A COMPARATIVE STUDY OF THE OPTICAL PROPERTIES OF NEMATIC HOMOLOGUES

BY

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A thesis submitted in partial fulfilment for the degree of Master of Science in Physics in the Department of Physics, Egerton University.

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DEDICATION

The author dedicates this work to his brothers and sisters alike and to those who cherish the works of researchers.

ABSTRACT

In recent years, a large number of nematogenic compounds have been synthesized in view of their immense potential with regard to applications in the display industry. Nematic liquid crystals are widely applied in the industry because of a wide range of appropriate suitable physical properties. In the display industry it is essential to make suitable choices of materials with requisite physical properties such as wide mesomorphic ranges around room temperature and good thermal stability. However, clear-cut guidelines for making such choices are not available.

A simple but useful method to obtain such guidelines is the investigation of the variation of optical properties such as orientational order parameter and optical and field anisotropies of nematic homologues with molecular length and different end groups of their molecules. For such investigations a number of theoritical approaches are available in literature. However, only two are widely used namely; Vuks' and Neugebauers' approaches which were originally meant for crystalline media but have since been modified for nematic liquid crystals.

In this work, an elaborate investigation of the optical properties of five nematic homologues has been done using the two approaches and some significant conclusions have been arrived at. These conclusions have enhanced our understanding of liquid crystalline compounds and have established the superiority of Neugebauer's approach over Vuks' approach. Recommendations have also been made concerning the possibility of extending such a comparative study to other homologous series, nematic mixtures, smectic and cholesteric liquid crystals.

PREFACE

Over the last two decades, research on liquid crystals has aimed at meeting the requirement of the electroptic display industry for improved liquid crystalline materials for device development and manufacture. However, the aspirations of device manufactures has placed increasingly stringent demands on the physical characteristics of the liquid crystal compounds to be used. This has meant that research on liquid crystal compounds must be geared towards finding those compounds meeting certain target values of physical characteristics such as high information density and wide mesomorphic ranges around room temperature.

In order to develop improved liquid crystal materials and hence meet the requirements of device producers, an understanding of the physical characteristics of liquid crystals such as optical properties and their structure- property relations is very essential. To this end detailed empirical studies have been done and results of optical properties obtained and analysed using various theoritical approaches available in literature. Such studies demand that only those approaches that give consistent and reliable results as compared to other standard techniques be applied. In view of this, a comparative study of the various approaches has been necessitated over time.Though a number of such studies have been done, they have by no means been exhaustive. This thesis incorporates the results of a comparative study of two most widely applied approaches namely Vuks' and Neugebauer's approaches. The comparisons has veen done through experimental and theoretical investigations of the optical properties of a homologous series of five nematic compounds. The compounds are listed in chapter 1. As indicated in the last chapter more comprehensive and convincing conclusions could be arrived at only by extending the investigation to more nematic homologues. However, both financial and time constraints have come in the way of such extensive investigations, but even in the absence of such elaborate investigations, significant conclusion regarding the optical properties of nematic liquid crystals were arrived at.

The initial part of chapter 1 is introductory in nature. In this part, the various types of liquid (LCs) i.e. smectic, cholesteric and nematic mesophases and the numerous applications of LCs have been described. The chapter then addresses itself to a brief discussion of the various theoritical approaches that are available in literature for the study of the variation of optical properties of nematogens with molecular parameters. Herein, the motivation for choosing the five compounds for the investigation has been mentioned . Even though all the three types of LCs have useful application in display industry, greater emphasis and interest is on nematics because of superior devices such as the twisted and supertwisted nematic devices derived from them. The last part of chapter 1 is a general review of literature on liquid crystals and their physical

properties such as aspects of molecular structure especially of homol gues and the relationship between transition temperature and molecular length and end groups. However, those discussed particularly are the physical characteristics of nematics such as optical anisotropy and its variation with molecular length, orientational order parameter "S" and the theories regarding its calculation, dielectric constants, refractive indices and their relationship with 'S', elastic constants and viscosity. Lastly is a discussion of the rotation of plane polarization of incident light by a LC and the importance of pitch in cholesterics and its variation with temperature.

Chapter 2 starts with a brief discussion of how orientational order parameter 'S' varies with change of phase. Since 'S' is a prominent optical parameter of nematic LCs, such a discussion was necessary. The later part of the chapter discusses the various theoritical approaches available in literature for the study of various optical parameters of nematics. As almost all the approaches are based on the concept of local field, a brief discussion of this concept and its relevance is taken up to start with. A somewhat detailed account of Lorentz-Lorenz approach is given though it only deals with spherically symmetric distribution of the molecules. This is because it forms an important part of Neugebauer's's approach. Approaches due to Zwetkoff, Derzhanski and Petrov, Dunmur and Blinov are not elaborately discussed owing to their limitations. Howevei , two approaches; one due to Neugebauer and originally used to investigate the optical properties of crystalline media but later modified by Subramhamyaam *et al* for liquid crystalline media and another originally due to Vuks but later modified by Chandrasekhar *et al* to suit crystalline media are discussed at length. In this chapter an explanation of why use was made of only these two approaches for our investigation is given by exposing the serious limitations of the other approaches and the extensive use of Neugebauer's and Vuks' approaches. Herein it has also been made clear that our major objective was to establish the edge if any, of one of the two approaches over the other through our investigations.

As already mentioned, the motivation for choosing these five nematic homologues was the ease with which they could be synthesized starting from MBBA and valerate which are commercially available at low costs. In chapter 3 a brief account of the experimental procedure is presented. In this investigation, the data required were the refractive indices and densities in crystalline and isotopic phases. While refractive index data in all the phases of the compounds were available in literature, the density data were not available. In chapter 3 therefore a discussion of the experimental determination of the density data in all the three phases of the compounds is presented. In particular, details of purification of samples, details id the hot chamber, experimental procedure and volume measurement for each sample are given. The experimentally determined values of densities are tabulated at the end of the chapter.

Chapter 4 of this thesis is the most crucial one in that not only have the calculations, results, data analysis and discussions been presented but it has also been established through various comparisons that Neugebauer's approach is superior to Vuks' approach. The chapter starts with the calculation of isotropic polarizability by variuos approaches such as Lorentz-Lorenz relation, Born's relation and bond polarizability technique. Next is the calculation of the effective polarizabilities in the nematic phase of the compounds and of optical anisotropy using the two approaches and the bond polarizability technique. Orientational order parameter 'S' was also calculated for each compound using Vuks' and Neugebauer's approaches and the resulting values compared with those obtained from standard methods such as from NMR splittings and Raman band analysis. The calculation of order parameter and optical anisotropy was extended to MBBA which is homologous to the last two of the five compounds and valerate which is homologous to the first three. Also discussed is the calculation of Lorentz field factors and field anisotropies in the crystalline and liquid crystalline phases. In this chapter graphical plots of orientational order parameters S_V and S_N versus temperature have veen made and for some of the compounds the plots have been made along with those of S_{Raman} and S_{NMR} on the same axes for the sake of comparison. A thorough discussion of the results was then made and it emerged that the isotropic polarizability values calculated using Lorentz- Lorentz relation which forms the basis of Neugebauer's approach are in more agreement with experimental values and broad based than those obtained using Born's relation which forms the of Vuks' approach. It also has been successfully shown that Born's relation is a particular form of Neugebauer's approach. Effective polarizabilities in the liquid crystalline phase and optical anisotropy in the crystalline phase calculated using Neugebauer's approach were similarly shown to fit experimental data better than those obtained from Vuks' approach. Also constancy of orientational order parameter S_N was shown to be much better than that of S_V values, Further, the values of optical anisotropy and those of 'S' calculated using Neugebauer's approach were found to be in better agreement with those obtained from other standard methods. In addition, some of the significant conclusion concerning Lorentz field factors could only be arrived at as a result of Neugebauer's approach to the concept of local field.

In chapter 5 a summary is presented of the various conclusions arrived at which have significantly showed that Neugebauer's approach is superior to Vuks' approach. These conclusions have also shown that to deal with anisotropic distribution of molecules in condensed matter problems Neugebauer's approach which gives due consideration to asymmetric distribution is more suited than Vuks' approach. Also discussed are some important additional features which were implicit in our discussion but ere not highlighted in earlier chapters.

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LIST OF ABBREVIATIONS

Abbreviation	Meaning
LC	Liquid crystal
LCs	Liquid crystals
PC	Phase change
DS	Dynamic scattering
GH	Guest-Host
ECB	Electrically Controlled Birefringence
LCDs	Liquid Crystal Displays
TN	Twisted Nematic
TFTs	Thin Film Transistors
TVs	Televisions
STN	Supertwisted Nematic
K-N	Crystalline to Nematic
N-I	Nematic to Isotropic
NMR	Nuclear Magnetic Resonance

CHAPTER ONE

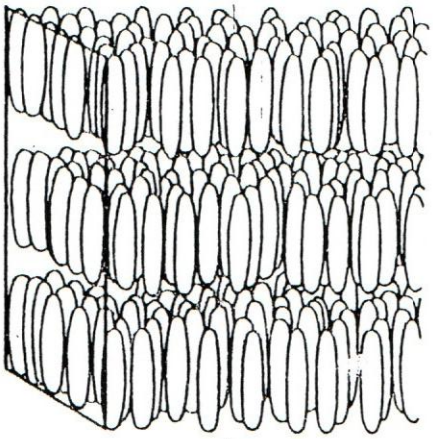
1.0. INTRODUCTION AND LITERATURE REVIEW

1.1. INTRODUCTION

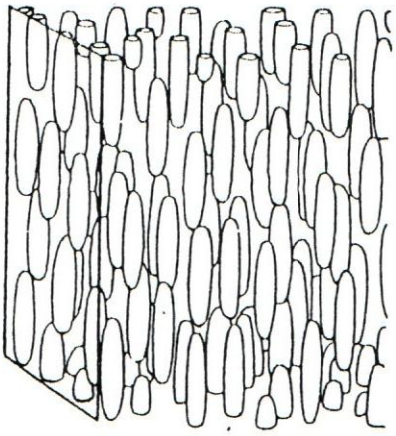
Most substances have a single melting point at which they change from a solid to a transparent liquid, but a group of compounds termed liquid crystals, first become opaque and cloudy liquids at one temperature and then turn to ordinary transparent liquids at a higher temperature. The term 'liquid crystal' represents the mesophase that is intermediate between the solid and liquid phases and any material that exhibits the liquid crystal phase (mesophase). Within a certain temperature range called mesomorphic range, a liquid crystalline substance behaves macroscopically as a fluid and simultaneously possesses a crystalline structure that exhibits optical double refraction. The liquid crystalline phase was discovered by the Austrian biologist F. Reinitzer in 1888 in benzoic acid and acetic acid esters of cholesterol (Matsumoto, S. 1990).

Majority of liquid crystalline substances are organic compounds with either long thin rod-shaped or flat molecules. Of late, compounds with disc-like molecules have also been found to exhibit this mesophase (Chandrasekhar *et al, 1990)*. In the liquid crystalline phase, molecular orientation takes up certain spatial organizations and based on differences in these spatial organizations, liquid crystals are classified into three main types namely: nematics, smectics and cholesterics (see Fig. 1 below). In smectics, the rod-shaped molecules are arranged in layers with their long axes parallel to each other. The binding between the molecular layers is relatively weak, so that they slip easily over each other. For this reason, a smectic liquid crystal behaves as a two-dimensional fluid, compared with an ordinary liquid. However, its viscosity is very high. Smectics are further classified into several categories denoted as S_A,S_B,S_C,S_D,.... depending on the nature of the arrangement of the molecules within each layer. The distribution of molecular centers in the plane of Smectic 'A' layer is totally random whereas in Smectic 'B', a hexagonal arrangement of molecular centers is found. Smectic 'C' differs from Smectic 'A' in that the long axis of the molecules in each layer make a certain constant angle with the normal to the layers. The molecular arrangements in 'S_D' which has a cubic symmetry and in the other higher order smectics are more complicated.

