2 - 1} + 2 \frac{n_o^2 + 2}{n_o^2 - 1} \right) \]

The scaling factors for the determination of order parameter are obtained in both the cases by plotting \( \log - \log \) plots between \( \left[ \frac{n_e^2 - n_o^2}{n + 1} \right] \) and \( f(B) \) in Vuks and Neugebauer methods respectively against the reduced temperature \( (T_{NI} - T)/(T_{NI} - T_{N/C}) \) (where \( T_{NI} \) and \( T_{N/C} \) are isotropic – nematic and nematic – crystal transition temperatures, respectively).

The order parameter, \( S \), from molecular polarizabilities is estimated by assuming Vuks and Neugebauer internal field models. The denominator i.e., the principal polarizabilities used are obtained by four different methods as stated above. The order parameter, \( S \), calculated using these methods are shown in Figures 4.3 and 4.4 for 6.012O.6 and 7.012O.7, respectively. The \( S \) values calculated directly from optical anisotropy are also included for the sake of comparison.
Table 4.6 Percentage of deviations of order parameter, S estimated assuming the two field models and using different methods from that obtained using Δn, the birefringence in perfect order in two dimeric compounds.

Table 4.6 shows the percentage of deviation of the order parameter calculated using Vuks and Neugebauer models for all methods from that calculated directly from optical anisotropy values, Δn, the birefringence in perfect order [73-76]. The values are underlined if the deviation is less than or equal to 10% which are considered in agreement with S calculated from Δn and is within the experimental error (which is be between -5% to +5%). From the figures 3 and 4 as well as from Table 4.6, following conclusions can be drawn: The S values obtained from Vuks model using the polarizability anisotropies calculated from Lippincott δ – function model, vibrational method, Haller extrapolation method and from scaling factor method are slightly larger than those calculated directly from optical birefringence (Δn) in both 6.O12O.6 and 7.O12O.7 as well as in reasonably good agreement with S values calculated from Δn directly. Whereas, in the case of S values obtained from Neugebauer model, the S values calculated from scaling factor method are slightly smaller than those calculated from Δn values directly and S values calculated from all other methods are slightly larger than those obtained from Δn values for both of the compounds. Also, the percent of deviation observed is rather large, except in case of the values obtained from scaling factor method for 6.O12O.6 and Haller’s extrapolation and scaling factor methods in case of 7.O12O.7. From all the methods employed, it can be seen that the largest value of S attained in N phase of 7.O12O.7 is slightly higher compared with that for 6.O12O.6. From this analysis a good agreement can be observed in the S values obtained from Δn directly with S values obtained from other
methods using Vuks model in the N phase of both of the compounds studied. Whereas this kind of agreement is rather poor in case of the calculated S values using Neugebauer method with those obtained from $\Delta n$ values directly. Finally, it may be concluded that the application of Vuks model for calculating molecular polarizabilities and order parameter gives good results in these two dimers than the Neugebauer model.

From these observations, it may be concluded that there is a broad agreement of S from $\Delta n$ with S from other methods with that of Vuks model rather than with Neugebauer.

In conclusion

- The variation of refractive indices ($n_e$, $n_o$) as a function of temperature are studied in 6.O12O.6 and 7.O12O.7, which compliments the density results as far as the nature of I-N transition is concerned, i.e., first order nature.
- Extraordinary and ordinary components of molecular polarizabilities were calculated using Vuks isotropic internal field model and Neugebauer’s anisotropic field model.
- The orientational order parameter values were calculated in the nematic phase of 6.O12O.6 and 7.O12O.7 using polarizability data. The parallel and perpendicular components of principal polarizabilities were calculated using Lippincot $\delta$ – function model, vibrational method, Haller extrapolation method and scaling factor method. S values were also calculated directly from birefringence values for the sake of comparison.
- The S value obtained from different four methods viz., Lippincott $\delta$ – function model, vibrational method, Haller extrapolation method and from scaling factor method agrees with the S value obtained from $\Delta n$ in the case of Vuks model in both the compounds.
- This is not so in the case of Neugebauer model though it is an anisotropic internal field model.
- It may be concluded that the compounds favor Vuks model which is an isotropic field model over that of Neugebauer model.
REFERENCES:


Figure 4.1 Variation of refractive indices $n_e$ and $n_o$ with temperature in the compound 6.O12O.6.

Figure 4.2 Variation of refractive indices $n_e$ and $n_o$ with temperature in the compound 7.O12O.7.
Figure 4.3(a) Variation of order parameter, $S$ versus the normalized nematic range for the compound 6.012O.6 using Vuks model.

Figure 4.3(b) Variation of order parameter, $S$ versus the normalized nematic range for the compound 6.012O.6 using Neugebauer model.

(1-Lippincott’s model; 2-Vibrational method; 3-Haller’s method and 4- Scaling factor method)
Figure 4.4 Variation of order parameter, $S$ versus the normalized nematic range for the compound 7.0120.7 using (a) Vuks model and (b) Neugebauer model.

(1-Lippincott’s model; 2-Vibrational method; 3-Haller’s method and 4- Scalling factor method)