In a nematic LC, the rod-shaped molecules are also aligned approximately parallel about



Smectic liquid crystal



Nematic liquid crystal

Cholesteric liquid crystal

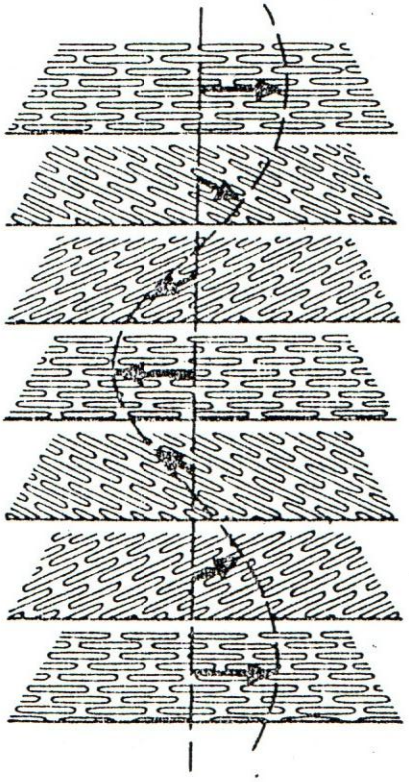


Figure 1: Molecular orientations in the three types of liquid crystals.

preferred direction called the 'director', but the individual molecules move relatively easily in the direction along their axis so that there is no layering structure. The nematic substance is therefore very fluid with low viscosity. A cholesteric LC has a layered structure like a smectic LC with the long axis of the molecules oriented about a preferred direction rotating smoothly as one progresses from layer to layer along the normal to the layers. Thus, the axis of alignment of molecules in neighboring layers slightly deviate one from another and therefore overall, the LC has a helical structure. The optical characteristics of a cholesteric LC such as optical rotatory power, selective light reflection and circular dichroism are due to this helical structure (Matsumoto, 1990). The molecular orientations in the three types of LCs are shown in figure 1 below. However, the structural organization of molecules in a liquid crystal is not rigid as in a crystalline structure. The molecules can therefore be easily reoriented by an external stimulus such as an electric field, a magnetic field, temperature or mechanical strain and consequently the optical characteristics of the LC change. It is precisely this flexibility in the molecular orientation and the anisotropy in physical characteristics such as refractive index, electric and magnetic susceptibilities, conductivity, and viscosity in LCs that are responsible for the applications of LCs in display and other optoelectronic devices and sensors.

The change in the optical characteristics of an LC due to a change in molecular orientation caused by an applied electric field is called an electrooptic effect of an LC. A number of electrooptic effects have been reported such as the phase change (PC) effect discovered by Wyscoki *et al* in 1968, and the dynamic scattering (DS) effect of Heilmeeir *et al* later the same year (Heilmeeir, G. *et al*, 1968). About the same time, Heilmeeir and Zanoni reported the Guest - host (GH) effect. In 1971, the twisted nematic (TN) effect was reported by Schadt *et al* while Schiekel *et al* and Hareng *et al* came up with electrically controlled birefringence (ECB) effect the same year. The discovery of the various electrooptic effects opened up the possibility of applications for liquid crystals particularly for display devices.

LCs have unusual but remarkable optical properties. For example nematics and Smectic A phases are uniaxial and their optical properties are extremely sensitive to weak external perturbations. Cholesterics, because of their periodic structure give rise to Bragg reflections at optical wavelengths. The pitch of a cholesteric and hence the wavelength of the Bragg reflected light depend on temperature and thus the color of the material can change drastically in a temperature interval of a

few degrees. This has led to a number of applications such as detection of hot points in microcircuits, localization of fractures and tumors in humans and conversion of infrared images (De Genes, P.G., 1975).

Nematics and cholesterics are very sensitive to magnetic and electric fields as was first shown by Fredericks and Tsvetkov in 1969 (Fredericks and Zohnia, 1969). However electric field effects are very spectacular and important for applications particularly for display systems. Because of their exotic optical and related physical properties the subject of LC has been a field of active research for the last twenty years and many applications have emerged as for example in displays.

LC displays (LCDs) are now well known for their low power consumption, low voltage operation, low cost, flat-panel construction and simple technology. They also give good readability in bright lighting conditions for example in the presence of sunlight because they modulate the reflected light and thus maintain good contrast and visibility. Besides liquid crystal displays (LCDs) are the first choice for equipment designers in many applications.

Owing to their numerous applications, interest in nematics and cholesterics has grown considerably since 1965. However, because of the practical importance of the twisted nematic (TN) effect, greater interest has been on nematics than cholesterics. A noteworthy feature of the TN device is that it can act as an electrically controllable optical shutter for light transmitted through a pair of polarizer as a function of field due to its 'bilevel' behavior. This phenomenon was first demonstrated by Schadt and Helfrich in 1971 (Schadt & Helfrich, 1971) and Arora *et al*, in 1973. This principle has found extensive industrial applications in the manufacture of LCDs for pocket calculators, automobile dashboards, miniature TVs, watches and clocks, test and measuring instruments, electronic toys and games, computers and large screen display boards.

In addition, unlike the dynamic scattering effect in which conductivity plays a crucial role, TN LCDs are field effect devices and thus work perfectly well with low conductivity materials. Further, the supertwisted nematic (STN) device has extended the application of LCDs to full page computer terminals and other high information content displays without having to resort to thin film transistors (TFTs) (Chandrasekhar, S. 1992).

Thus the importance of LCs, particularly nematics in industrial applications cannot be overemphasized and in view of this, a large number of nematogens have been synthesized in an

attempt to obtain nematic LCs with suitable physical properties for the manufacture of LCDs. However, it remains true that the targets set for LC materials by users have always outstripped the ability of chemists to supply them and probably exceed in several respects what can be achieved in real molecules. Nevertheless, sufficient progress has been made toward such targets to extend the range of applicability of LCDs. Incremental improvements in materials are likely to continue particularly in fluids for the established twisted nematic display mode until a considerably superior device technology is discovered.

The problem of developing improved LC material for devices may be considered in two ways. Firstly, an understanding of the operation of the device is necessary to deduce which physical properties of the fluid will affect its performance. This includes the effect of an applied electric field or current on the alignment of the LCs and the accompanying change in the optical properties. This leads to target values for the physical properties of LCs. Secondly, it is necessary to understand the structure-property relationships which exist in LC materials in order todesign fluids that approach these targets. Although sufficient progress has been made regarding the first of these problems, our understanding of how given physical properties may be obtained in useful or practical LCs is far from perfect. Much of the groundwork has been carried out and most progress in LC formulation has probably been made by detailed empirical experimentation. However a lot still remains to be done.

The physical properties of nematics such as transition temperature, mesomorphic range, orientational order parameter 'S' and Lorentz field factors have been found to be strongly dependent on the symmetry and asymmetry of the molecules forming the nematogenic material (Bahadur, 1990). Further a detailed study and an understanding of the mode of variation of these properties with such parameters as density, birefringence, temperature, molecular structure and length are of considerable importance as it greatly simplifies the choice and applicability of the LC materials for use in LCDs. For such a study, numerous theoretical approaches, almost all of which are based on the concept of local field, are available in literature. The prominent ones among these approaches are those developed by:-

(i) Neugebauer for crystalline media (Neugebauer, 1950) and adapted with suitable modifications for LCs by Subramhanyam *et al* (1973,1974),

(ii) Vuks for crystalline media and adapted with suitable modification for LCs by Chandrasekhar *et al* (1969),

(iii) Derzhanski and Petrov (1971),

(iv) Dunmur (1972),

(v) Zwetkoff (1942) and

(vi) Blinov *et al* (1985).

A detailed account of some of these approaches is given in chapter 2 of this thesis. The approaches in (iii), (iv), (v) and (vi) have a number of limitations, which are discussed in chapter 2, and hence have not been widely employed. However the approaches in (i) and (ii) have been employed by a large number of investigators for a variety of investigations dealing with nematics. The question of which approach among the two is superior has not been satisfactory settled. In this thesis an attempt has been made to study the relative merits of these two approaches namely Neugebauer's and Vuks' approaches through an investigation of the optical properties of a homologous series of nematic LCs. The compounds chosen for investigation are;

A. p-(p-ethoxyphenylazo) phenyl hexanoate.

B. p-(p-ethoxyphenylazo) phenyl heptanoate,

C. p-(p-ethoxyphenylazo) phenyl undecyclenate,

D. n-(p-propoxybenzylidene) p-pentylaniline (PBPA) and

E. n-(p-butoxybenzylidene) p-pentylaniline (BBPA).

For simplicity and ease of writing, these compounds are hereafter abbreviated as hexanoate, heptanoate, undecyclenate, PBPA and BBPA respectively. The structural formulae of these LC compounds are shown in figure 3 of chapter 3. The choice of these nematogens was arrived at because their birefringence data in all the three phases as well as their crystalline to nematic and nematic to isotropic phase transition temperatures (K-N and N-I respectively) have been reported by Revanna Siddaiah *et al* (1992). In addition they exhibit mesophases at ambient temperatures and are thus available for direct investigation without the use of very low or high temperature equipment. Their mesomorphic ranges persist over a large temperature range and hence allows an extensive study of their mesomorphic behavior to be made. Further, they are thermally stable,i.e., they do not decompose on heating and thus their K-N and N-I transition temperatures do not change. Lastly and

most important, synthesis of these compounds was easier and less costly than if they had been procured by direct buying.

Apart from the birefringence data which are available, the data also required for the investigation were the densities in all the three phases of these compounds. Hence at the outset, experimental determination of these densities in the crystalline and liquid phases and at various temperatures in the liquid crystalline phase of each of the homologues was taken up. The details of this determination of the densities are discussed in chapter **3** of this thesis. Based on the available index data and the measured values of densities, various physical parameters such as isotropic polarizabilities, effective polarizabilities, optical anisotropy, Lorentz field factors and orientational order parameter were calculated for each of the five homologues using expressions associated with each of the two approaches; Neugebauer's and Vuks' as well as other relevant methods such as Born's relation, bond polalizability technique, and the principle of additivity of bond polarizabilities. The details of these calculations are discussed in chapter **4** of this thesis, along with the results obtained from these calculations. Some of the results were also represented graphically to determine their mode of variation with temperature. A comparison of the results from the two approaches with those obtained from other standard methods such Nuclear magnetic resonance and Raman spectroscopy was also made. These comparisons and the accompanying discussions are given partly in chapter **4** and mainly in chapter **5** of this thesis.

On the basis of the results of the five compounds, the study was extended to two other LC compounds closely related to the five compounds. The compounds are p -(p- ethoxyphenylazo) phenylvalerate [valerate] which is homologous with hexanoate, heptanoate and undecyclenate and (p- methoxy benzylidene) p-(n- butyl)aniline [MBBA] which is homologous with PBPA and BBPA. Certain optical properties of MBBA have been extensively studied by Rose (1972) while those of Valerate have been reported by Subramhanyam (1976). In chapter **5** of this thesis further discussion of the results, the conclusions and recommendations are presented.

However in section **1.2** below of this chapter, a general review of literature on liquid crystals and their physical properties is presented. But as this study was concerned with nematic LCs only, the review mainly deals with the properties of nematic LCs.

1.2. LITERATURE REVIEW

1.2.1 General aspects of molecular structure of LC compounds.

Liquid crystals (LCs) were initially of interest only as examples of a new state of matter and until 1965, most research work involved the preparation of homologous series of compounds with a particular core structure and a study of how the transition temperatures and types of mesophase changed within the series. Then, the types of mesophases encountered were limited mainly to nematic and smectic A, B or C phases, but from 1965 onwards with the expectation and eventual discovery of effective electrooptical display devices using LCs, research in the area has increased significantly and all the three main classes of mesophases are now used in technological applications. Liquid crystal compounds are either aromatic or alicyclic systems. However most of the compounds such as those listed by Demus *et al* (1974, 1984) and Kelker *et al* (1980) which are suitable for use as LC materials are aromatic systems probably because such systems give mesophases of good thermal stability as reported by Schubert *et al* (1972) and in general are relatively easy to prepare. Generally any structural feature (see figure **2** below) such as increased core length (e.g., n changed from 1 to 2), terminal groups (A or C) or linking groups (B) which give reasonable rigidity to an almost linear molecule is conducive to liquid crystal formation: even small lateral groups (D) may often be tolerated. However larger lateral groups would be expected to decrease the broadside association of molecules and lead to a reduction of mesophase thermal stability. Any terminal group (A or C) which extends the molecule along the molecular axis without increasing the molecular breadth too much, increases the thermal stability of a mesophase (Gray, 1987).

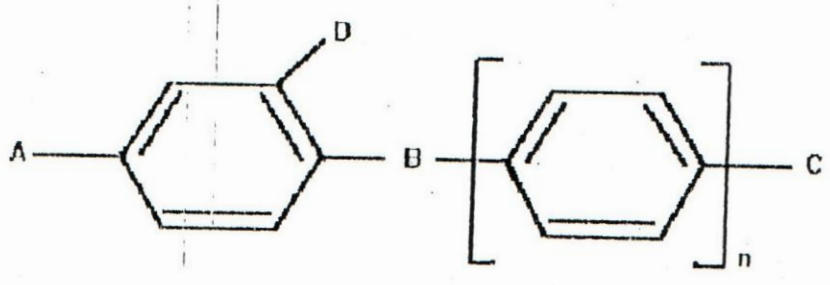


Figure 2: Structural formulation of aromatic LC compounds.

Such substituents increase the anisotropy of molecular polarizability ($\Delta\alpha$), particularly if they conjugate with the aromatic ring and the theory of Maier and Saupe (1960) suggests a link between the N-I transition temperature (T_{N-I}) and $\Delta\alpha$. A common terminal substituent is the n-alkyl or n-alkoxy group and by plotting the transition temperature (mesophase to mesophase or mesophase to isotropic liquid) against the number of carbon atoms in the alkyl ($C_n H_{2n-1}$) or alkoxy ($C_{n-1} H_{2n-1}0$) group of an homologous series, one of several possible curves is revealed as shown in figures **3a** and **3b** below.

As the series is ascended, the values for the transition temperatures alternate but usually members with odd value of n have higher and members with even n have lower values and for the alkoxy compounds, the oxygen atom is equivalent to a CH_2 group, and the alternation effect thebecomes less pronounced. The shape of the curve varies and the lines for the odd or even series may for example both fall gradually, rise gradually or rapidly, one may fall and the other mayrise,both may fall initially to minima and then rise again, etc. Examples of two important structurally related systems which give quite different shapes are shown in figures **3a** and **3b** below. The alternation in simple cases is thought to be related to the change in $\Delta\alpha$ as the chain lengthincreases and assuming a rigid, extended zigzag alkyl chain, the odd series have more C-C bonds along molecular axis giving the higher $\Delta\alpha$ (de Jeu *et al,* 1973). Although a single extended s- trans conformation is unlikely, it is believed to be a major preferred conformation. (Samulski, 1983; Avent *et al*, 1984; Luckhurst, 1985; Chapoy *et al*, 1985). With longer alkyl chains the differences between the two curves will decrease as the flexibility of the chain increases and even for initially rising curves, the T_{N-I} values should eventually fall as the increasing chain flexibility begins to disrupt the nematic ordering (Toyne,1987).

Suitable linking groups (B in figure **2** above) which preserve the linearity of the molecule and by being unsaturated also extend conjugation between the two rings include;

$(CH=CH)_n$, -C≡C-, -CH=N-, -N=N-, -CH=$\overset{O}{\uparrow}$N-, -N=$\overset{O}{\uparrow}$N-, -C-O- and -CH=CH-$\overset{O}{\overset{\|}{C}}$-O. Linking groups such as $-CH_2CH_2-$ and $-CH_20-$ which do not permit conjugation from one ring to the next do not enhance the molecular rigidity and are poor linking groups between aromatic rings but may be acceptable in alicyclic systems (Toyne, 1987).

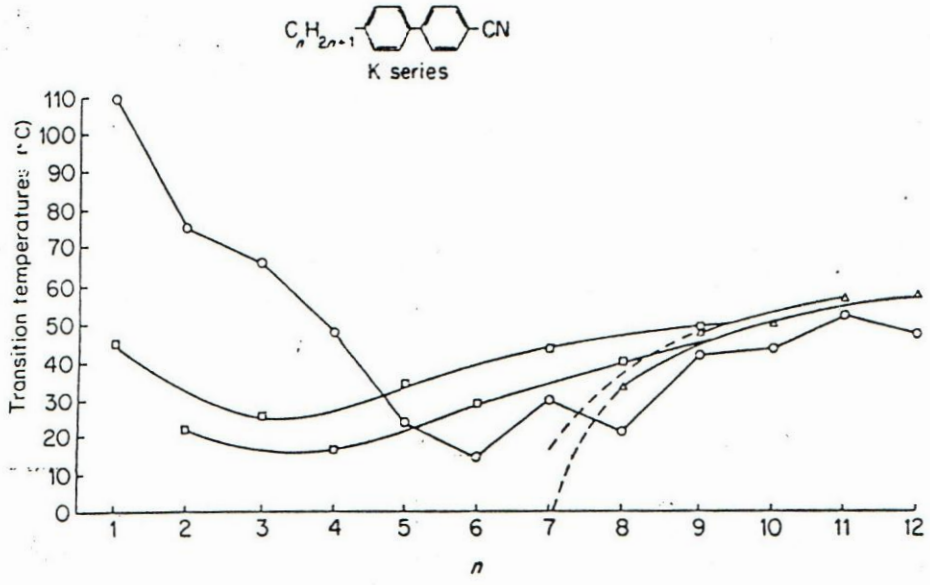


Figure 3a.

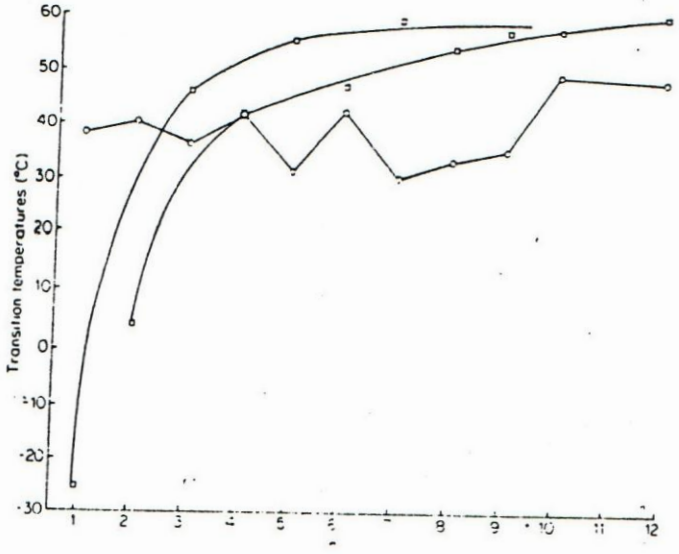


Figure 3b.

Figure 3a and 3b: Transition temperatures (^{0}C) versus n for compounds of the K and PCH series.

Thermotropic LCs such as nematogens are generally rod-like and even small lateral substitutions usually perturb the structure and cause a significant depression in the clearing point. An important potential use for laterally substituted compounds lies in producing nematogens suitable for high information content, highly multiplexed twisted nematic displays. For substitution in a terminal chain to give branched terminal groups, Gray and Kelly (1984) compared some alkyl and alkoxy terminated systems in which a methyl group is systematically moved along the carbon chain and their results are similar to those in earlier works with different types of mesogens (Gray *et al*, 1971). Osman (1983, 1985) has discussed the nature of the core terminal substituents in influencing the thermodynamic stabilities of mesophases.

1.2.2. Physical characteristics.

1.2.2.1 Anisotropy of physical characteristics of LCs.

The various types of LCs share the fact that their molecules are aligned with their long axes parallel. As a result, the various physical characteristics such as refractive index n, dielectric constant ϵ, magnetic susceptibility χ, conductivity σ and viscosity η of the LC substance have different values in the direction parallel ($\parallel$) and orthogonal ($\perp$) to the molecular axis or in other words are anisotropic (i.e. $n_{\parallel} \neq n_{\perp}$, $\epsilon_{\parallel} \neq \epsilon_{\perp}$, $\chi_{\parallel} \neq \chi_{\perp}$, $\sigma_{\parallel} \neq \sigma_{\perp}$ and $\eta_{\parallel} \neq \eta_{\perp}$) (Matsumoto, 1990). In considering the anisotropy of LC physical characteristics, it is important to discover the extent to which the liquid crystal molecules are properly aligned with each other. The degree of orderliness of LC molecular orientations is described by the molecular alignment order parameter 'S', which is discussed in section **1.2.3.1**. below.

1.2.3. Nematic liquid crystal properties.

1.2.3.1. Nematic phase range and order parameter.

The nematic liquid crystal (hereafter abbreviated as NLC) phase is commonly bounded by a smectic (S) or crystalline phase at low temperature and an isotropic liquid at high temperature. The NLC phase is distinguished from an isotropic liquid by the long-range ordering of the rod-like molecules which is never perfect but is the basis of the observed anisotropy of the various physical properties of the nematic phase (de Genes, 1974; de Jeu, 1980). It is convenient to define an order

parameter which on one hand reflects the ordering symmetry of the phase on a molecular level, while on the other hand provides a scaling factor for the observed physical properties of the bulk liquid. It is the latter role which is paramount for the discussion of the display related materials, for it is the anisotropy, particularly of optical and dielectric properties that make LCs into useful display components (Sage, 1987).

The director of a NLC is defined as a unit vector, **n**, pointing in the preferred local alignment direction of the molecular long axes. NLCs behave as uniaxial materials on which many physical properties display two principal values measured parallel and perpendicular to the director; the anisotropy of the property being defined as the difference between these principal values and is always positive for nematics. All observed properties of NLC are invariant under reversal of the director, that is, nematic molecules with different end groups have an equal probability of pointing either one in a given direction. An order parameter is a scalar quantity that describes the average alignmen of molecules with the director, incorporates this symmetry, has a value of zero for the disordered isotropic phase and unity for a (hypothetical) perfectly aligned NLC. The simplest such order parameter is defined by the following relation;

$$S = \frac{1}{2}\left(3\langle\cos^2\theta\rangle - 1\right) \qquad (1.1)$$

where θ is the angle between the preferential direction of alignment called the director and the long axis of each molecule, the molecule being regarded as cylindrically symmetric while $\langle\cos^2\theta\rangle$ denotes a statistical average over the ensemble of molecules. For a typical NLC, S has a value between 0.3 and 0.8 depending on the temperature. S is directly related to quantities like optical anisotropy, dielectric anisotropy, curvature elasticity, etc.

The theoretical treatment of nematic ordering has been a subject of intense research and has achieved some notable success, but in common with the theory of almost all LC properties, it has not reached the point where quantitative predictions of the order parameter or qualitative trends in structure-property relations can be derived (Sage, 1987). The relatively simple theory of Maier and Saupe (Maier *et al*, 1960) gives good semi quantitative agreement with experiment by regarding

NLC molecules as cylinders which interact only by long-range dispersion forces (Luckhurst, 1977).

The experimental determination of order parameter 'S' is normally carried out by measuring an appropriate physical quantity proportional to S. In order to obtain absolute values, the property must be known in the perfectly aligned state and this is achieved by fitting data to an approximate function of S, such as Maier-Saupe relation and extrapolating to 0 K (Haller, 1975). The form of the fitting equation is important and alternatives have been suggested by Tough *et al* (1983) including in a few cases measurements made on the crystalline solid. The most usual quantities chosen are (Sage, 1987);

$$S \propto \left(\frac{n_e^2 - n_o^2}{\bar{n}^2 - 1}\right) \tag{1.2}$$

where

$$\bar{n}^2 = \frac{n_e^2 + 2n_o^2}{3}$$

and

$$S \propto (\chi_{\parallel} - \chi_{\perp}) \tag{1.3}$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ denote the magnetic susceptibilities in a direction parallel and orthogonal to the long axis of the molecule respectively. The use of magnetic anisotropy in equation (1.3) leads to a high degree of confidence in the theoretical treatment of data but it is difficult to make sufficiently accurate experimental measurements. Refractive indices may be measured accurately for use in equation (1.2) but their interpretation is complicated by local field effects (Haller, 1975). The use of more advanced techniques such as NMR allows for the measurement of 'S' for individual NLCs, components of a mixture or even for different structural groups within a flexible molecule (Emsley, 1985).

1.2.3.2. Dielectric constants.

When an electric field is applied to a LC with particular initial orientation, then with a transition to a new molecular orientation, termed Freedericksz transition, there is an accompanying change in optical characteristics of the LC. This transition phenomenon is due to the dielectric anisotropy of the LC which is defined as;

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} \qquad (1.4)$$

where $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ denote respectively the dielectric constants in a direction parallel and orthogonal to the molecular long axis. The value of $\Delta\epsilon$ for a LC may be positive or negative depending on the molecular structure of the LC. Depending on whether $\Delta\epsilon$ is positive or negative, the initial molecular orientation of the LC will normally be with the LC molecular axis (director, **n**) either parallel or orthogonal to the plane of the two electrode substances. For electrooptic display devices, $\Delta\epsilon$ is a quantity of paramount importance as its magnitude directly determines the strength of the interaction between a LC and an applied electric field. Its sign also determines the geometry of display devices; under a large applied field the LC director aligns so that the larger dielectric constant lies parallel to the field (Sage, 1987).

A predictively useful insight into the relation between dielectric constants and molecular structure is provided by the theory of Maier and Meier (1961). By considering mesogenic molecules as centers of anisotropic polarizability with point dipoles, they derived equations for dielectric constants in terms of molecular properties and order parameter given by;

$$\Delta\epsilon \propto S\ [\Delta\alpha - c\mu^2(1 - 3\cos^2\beta)] \qquad (1.5)$$

where $\Delta\alpha$ is the polarizability anisotropy, μ is the dipole moment, β is the angle between the molecular long axis and the dipole moment. If $\beta \simeq 54.7°$, the second term in brackets becomes zero and a small positive $\Delta\epsilon$ is expected due to the positive $\Delta\alpha$ of the molecules. For other values of β, the dipole moment makes a contribution and the constant c is such that it often dominates the $\Delta\alpha$ term. Design of molecules with a given $\Delta\epsilon$ would thus appear to depend on the introduction of a

suitable dipole moment parallel or perpendicular to the molecular long axis. Although this is largely true, other factors complicate the true situation.

1.2.3.3. Elastic Constants

In LC electrooptic devices it is the operation of an electric field on the dielectric anisotropy of the fluid that turns on the cell, while the turn-off is usually driven by elastic forces. The elastic behavior of LCs is very weak when compared to that of solids and is difficult to detect by mechanical means (Grupp, 1983), but is sufficient to drive the realignment of the LC director in a time scale of the order of milliseconds. Elasticity in LCs is not dimensionally equivalent to that of solids; all deformations in LCs are curvatures and can be expressed as a combination of the basic operations of splay, twist and bend of the director, mediated by elastic constants K_{11}, K_{22} and K_{33} respectively whose units are those of force, i.e. Newtons (See figure 4 below).

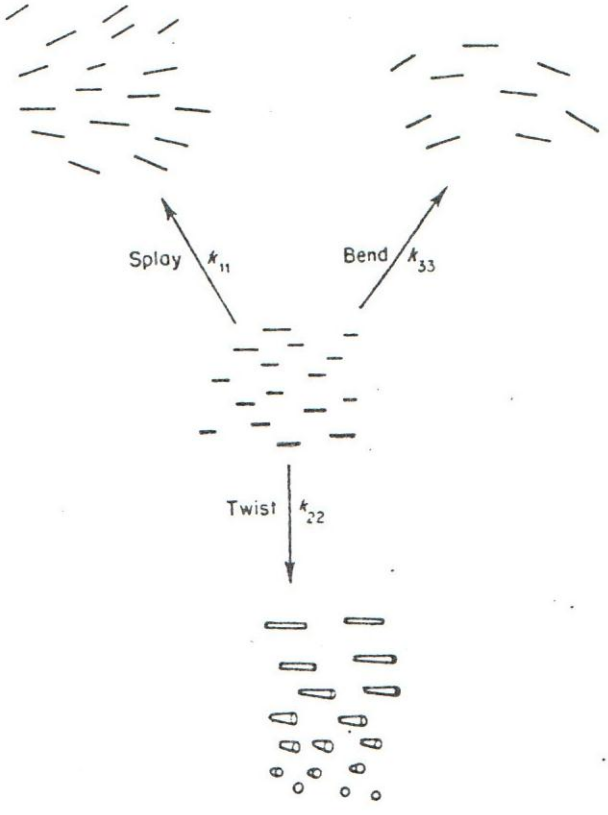


Figure 4: Three fundamental elastic distortions of the nematic phase

Although the absolute values of elastic constants help to determine the relaxation speed of display devices, it is the ratio of the elastic constants particularly K_{33}/K_{11} that has received the most attention because of its effect on the shape of the electrooptic switching curve in displays especially for the twisted nematic cell.

No useful theory exists for the prediction of elastic constants or their ratios. Although analyses have been performed, the results are at variance with experiment perhaps because only the grossest aspects of molecular structure are considered and it is necessary to rely on empirical rules based on experimental measurements (Leenhouts *et al*, 1979; Bradshaw *et al*, 1981). In general a low value of K_{33}/K_{11}, which is desirable in many display modes, can best be obtained by using aromatic and heterocyclic ring systems, high members of homologous series and by excluding lateral substituents. Absolute values of elastic constants appear to correlate approximately with clearing points and only approximately follow the theoretical prediction that,

$$K_{11} \propto S^2 \tag{1.6}$$

The elastic constants K_{22} and K_{33} commonly diverge to large values on approaching a smectic phase (Sage, 1987).

1.2.3.4. Viscosity

The dynamic response of LC displays is limited by the viscosity of the fluid (Jakeman *et al*, 1972). In an NLC, the viscosity is anisotropic like other physical parameters, but both the theory and phenomenology of LC viscosities is rather complex. Five independent viscosities are required to characterize a NLC; three of these called the Miesowiez viscosities represent conventional shear flow with different dispositions of the director while the other two include director rotation or coupling between the director and flow pattern. Experimental determination of these quantities is hindered by the tendency for shear to rotate the director, so very few complete sets of viscosity data exist for LCs. It is normal practice to determine a capillarity flow viscosity or other bulk viscosities (Schadt *et al*, 1987; Clark, 1985). The bulk viscosity is not principally dependent on order parameter although a discontinuity in the plot of η against temperature at a clearing point reveals

that the effect of long-range order is significant (Sage, 1987).

1.2.3.5. Refractive indices

A LC has an anisotropy of refractive indexes similar to that of an optical uniaxial crystal and exhibits double refraction. A uniaxial crystal has two different principal refractive indices n_o and n_e. These are the refractive indices of ordinary rays in which the axis of oscillation of the electrical vector is orthogonal to the optical axis of the crystal and extraordinary ray for which it is parallel.

In NLCs, the direction of the LC director corresponds to the optical axis of the uniaxial crystal and therefore the refractive indices are $n_\perp$ and $n_\parallel$ for rays whose oscillation is respectively orthogonal and parallel to the director , that is, $n_0 = n_\perp$ and $n_e = n_\parallel$. Thus, the refractive index anisotropy Δn is given by;

$$\Delta n = n_e - n_o = n_\parallel - n_\perp \qquad (1.7)$$

n_0 is never greater than n_e and the two coincide on the direction of the director. Therefore, always $n_\parallel$ is greater than $n_\perp$ and Δn is positive. For this reason, NLCs are said to be optically positive (Matsumoto, 1990; Hartshone *et al*, 1970). The refractive indices of a LC are determined by the polarizability of the molecules at optical frequencies and therefore depend largely on the extent of the conjugated π bonding throughout the molecule. Although the dependence of refractive indices on order parameter 'S' is most accurately represented by equation (1.2) above, for practical values and purposes it may be taken that Δn is proportional to S, i.e. $\Delta n \propto S$ (Sage, 1987). Although the refractive indices of LCs can be treated fairly successfully by theory, it is relatively easy to estimate values for new materials by analogy with numerous published data for a wide range of LC systems. As indicated above, birefringence is largely determined by the presence of aromatic rings and π-bonded terminal or linking groups in a LC molecule.

1.2.3.6. Optical Characteristics of LCs.

Due to the anisotropy of refractive index, LCs exhibits the following useful characteristics which form the basis of LCDs;

1. Deflection of the direction of travel of light to the direction of the director (molecular long axis).
2. A change in the polarization state (linearly, elliptically or circularly polarized light) or direction of polarization.
3. Reflection or transmission of incident polarized light according to whether the optical rotation is to the right or left.

The direction of travel of light incident on a LC in the direction of the director is because within the LC $n_{\parallel}$ is greater than $n_{\perp}$ so that the speed of light $v_{\parallel}$ in the parallel direction is higher than $v_{\perp}$ in the orthogonal direction. What happens when linearly polarized light is incident on a LC with a twisted director will be seen by considering figure 5 below.

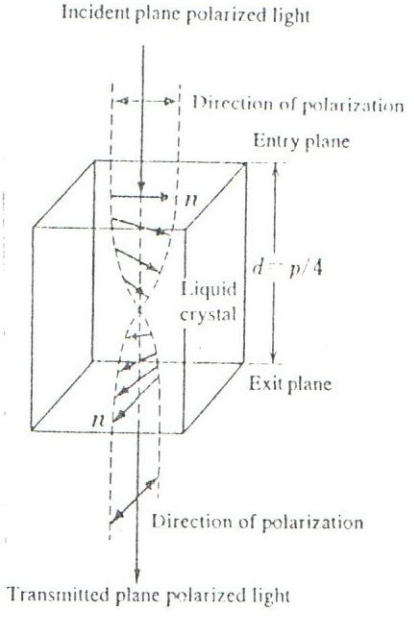


Figure 5: Rotation of plane polarization of incident light by a LC with twisted orientation.

When the pitch p of the LC twist is sufficiently greater than the wavelength λ of the incident light, the light that is incident with its direction of oscillation parallel to the director at the entry surface rotates together with the twist of the director and emerges at the opposite side with its direction of oscillation still parallel to the director. Light incident with its direction of oscillation orthogonal to the director emerges with its oscillation still orthogonal to the director at the plane of emergence. However, light incident with any other direction of oscillation will emerge with its polarization either elliptical, circular or linear depending on the phase difference [$= (n_{\parallel} - n_{\perp}) wd/c$] from the incident to the emergence surface, where w is the angular frequency of light, c is its speed and d is the thickness of the LC layer.

If the pitch p of the twist is of the same order of magnitude as wavelength λ of light, as in an ordinary cholesteric LC, the component of the incident polarized light in the same direction as the optical rotation direction of the LC is reflected and the rotation component in the opposite direction only is transmitted. This phenomenon is termed selective optical scattering (Matsumoto, 1990).

CHAPTER TWO

2.0. THEORY.

2.1. INTRODUCTION.

In Section **2.2** below, a discussion of the merits and limitations of the various approaches available for the calculation of the various optical parameters of nematic liquid crystals (NLCs) such as local field factors, optical anisotropy and orientational order parameter is presented. However, the main emphasis is on only two of these approaches namely: Neugebauer's and Vuks' approaches as these are the ones will be employed in this thesis for the calculation of the various parameters.

The most important of these parameters is the orientational order parameter 'S' which is a measure of the degree of alignment of the molecules in a liquid crystal, in this case a nematic liquid crystal and is defined by equation (1.1) of chapter 1 (Zwetkoff, 1942). For the ordered crystalline phase $\langle\cos^2\theta\rangle = 1$ and therefore 'S' assumes a value of unity while for the random distribution in the liquid state, 'S' is equal to zero since $\langle\cos^2\theta\rangle = 1/3$ for this state.

Many of the macroscopic physical properties and applications of liquid crystals depend on the value of 'S' and its variation with temperature over the mesomorphic range. This applies for the other parameters as well and therefore the determination of the parameters mentioned above is of paramount importance. Different tensorial properties of the liquid crystal medium such as optical dichroism, diamagnetic susceptibility, infrared and Raman band frequencies and intensities, NMR splittings have been used to calculate the parameters in general and in particular the orientational order parameter 'S'. However, a simpler and more elegant method for the calculation of 'S' is by expressing the same in terms of α_e and α_o, the effective polarizabilities of the molecule in the nematic phase and $\alpha_\parallel$ and $\alpha_\perp$, the polarizabilities of the molecule along and transverse to the molecular axis respectively in the crystalline phase. The expression is given by (Subramhanyam *et al, 1973;* Mukhebi, 1995);

$$S = \frac{\alpha_e - \alpha_o}{\alpha_\parallel - \alpha_\perp} \qquad (2.1)$$

A number of investigators have obtained relationships between the polarizabilities α_e, α_o,

$\alpha_{\parallel}$ and $\alpha_{\perp}$ on the one hand and density data in various phases of the liquid crystal on the other hand. The nature of these relationships are different for the various approaches and are based on certain assumptions concerning the local fields at the site of the molecule. Therefore, birefringence and density studies on nematic liquid crystals should provide an elegant and simple method for calculating 'S' and other parameters of nematic liquid crystals.

2.1.1. The Concept of Local Field.

In view of what was mentioned in the previous section, it is important that a brief discussion of the concept of the local field is presented prior to discussing the various approaches.

When an electric field **E** is applied to a medium in the condensed phase, the resultant field will be the sum of the applied field **E** and the field $\mathbf{E}_p$ developed due to the polarization of neighboring molecules of the designated site. The resultant field $\mathbf{E}_{loc.}$ is given by the expression (Born & Huang, 1954);

$$\boldsymbol{E}_{loc} = \boldsymbol{E} + \boldsymbol{E}_{p} \qquad (2.2)$$

Lorenz assumed a spherically symmetric distribution of polarizable molecules and gave an expression for $\mathbf{E}_p$ as;

$$\boldsymbol{E}_{p} = \frac{4\pi \boldsymbol{P}}{3} \qquad (2.3)$$

where **P** is the polarization of the medium (dipole moment per unit volume). In the case of; (i) amorphous solids such as optical glasses, (ii) liquids and (iii) crystalline solids belonging to the cubic system, the induced dipole moment per molecule is given by;

$$\boldsymbol{P} = \alpha \boldsymbol{E}_{loc} \qquad (2.4)$$

where α is the electronic polarizability of the molecule and it is isotropic. The polarization **P** of an optically isotropic medium with only one species of molecules with isotropic polarizability α may

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therefore be written as;

$$\boldsymbol{P} = N\alpha \boldsymbol{E}_{loc} \tag{2.5}$$

where N is the number of molecules per unit volume and $\bar{\alpha}$ is the mean polarizability of the molecule and is given by $\bar{\alpha} = (\alpha_1+\alpha_2+\alpha_3)$, in which α_1, α_2 and α_3 are the principal polarizabilities of the molecule.

As **D**, the displacement vector is related to **E** and **P** by the expression;

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi \boldsymbol{P} = \varepsilon \boldsymbol{E} = (n^2 - 1)\boldsymbol{E} \tag{2.6}$$

it can easily be shown that,

$$(n^2 - 1) = 4\pi N\alpha \frac{\boldsymbol{E}_{loc}}{\boldsymbol{E}} \tag{2.7}$$

From equations (2.2) and (2.3) above, $E_{loc.}$ as,

$$\boldsymbol{E}_{loc} = \boldsymbol{E} + \frac{4\pi \boldsymbol{P}}{3} \tag{2.8}$$

combining equations (2.3), (2.6) and (2.7) leads to the well-known Lorentz - Lorenz relation (Born and Wolf, 1959) shown below:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N}{3} \alpha \tag{2.9}$$

2.2. VARIOUS APPROACHES FOR THE CALCULATION OF OPTICAL PARAMETERS OF NEMATIC LIQUID CRYSTALS.

2.2.1. Zwetkoff's approach.

The earliest calculations of the principal polarizabilities in terms of refractive indices and densities were carried out by Zwetkoff (1942). Using equations (2.2), (2.3) and (2.6) above, he obtained the following relations for the polarizabilities in the crystalline phase:

$$\frac{(n_g^2 - 1)}{(n_g^2 + 2)} = \frac{(4\pi N_C \ \alpha_g)}{3} \tag{2.10}$$

$$\frac{(n_m^2 - 1)}{(n_m^2 + 2)} = \frac{(4\pi N_C \ \alpha_m)}{3} \tag{2.11}$$

and

$$\frac{(n_p^2 - 1)}{(n_p^2 + 2)} = \frac{(4\pi N_C \ \alpha_p)}{3} \tag{2.12}$$

where N_C [$= (\rho_C N_A)/M$] is the number of molecules per unit volume (concentration) in the crystalline phase, ρ_C is the crystalline density, M is the molecular weight and N_A ($= 6.023 \times 10^{23}$) is the Avogadro number. The subscripts g, p and m in the polarizabilities and refractive indices refer to the great, petty and minor axes respectively of the crystal. The principal polarizabilities of the molecules $\alpha_{\parallel}$ ($= \alpha_g$) and $\alpha_{\perp}$[$= (\alpha_p + \alpha_m)/2$] are hence calculable from equations (2.10), (2.11) and (2.12) above. For the nematic phase, Zwetkoff obtained the following relations:

$$\frac{(n_e^2 - 1)}{(n_e^2 + 2)} = \frac{(4\pi N_{LC} \ \alpha_e)}{3} \tag{2.13}$$

and

$$\frac{(n_o^2 - 1)}{(n_o^2 + 2)} = \frac{(4\pi N_{LC}\ \alpha_o)}{3} \qquad (2.14)$$

where N_{LC} [$=(\rho_{LC}N_A)/M$] is the concentration of molecules in the nematic (liquid crystalline) phase. Hence Zwetkoff provides a method for calculating $\alpha_{\parallel}$, $\alpha_{\perp}$, α_e and α_o from refractive index and density data. However the use of equations (2.2), (2.3) and (2.6) to derive equations (2.10) to (2.14) is justifiable only in cases with spherically symmetric positional arrangement of the molecules. For a condensed phase in which there is close packing of the long molecules like liquid crystals, it is evident that this approach would not be justifiable and the field due to induced electric moments of the molecule within the cavity will not vanish. Therefore, it is clear that this approach in which the anisotropic nature of the polarization field is not taken into consideration, is not realistic and hence is not applied in this investigation.

2.2.2. Vuks' approach and Born's relation.

A simpler formula for the local field was proposed by Vuks (1966) in connection with his investigations on Kerr effect (1957) for strongly anisotropic molecules. Vuks assumed that the local field is given by the relation;

$$(\boldsymbol{E}_{loc})_i = (\frac{\bar{n}^2 + 2}{3})\boldsymbol{E}_i \qquad (2.15)$$

where $\bar{n}^2$ is the mean square of the principal refractive indices of the medium. For the crystalline phase, $\bar{n}^2=(n_g^2 + n_m^2 + n_p^2)/3$ and for the nematic phase, $\bar{n}^2=(n_e^2 + 2n_o^2)/3$. From equation (2.15), it is evident that the local field factor $(\bar{n}^2 + 2)/3$ is independent of the rotational direction of the incident electric vector. According to Vuks, the principal refractive indices and polarizabilities are related by the expressions;

$$\frac{n_i^2 - 1}{\bar{n}^2 + 2} = \frac{4\pi N \alpha_i}{3} \qquad (2.16)$$

where i (= x, y or z) refer to the directions of the principal refractive indices and polarizabilities and N is the concentration (number of molecules per unit volume) of the medium and is as defined in section **2.2.1** above. For the crystalline phase, the principal polarizabilities α_x, α_y and α_z are given by;

$$\alpha_x = \frac{3}{4\pi N_C} \left(\frac{n_x^2 - 1}{\bar{n}^2 + 2}\right) \qquad (2.17)$$

$$\alpha_y = \frac{3}{4\pi N_C} \left(\frac{n_y^2 - 1}{\bar{n}^2 + 2}\right) \qquad (2.18)$$

$$\alpha_z = \frac{3}{4\pi N_C} \left(\frac{n_z^2 - 1}{\bar{n}^2 + 2}\right) \qquad (2.19)$$

where symbols are as already defined above. The principal polarizability α_z for the electric vector parallel to the long axis of the molecule is expected to be larger than α_x and α_y and it will be denoted by $\alpha_{\parallel}$ hereafter. The principal polarizabilitiies α_x and α_y for the electric vector perpendicular to the long axis of the molecule are less than α_z and approximately equal to each other and hence may be denoted by $\alpha_{\perp}[= (\alpha_x + \alpha_y)/2]$. Substituting for α_x, α_y and α_z in equations (2.17), (2.18) and (2.19) above gives,

$$\alpha_{\parallel} = \frac{3M}{4\pi\rho_C N_A}\left(\frac{n_{\parallel}^2-1}{\bar{n}^2+2}\right) \qquad (2.20)$$

and

$$\alpha_{\perp} = \frac{3M}{4\pi\rho_c N_A}\left(\frac{n_{\perp}^2-1}{\bar{n}^2+2}\right) \qquad (2.21)$$

where $\bar{n}^2 = (n_g^2 + n_m^2 + n_p^2)/3$, $n_{\perp}^2 = (n_m^2 + n_p^2)/2$ and $n_{\parallel}^2 = n_g^2$. Other symbols are as defined in previous sections. The mean polarizability $\bar{\alpha}$ of the medium is then given by

$$\bar{\alpha} = \frac{(\alpha_{\parallel} + 2\alpha_{\perp})}{3} \qquad (2.22)$$

Equations similar to equation (2.16) have also been applied to the nematic (liquid crystalline) phase and the equations are:

$$\alpha_e = \frac{3}{4\pi N_{LC}}\left[\frac{n_e^2 - 1}{\bar{n}^2 + 2}\right] \qquad (2.23)$$

and

$$\alpha_o = \frac{3}{4\pi N_{LC}}\left(\frac{n_o^2 - 1}{\bar{n}^2 + 2}\right) \qquad (2.24)$$

in which all the symbols are as defined in previous sections. The above expressions obtained from Vuks' relation for the local field were first applied by Chandrasekhar *et al* (1969, 1971, 1976) to evaluate the polarizabilities and orientational order parameters of PAA (p-azoxyanisole), p-azoxyphenetole (PAP) and Anisaldazine and later by others such as Hanson *et al* (1976).

Further from Vuks' formulae in equations (2.17) to (2.24), it can be shown that the mean

polarizability of the molecule in crystalline and liquid crystalline phases is given respectively by:

$$\bar{\alpha} = \frac{(\alpha_g + \alpha_m + \alpha_p)}{3} = \frac{3}{4\pi N_C}\left(\frac{\bar{n}_i^2 - 1}{n_i^2 + 2}\right) \qquad (2.25$$

where $n_i^2 = (n_g^2 + n_m^2 + n_p^2)/3$ and also

$$\bar{\alpha} = \frac{(\alpha_e + 2\alpha_o)}{3} = \frac{3}{4\pi N_{LC}}\left(\frac{\bar{n}_i^2 - 1}{n_i^2 + 2}\right) \qquad (2.26)$$

in which $n_i^2 = (n_e^2 + 2n_o^2)/3$. Equations (2.25) to (2.26) are also referred to as Born's relations (Born *et al*, 1916). In the next paragraph a discussion of Bom's relations is presented as it is treated as part of Vuks' approach.

As early as 1916, Born had shown that for an anisotropic medium, the mean polarizability of the molecules of the medium is calculable from the relation (Born *et al*, 1916);

$$\bar{\alpha} = \frac{3}{4\pi N_L}\left(\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right) \qquad (2.27)$$

where $n^2 = (1/3)\sum n_i^2$.

This relation is derived from the Lorenz expression for the local field (equation 2.7). As already indicated Born's relation automatically follows from Vuks' formulae owing to the very nature of the assumptions made therein. Even though Vuks' approach has some limitations, which are pointed out in the last chapter of this thesis, the approach has been employed by a good number of investigators to calculate orientational order parameter and other parameters for a number of nematics. For example, Chandrasekhar *et al* used Vuks approach to calculate orientational order parameter and other parameters for PAA and PAP (Chandrasekhar *et al*, 1969). Other investigators who have applied the same approach to interpret birefringence data for other nematic compounds include Madhusudana *et al* (1971), Huang *et al* (1974), Shaya and Yu (1975), Karat and Madhusudana

(1976), Schulze and Burkerarode (1986), Hanson and Shen (1976), Trotimov *et al* (1977) and Nagappa (1992).

Owing to the extensive usage of this approach by investigators, it has been adopted for use in the calculations in this thesis and the results obtained compared with those obtained from Neugebauer's approach.

2.2.3. Approach due to Derzhanski and Petrov.

The concepts of local field and hence the calculation of polarizabilities from refractive index and density data, were also undertaken by Derzhanski and Petrov in 1971. They assumed that the molecule occupies a spheroidal shaped cavity whose volume equals to the volume available to the molecule and that the spheroidal cavity is a homogeneous anisotropic dielectric. The principal polarizabilities $\alpha_{\parallel}$ and $\alpha_{\perp}$ in the crystalline phase were shown by them to be given by:

$$\alpha_{\parallel} = \frac{1}{4\pi N_C}\left[\frac{n_{\parallel}^2 - 1}{1 + L_{\parallel}(n_{\parallel}^2 - 1)}\right] \qquad (2.28)$$

and

$$\alpha_{\perp} = \frac{1}{4\pi N_{LC}}\left[\frac{n_{\perp}^2 - 1}{1 + L_{\perp}(n_{\perp}^2 - 1)}\right] \qquad (2.29)$$

The corresponding expressions for α_e and α_o in the nematic phase are:

$$\alpha_e = \frac{1}{4\pi N_{LC}}\left[\frac{n_e^2 - 1}{1 + L_e(n_e^2 - 1)}\right] \qquad (2.30)$$

and

$$\alpha_o = \frac{1}{4\pi N_{LC}}\left[\frac{n_o^2 - 1}{1 + L_o(n_o^2 - 1)}\right] \qquad (2.31)$$

$L_{\parallel}$ and $L_{\perp}$ are called shape factors for the molecules which satisfy the condition $L_{\parallel}+2L_{\perp} = 1$ and are related to the ratio of the major to the minor axis of the spheroid. Though equations (2.28) and (2.29) lead to Neugebauer's relations, which are discussed in the next section, the values of $L_{\parallel}$ and $L_{\perp}$ obtained from the approaches are quite different. However, the assumptions made by Derzhanski and Petrov, that the molecule is a spheroid and that the surrounding of a molecule is equivalent to a homogeneous dielectric are simplistic in nature. This is because the immediate vicinity of any molecule surrounded by other molecules cannot obviously be treated as a homogeneous dielectric. Because of these assumptions, it appears that the calculation of Lorenz factors and polarizabilities directly on the basis of the shape of the crystal as was done by Derzhanski and Petrov cannot lead to reliable values of Lorenz factors, polarizabilities and consequently orientational order parameters. This approach, probably because of these limitations, has not been widely employed unlike Vuks' and Neugebauer's approaches. Consequently, it has not been used in this investigation.

2.2.4. Dunmur's Approach.

The approach due to Dunmur (Dunmur, 1972) leads to the following expressions for the Lorenz field factors, $L_{\parallel}$ and $L_{\perp}$ in the crystalline phase. They are given by:

$$L_{\parallel} = \frac{1}{3}\left(1 - \frac{3A_{\parallel}}{4\pi N}\right) \qquad (2.32)$$

and

$$L_{\perp} = \frac{1}{3}\left(1 - \frac{3A_{\perp}}{4\pi N}\right) \qquad (2.33)$$

where $A_{\perp}$ and $A_{\parallel}$ satisfy the relation $A_{\parallel} + 2A_{\perp} = 0$. Dunmur expressed the polarizabilities in terms of these A factors and assumed that the polarizable units, that is the molecules, are points situated at different lattice sites of the crystal. This assumption is valid for molecules which are far from the point at which the field is calculated and only approximately for molecules close to the reference point. Dunmur considered the problem of local field for crystals from a standpoint similar to that

adopted by Mueller (Mueller, 1935) in his theory of photoelectric effect of cubic crystals. Using his calculated values of A factors of a few organic crystals, Dunmur calculated the polarizabilities and made a significant observation that the mean value of these polarizabilities did not agree with that determined from studies on the refractive indices of solutions of the same compounds. This disagreement arose essentially because of his assumptions that the polarizable units are points situated at different lattice sites of the crystal. This approximation is not likely to be accurate for molecules which are close to the reference point at which the local field is calculated.

As a consequence of this drastic assumption, the polarizabilities, orientational order parameters , etc calculated directly from the structure of the crystal, as in Dunmur's approach cannot lead to accurate values. In view of this limitation, this approach has not been used for our calculations.

2.2.5 Neugebauer's Approach.

The anisotropic nature of the local field was taken into account by Neugebauer (1950, 1954) by considering the local field at the center of a fictitious spherical cavity of sufficiently large size to include within it a large number of molecules. As a result he obtained the well-known Neugebauer's relations for the crystalline phase. However, first is a consideration of how these analogous relations can be obtained for the nematic phase and later on to the crystalline phase.

When the molecular distribution is spherically symmetric, the field arising due to the induced dipoles within the fictitious cavity is equal to zero and it is well known that the net electric field at the center of the cavity, that is, the local field is equal to $\mathbf{E} + (4\pi\mathbf{P})/3$. In general where the molecular distribution is anisotropic, the part of the field arising due to induced dipoles within the cavity will not vanish and it can be shown on the basis of Neugebauer's approach (1950, 1954) that the effect of the induced dipoles within the cavity would give an additional term to $\mathbf{E} + (4\pi\mathbf{P})/3$, say $\mathbf{E}_d$ which is non-zero. This additional part of the field is given by the well-known relation (Botcher, 1952)

$$\boldsymbol{E}_d = \Sigma\ [3(\boldsymbol{P}_s.\boldsymbol{r}_s)\boldsymbol{r}_s - r_s^2\boldsymbol{P}_s]\ r_s^{-5} \qquad (2.34)$$

where $\mathbf{P}_s$ is the induced dipole moment at the S^{th} molecule and $\mathbf{r}_s$ is the position vector. The summation has to be carried out over all the molecules within the cavity including the one at the center. By adding the same to $\mathbf{E} + (4\pi\mathbf{P})/3$ and simplifying, the following relations will result for the three components of the local field; $(\mathbf{E}_{loc})_x$, $(\mathbf{E}_{loc})_y$ and $(\mathbf{E}_{loc})_z$. The relations are;

$(\mathbf{E}_{loc})_x = \mathbf{E} + (4\pi L_z P_z)$ where

$$L_z = \frac{1}{3} + \frac{1}{4\pi N_{LC}} (3z_s^2 - r_s^2)\, r_s^{-5} \qquad (2.35)$$

$(\mathbf{E}_{loc})_y = \mathbf{E} + (4\pi L_y P_y)$ where

$$L_y = \frac{1}{3} + \frac{1}{4\pi N_{LC}} (3y_s^2 - r_s^2)\, r_s^{-5} \qquad (2.36)$$

and $(\mathbf{E}_{loc})_x = \mathbf{E} + (4\pi L_x P_x)$ where

$$L_x = \frac{1}{3} + \frac{1}{4\pi N_{LC}} (3x_s^2 - r_s^2)\, r_s^{-5} \qquad (2.37)$$

P_x, P_y , P_z are the principal polarization components while $\mathbf{r}_s$ is the position vector and x_s, y_s, z_s are its components. Lorenz factors L_x, L_y and L_z are related by $L_x + L_y + L_z = 1$ since $(x_s^2 + y_s^2 + z_s^2) = 1$ and for cylindrical distribution as in the case of nematic LCs, $L_x = L_y$. The optic axial direction of the nematic LC is taken to be the z-direction and thus without any loss of generality, it can be written that $L_z = L_e$, by associating the extraordinary vibration direction without the z-direction. Consequently, $L_x = L_y = L_o$ where the subscript `o' represents the ordinary vibration direction. Further, for a long molecule, P_s is given by;

$$\boldsymbol{P}_s = (\alpha_{\parallel} - \alpha_{\perp})\, (\boldsymbol{E}_{loc}.\boldsymbol{a}_s)\, \boldsymbol{a}_s + \alpha_{\perp} \boldsymbol{E}_{loc} \qquad (2.38)$$

in which $\mathbf{a}_s$ is the unit vector along the long axis of the molecule and $\alpha_{\parallel}$ is the principal polarizability of the molecule parallel to its long axis and $\alpha_{\perp}$ is the mean value of the two principal polarizabilities transverse to the long axis of the molecule. It can also be shown that the effective polarizabilities α_e and α_o in the nematic phase are related to $\alpha_{\parallel}$ and $\alpha_{\perp}$ by the expressions below;

$$\alpha_e = (\alpha_{\parallel} - \alpha_{\perp})\,(\boldsymbol{a}_s.\boldsymbol{k})^2 + \alpha_{\perp} \qquad (2.39)$$

and

$$\alpha_o = (\alpha_{\parallel} - \alpha_{\perp})\,(\boldsymbol{a}_s.\boldsymbol{i})^2 + \alpha_{\perp} \qquad (2.40)$$

where **i**, **k** are unit vectors along x- and z- directions. P_z and P_x are respectively given by $P_z = N_{LC}\alpha_z (E_{loc})_z$ and $P_x = N_{LC}\alpha_x (E_{loc})_x$ using the components of the displacement vector D in the two directions which are given by;

$$D_z = n_z^2 E_z = E + 4\pi P_z \qquad (2.41)$$

and

$$D_x = n_x^2 E_x = E + 4\pi P_x \qquad (2.42)$$

With the help of the above set of equations (2.35) to (2.42), it can easily be shown that the effective polarizabilities α_e and α_o, the Lorenz field factors L_e and L_o, and the extraordinary and ordinary refractive indices n_e and n_o respectively in the nematic phase are related by the following expressions;

$$(n_e^2 - 1) = 4\pi N_{LC}\alpha_e\,(1 - 4\pi N_{LC}L_e\alpha_e)^{-1} \qquad (2.43)$$

and

$$(n_o^2 - 1) = 4\pi N_{LC}\alpha_o\,(1 - 4\pi N_{LC}L_o\alpha_o)^{-1} \qquad (2.44)$$

where $\bar{\alpha}$, the mean polarizability in the nematic phase is given by;

$$\bar{\alpha} = \frac{(\alpha_e + 2\alpha_o)}{3} \tag{2.45}$$

Using equations (2.35) to (2.45) Subramhanyam *et al*, (1973) and Mukhebi *et al* (1995) showed that the following expression results;

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N_{LC}}{3}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + 2\left(\frac{n_o^2 + 2}{n_o^2 - 1}\right)\right] \tag{2.46}$$

where N_{LC} has the same meaning as defined in section 2.2.1 above. In the liquid phase $n_e = n_o = n_l$ the refractive index in the liquid phase and hence equation (2.46) reduces to the well-known Lorenz-Lorenz relation viz;

$$\bar{\alpha} = \frac{\alpha_e + 2\alpha_o}{3} = \frac{3}{4\pi N_l}\left(\frac{n_l^2 - 1}{n_l^2 + 2}\right) \tag{2.47}$$

where $N_l [=(\rho_l N_A)/M]$ is the concentration in the liquid phase and ρ_l is the isotropic density of the nematic compound. Therefore if the indices n_e, n_o, n_l and the densities ρ_{LC}, ρ_l are known, then equations (2.46) and (2.47) can be solved simultaneously to obtain the values of α_e and α_o at any temperature in the liquid crystalline phase of the nematic compound. L_e and L_o can similarly be calculated using equations (2.43) and (2.44) above respectively.

An expression similar to equation (2.46) is obtainable for the crystalline phase of the nematic compound wherein it is assumed that the long axes of the molecules are arranged parallel to one another. Using similar considerations concerning $\mathbf{E}_{loc}$ as in the nematic phase and based on the set of equations given by;

$$P_i = N_C \alpha_i (E_{loc})_i \tag{2.48}$$

where N_C [= $(\rho_C N_A)/M$] is the molecular concentration in the crystalline phase and i = g, m, p. It can be shown that the following relations results;

$$(n_g^2 - 1) = 4\pi N_C \alpha_g (1 - 4\pi N_C L_g \alpha_g)^{-1} \quad (2.49)$$

$$(n_m^2 - 1) = 4\pi N_C \alpha_m (1 - 4\pi N_C L_m \alpha_m)^{-1} \quad (2.50)$$

\and

$$(n_p^2 - 1) = 4\pi N_C \alpha_p (1 - 4\pi N_C L_p \alpha_p)^{-1} \quad (2.51)$$

where n_g, n_m, and n_p are the three principal refractive indices in the crystalline phase while L_g, L_m and L_p are the corresponding Lorenz field factors which satisfy the relation $L_g + L_m + L_p = 1$. Combining equations (2.49), (2.50) and (2.51) gives the following Neugebauer's relation for the crystalline phase:

$$\frac{1}{\alpha_g} + \frac{1}{\alpha_m} + \frac{1}{\alpha_p} = \frac{4\pi N_C}{3} \left[\frac{n_g^2 + 2}{n_g^2 - 1} + \frac{n_m^2 + 2}{n_m^2 - 1} + \frac{n_p^2 + 2}{n_p^2 - 1}\right] \quad (2.52)$$

As the `g' axis of the crystal corresponds to the long axes of the molecules which are all parallel to one another in the crystalline phase, α_g is replaced by $\alpha_\parallel$ hereafter. α_m and α_p are very nearly equal and hence the approximation that $\alpha_\perp = (\alpha_m + \alpha_p)/2$ is valid. On making these substitutions equation (2.52) above then reduces to;

$$\frac{1}{\alpha_{\parallel}} + \frac{2}{\alpha_{\perp}} = \frac{4\pi N_C}{3}\left[\frac{n_g^2 + 2}{n_g^2 - 1} + \frac{n_m^2 + 2}{n_m^2 - 1} + \frac{n_p^2 + 2}{n_p^2 - 1}\right] \qquad (2.53)$$

where symbols are as defined in previous sections. Similarly L_g in equation (2.49) can be replaced by $L_{\parallel}$ while the average $(L_m+L_p)/2$ in equations (2.50) and (2.51) can be replaced by $L_{\perp}$ with the proviso that;

$$L_{\parallel} + 2L_{\perp} = 1 \qquad (2.53a)$$

Equation (2.49) now takes the form;

$$(n_g^2 - 1) = 4\pi N_C \alpha_{\parallel} (1 - 4\pi N_C L_{\parallel} \alpha_{\parallel})^{-1} \qquad (2.53b)$$

Equation (2.53b) can be used to calculate $L_{\parallel}$ while $L_{\perp}$ can be calculated using equation (2.53a) above. In the isotropic (liquid) phase, $n_g = n_m = n_p = n_l$, the refractive index in the liquid phase and hence equation (2.53) above reduces to;

$$\bar{\alpha} = \frac{\alpha_{\parallel} + 2\alpha_{\perp}}{3} = \frac{3}{4\pi N_l}\left(\frac{n_l^2 - 1}{n_l^2 + 2}\right) \qquad (2.54)$$

Therefore if the values of n_g, n_m, n_p, ρ_c, ρ_l and n_l are known for any nematic compound, equations (2.53) and (2.54) can be solved simultaneously to obtain the values of $\alpha_{\parallel}$ and $\alpha_{\perp}$. Likewise solving equations (2.53a) and (2.53b) gives the values of Lorenz field factors $L_{\parallel}$ and $L_{\perp}$ in the crystalline phase. The details regarding the various assumptions made and the steps involved in the derivation of the crucial equations (2.43), (2.44), (2.46), (2.47), (2.49), (2.50), (2.51) (2.52), (2.53), (2.53b) and (2.54) are discussed by Mukhebi *et al* (Mukhebi, 1995). These sets of equations will be referred to as Neugebauer's relations hereafter. These relations involving point-dipole approximations and taking into account an anisotropic local field were first employed by Subramhanyam and Krishnamurti (1973), Subramhanyam and Prabha (1975), Subramhanyam (1976), Subramhanyam

and Prasad (1976), Isaert and Billard (1977) for nematic compounds; Subramhanyam and Krishnamurti (1975), Mukhebi (1995) for smectic LCs and Maghanga (1996) for cholesteric LCs. Several other investigators have also employed the same approach for various investigations concerning nematic, smectic and cholesteric LC compounds. In view of the extensive usage of this approach, it has also been applied for the calculation of the various parameters of the compounds in this study.

2.2.6. Blinov's approach.

Blinov *et al* (1985) adopted a very different procedure from the other approaches for the calculation of orientational order parameter for the nematic compounds in particular. They estimated Lorenz field factors and order parameter of nematics by measuring the dichroism of rod-like probe molecules dissolved in a nematic matrix. By orienting the polarizer perpendicular or parallel to the rubbing direction of the cell walls containing the nematic matrix, the optical densities D_o and D_e of dye solutions were determined and hence ratio $N^* = (D_e/D_{o})$ was calculated. They related the orientational order of parameter 'S' to a quantity N^* by the relation;

$$S = \frac{(N^{*} - 1)}{(N^{*} + 2)} \qquad (2.55)$$

where $N^* = gN$, where 'g' is a correction factor. They made a drastic assumption that $\mathbf{E}_{loc}$ for the ordinary direction of the polarizing field equals to the corresponding $\mathbf{E}_{loc}$ for the extraordinary field direction, that is, $(\mathbf{E}_{loc})_o = (\mathbf{E}_{loc})_e$ and showed that the correction factor g is given by;

$$g = \frac{n_e}{n_o} \qquad (2.56)$$

Since the assumptions made in the derivation of equation (2.56) are simplistic in nature, we feel that this correction factor 'g' should vary from dye to dye depending on dye length and its exact molecular structure. Therefore 'g' derived without considering the dye formula may not be realistic. Because of these limitations of Blinov's approach, it has not been applied in our calculations, pending the derivation of an involved expression for the correction factor 'g'.

In the light of the discussion of the various approaches that has been presented in the previous sections of this chapter, it emerges that two of the approaches namely: Vuks' and Neugebauer's approaches are worth serious consideration. They have therefore been applied in the subsequent chapters of this thesis for the calculation of the various parameters such as orientational order parameter, Lorenz field factors, optical anisotropy, etc for the five nematic compounds choosen for our investigation. The results from the two approaches have then been compared and discussed. In addition, significant conclusions and recommendations have been made.

CHAPTER 3.

3.0.EXPERIMENTAL DETERMINATION OF DENSITIES OF THE NEMATIC HOMOLOGUES.

3.1. INTRODUCTION.

The five nematic liquid crystalline compounds whose densities were measured are the following;

(i) p-(p-ethoxyphenylazo) phenyl hexanoate,

(ii) p-(p-ethoxyphenylazo) phenyl heptanoate,

(iii) p-(p-ethoxyphenylazo) phenyl undecyclenate,

(iv) n-(p-propoxybenzylidene) p-pentylaniline and

(v) n-(p- butoxybenzylidene) p-pentylaniline.

Their structural formulae along with those of p-(p-ethoxyphenylazo) phenyl valerate [valerate] and p-(methoxybenzylidene) p-butyl aniline [MBBA] are shown in the figure 6 below. These five compounds were chosen because of the following criteria:-

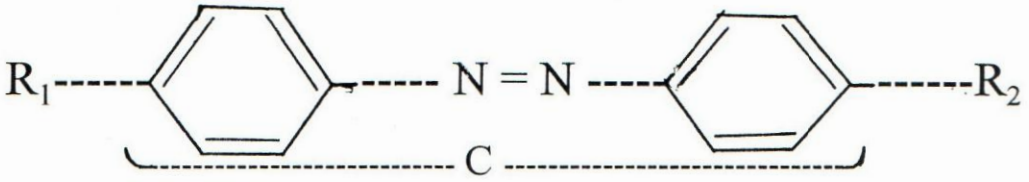
i) The first three compounds are homologous with valerate and the last two are homologous with MBBA. The birefringence data of MBBA and valerate have been reported and their optical properties extensively studied by earlier investigators,

ii) they exhibit the nematic phase at mesomorphic ranges within which it is not difficult to measure their densities,

iii) their nematic mesophases persist over a large temperature range and thus an extensive study of their mesomorphic behaviour is possible,

(iv) they do not decompose on heating as confirmed by the fact that the nematic-isotropic transition temperatures remain unaltered during the heating and cooling processes.

The first three of the five nematic compounds namely hexanoate, heptanoate and undecyclenate have the general formula given by;



in which;

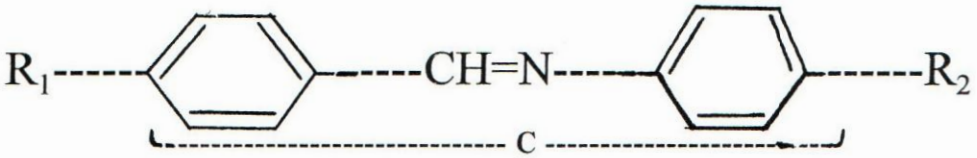
(i) $R_1 = CH_3CH_2O$ and $R_2 = O\text{-}CO\text{-}(CH_2)_4CH_3$ for hexanoate,

(ii) $R_1 = CH_3CH_2O$ and $R_2 = O\text{-}CO\text{-}(CH_2)_5CH_3$ for heptanoate,

(iii) $R_1 = CH_3CH_2O$ and $R_2 = O\text{-}CO\text{-}(CH_2)_8CH{:}CH_2$ for undecyclenate and

(iv) $R_1 = CH_3CH_2O$ and $R_2 =$ $O\text{-}CO\text{-}(CH_2)_3CH_3$ for valerate.

The fourth and fifth compounds namely PBPA and BBPA have the general formula given by;



in which;

(v) $R_1 = O(CH_2)_2CH_3$ and $R_2 = (CH_2)_4CH_3$ for PBPA

(vi) $R_1 = O(CH_2)_3CH_3$ and $R_2 = (CH_2)_4CH_3$ for BBPA.

(vii) $R_1 = O\text{-}CH_3$ and $R_2 = (CH_2)_3CH_3$ for MBBA.

Figure 6: Structural formulae of the five nematic compounds along with those of valerate and MBBA.

Further synthesis of these compounds could be done comparatively easily in that PBPA and BBPA could be synthesized starting with MBBA while hexanoate, heptanoate and undecyclenate could be synthesized starting with valerate. Both MBBA and valerate are commercially available at low costs. In addition, the crystalline to liquid crystalline (K-N) and liquid crystalline to liquid (N-I) phase transition temperatures of all the five compounds have been measured by Revanna Siddaiah *et al* (1992). These data along with the molecular weights of the five homologues are given in the table

1 below. Similarly the same investigators have also determined the refractive indices in the liquid crystalline and the liquid phases of the five compounds and in the crystalline phase of hexanoate, heptanoate and undecyclenate. No data on refractive index in the crystalline phases of the last two compounds, PBPA and BBPA has been reported probably due to the difficulties experienced in the recrystallization and orientation of these two compounds. The birefringence data for all the five compounds for various wavelengths are given in tables **1** to **8** of Appendix **I**.

Table 1: Molecular weights and transition temperatures of the five compounds.

Compound	Molecular Weight, M(gm)	Crystalline to Nematic (K-N) or $T_{CLC}(^0C)$	Nematic to Isotropic (N-I) or T_{LCL} (^0C)
Hexanoate	340.42	75.0	126.0
Heptanoate	354.45	59.5	119.0
Undecyclenate	408.54	65.6	110.0
PBPA	309.45	34.0	69.1
BBPA	323.48	42.5	80.5

As Revanna Siddaiah *et al* did not require in their investigation the density data in all the phases of the homologues , they did not undertake to determine the same. However, as the data were needed in this investigation, one of the major tasks therefore was to experimentally determine the densities in all the phases of each of the homologues. This was done by following the procedure discussed in the section below. However it was not possible to measure the densities in the crystalline phase of PBPA and BBPA owing to the difficulties encountered in the recrystallization of these two compounds.

3.2. SAMPLE PREPARATION

3.2.1. Introduction

Synthesis of the five compounds does not form a part of this thesis. In fact, we initially tried to buy a few grams of each compound from Eastman Kodak and Merk Limited of India but owing to the exhorbitant costs involved and the unavailability of such huge funds, the supervisor Prof. Subramhanyam decided to synthesize the same at a much lower cost during his visit to India in

December, 1995. More details about synthesis are not presented here as it forms the subject matter of a research paper to be published by Subramhanyam *et al* in due course.

3.2.2. Sample purification.

After procurement of the required quantities of each of the five compounds, purification was done to ensure that pure samples were used in experimentation. Purification was done by repeated recrystallization of each compound from its solution in benzene or salicylic acid. However, difficulties were experienced in the recrystallization of the last two compounds, PBPA and BBPA. Hence the densities of these two compounds were measured only in the liquid crystalline and liquid phases and not in the crystalline phase.

3.3. MEASUREMENT OF DENSITIES

3.3.1 Measurement of densities in the crystalline phase.

The densities in the crystalline phase of the compounds: hexanoate, heptanoate and undecyclenate were measured using the floatation technique. A known mass of each compound in turn was placed so as to float on a solution of sodium potassium tartarate in pure water of known volume contained in a measuring cylinder. The purpose of dissolving sodium potassium tartarate in water was to lower the density of water so that a small mass of the compound could cause an appreciable change in the volume of the solution. Using the measured volume of the displaced solution the density of the compound was calculated using the expression,

$$\text{density, } \rho_c = \text{(Mass, m)/(Volume, v)}$$

where m is the mass of the sample of compound used and volume v was obtained by measuring the height change of the water level and the internal radius R of the measuring cylinder using a travelling microscope. The volume was then calculated using $V=\Pi R^2 h$, where h is the difference in water levels before and after displacement.

3.3.2. Measurement of densities in the liquid crystalline and liquid phases.

The densities in the liquid crystalline and liquid phases were determined by measuring the lengths of a specimen of the compound inside a capillary tube placed in a specially constructed electrically controlled hot chamber. The details of the chamber are described in section **3.3.2.1** below.

In the liquid crystalline phase, densities were determined at various temperatures within the mesomorphic range while in the liquid phase, the densities were measured at a single temperature just beyond the N-I transition temperature. The capillary tube was wrapped all round with copper foil to improve thermal contact, leaving a few millimetres on either side of the specimen for observation. A thermometer of accuracy 0.1^0C was used to measure the temperature while the mass of the thread of the sample was measured using a single pan electrical microbalance of accuracy 0.0001gm. As the temperature of the specimen was increased, the corresponding value of length l of the specimen were read using a high resolution travelling microscope of accuracy 0.001cm. For each measuremet of length taken, a correction was made for the thermal expansion of the glass. The densities of the compound at various temperatures were calculated using the expression,

$$\rho = \frac{m}{\pi R^2 l} \qquad (3.1)$$

where m is the mass of the thread of the sample at room temperature and R is the internal radius of the capillary tube measured using the travelling microscope.

3.3.2.1. Details of the Chamber.

The chamber was constructed from a rectangular aluminium block of dimensions 20cm by 8cm by 10cm, with the following modifications made on it:

(i) A groove of dimensios about 15 cm by 2 cm by 2 cm was made at the centre of the top surface along the length of the block and covered with a transparent glass plate to make an observation window. This groove served the purpose of holding the capillary tube containing the sample and a themometer.

(ii) A cylindrical hole of dimensions 2 cm by 15cm, into which another thermometer was to be placed was drilled at the centre and along the length of the block directly below the window.

(iii) A groove measuring 2 cm by 1 cm by 6 cm was made on each of the two opposite and vertical faces and along the length of the block. These modifications on the aluminium block are shown on the sketch (not drawn to scale) in figure 7 below.

Araldite adhesive mixed with cement powder was used to hold in place four heating elements made from tungsten wire and connected in series, two on each of the grooves on the vertical faces.

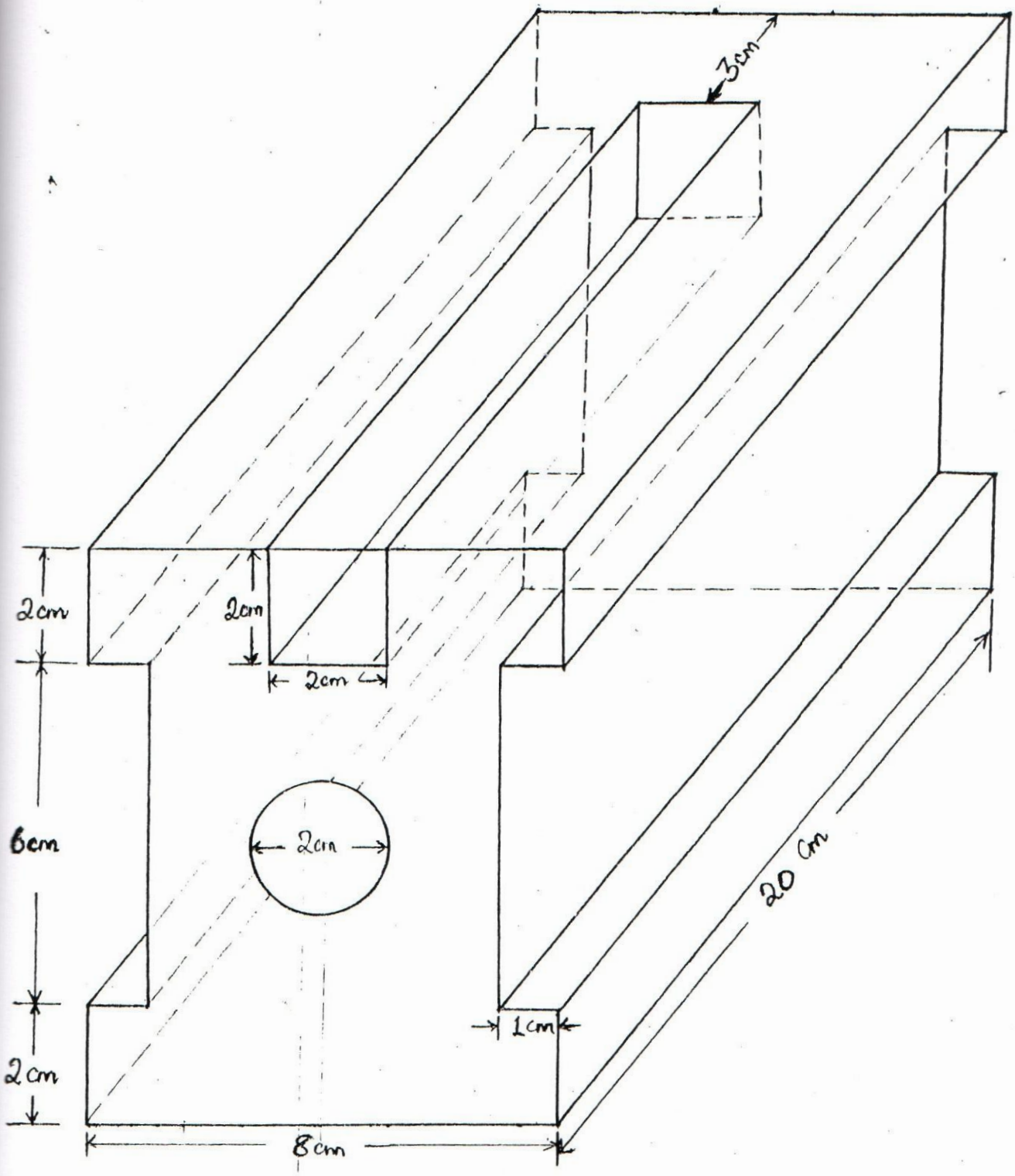


Figure 7: Diagram showing the modifications made on the aluminium block.

The gap was then packed with a paste of asbestos powder, insulated with mica sheets and finally covered fully with asbestos powder. Two wire leads provided connections to the power supply. The chamber was then left for about two days to dry. When it was ready for use, an exploratory study was done on it to determine the mode of variation of voltage from the powder supply with temperature in the chamber. This was necessary to determine values of voltage required for particular temperatures.

3.3.2.2 Experimental Procedure.

Purified crystals of each compound were pushed into a clean capillary tube sealed at one end by heating with a flame. The capillary tube containing the sample was placed in the hot chamber such that the specimen could be observed through the glass window. The ends of the wire leads from the chamber were connected to a variable autotransformer fitted with a voltage stabiliser. The temperature of the sample could thus be varied and maintained at a desired value by varying the current through the tungsten wire making up the heating element, in the chamber. Figure 8 below shows a block diagram of the experimental setup.

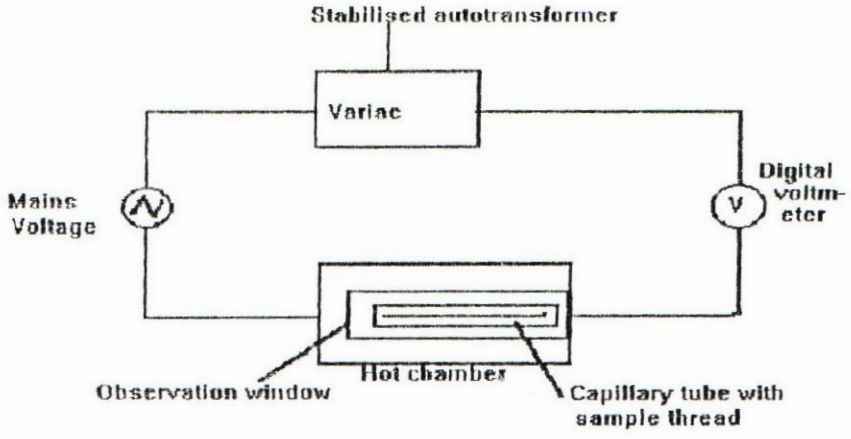


Figure 8: Block diagram of the experimental setup.

The lengths of the sample thread in the capillary tube were measured at various temperatures in the nematic phase using a high resolution travelling microscope. To be absolutely sure of the lengths, this procedure was done during both the heating and cooling processes of the sample. The internal diameter of the tube was also measured using the travelling microscoope and the corresponding values of density at various temperatures were calculated using equation (3.1) of this chapter. The measured densities in the crystalline phases of the first three compounds: hexanoate, heptanoate and undecyclenate are given in table 2 below, while the measured densities in the liquid crystalline and liquid phases of all the five compounds are presented in tables **3, 4, 5, 6** and 7 of this chapter.

Table 2: Densities in the crystalline phase of hexanoate, heptanoate and undecyclenate.

Compound	Hexanoate	Heptanoate	Undecyclenate
Crystalline ρ_C(gm/cm^3)	1.210	1.190	1.160

Table 3: Densities in the liquid crystalline and liquid phases of hexanoate.

$(t_c-t)^0$c	Density, ρ(gm/cm^3)
-0.5 (liquid)	1.044
4.0	1.051
8.0	1.055
12.5	1.059
19.5	1.065
24.0	1.069
28.5	1.073
32.0	1.076
37.0	1.080
44.5	1.086
48.5	1.090

Table 4: Densities in the liquid crystalline and liquid phases of heptanoate.

$(t_c-t)^0c$	Density, $\rho(gm/cm^3)$
-1.0 (liquid)	1.040
4.0	1.046
6.0	1.048
9.0	1.051
13.0	1.055
19.0	1.060
21.5	1.062
25.0	1.065
28.0	1.067
34.0	1.072
39.0	1.076

Table 5: Densities in the liquid crystalline and liquid phases of undecyclenate.

$(t_c-t)^0c$	Density, $\rho(gm/cm^3)$
-0.5 (liquid)	1.037
2.0	1.042
6.0	1.050
9.5	1.055
14.5	1.062
20.5	1.067
25.0	1.067
30.0	1.072
35.0	1.078
40.0	1.083
44.0	1.086

Table 6: Densities in the liquid crystalline and liquid phases of PBPA.

$(t_c - t)^0c$	density (gm/cm^3)
-0.5 (liquid)	0.992
4.6	1.001
6.8	1.004
10.2	1.007
15.6	1.011
22.6	1.016
27.3	1.019
30.6	1.022
34.6	1.025

Table 7: Densities in the liquid crystalline and liquid phases of BBPA.

$(t_c - t)^0c$	density, ρ(gm/cm^3)
-0.5 (liquid)	0.981
3.2	0.985
6.0	0.988
10.9	0.993
13.5	0.996
18.0	0.999
22.5	1.003
25.9	1.005
31.4	1.010
35.0	1.013

CHAPTER FOUR

4.0. CALCULATIONS, RESULTS AND DATA ANALYSIS

4.1. INTRODUCTION.

As indicated in the previous chapters in general and at the end of chapter **2** in particular, the intention is to apply Neugebauer's and Vuks' approaches to calculate the various optical parameters such as isotropic polarizability $\bar{\alpha}$, effective polarizabilities α_e and α_o, parallel and perpendicular to the optic axis respectively, optical anisotropy $\Delta\alpha$ $[=(\alpha_{\parallel}-\alpha_{\perp})]$, orientational order parameter 'S', Lorentz field factors L_e, L_o in the liquid crystalline phase and $L_{\perp}$,$L_{\parallel}$ in the crystalline phase and field anisotropies, $(L_o - L_e)$ and $(L_{\perp} - L_l)$in the nematic and crystalline phases respectively for each of the five nematic compounds. The results obtained from these two approaches will be compared with a view to establishing the merits, if any, of one approach over the other.

Foremost, a presentation of the varous calculations is done. For the calculation of the aforementioned parameters, the data required were;

(i) the refractive indices n_g, n_m and n_p in the crystalline phases of all the five compounds for various wavelengths,

(ii) the refractive indices n_e and n_o in the liquid crystalline phases of the compounds at various temperatures and for various wavelengths,

(iii) the refractive indices n_l in the liquid phases of the compounds for various wavelengths,

(iv) the densities ρ_c and ρ_L in the crystalline and liquid phases respectively and ρ_{LC} at various temperatures in the liquid crystalline phases of the compounds.

The data in (i), (ii) and (iii) have been reported by Revanna Siddaiah *et al* (Revanna Siddaiah, 1995) for all the five compounds and are presented in tables **1** to **8** of Appendix **I**. The data in (iv) have been experimentally determined by us following the methodology described in chapter **3** of this thesis and the results are presented in tables **1** to **6** of the same chapter.

4.2. CALCULATION OF ISOTROPIC POLARIZABILITIES.

The calculation of isotropic polarizability $\bar{\alpha}$ using Neugebauer's approach is based on Lorentz-Lorenz relation whereas in Vuks' approach it is effectively based on Born's relation.

However, it can also be calculated from the data on bond polarizabilities. For purposes of comparison and analysis of results, a presentation of the calculation of isotropic polarizability $\bar{\alpha}$ by the various methods is made in the following sections.

4.2.1. Calculation of $\bar{\alpha}$ using Lorentz-Lorenz relation.

Using the available refractive index data in the liquid phase presented in tables 4 to 8 of Appendix I and the isotropic densities of the five nematic compounds experimentally determined by us and presented in tables 3 to 7 of chapter 3, isotropic polarizability $\bar{\alpha}$ was calculated using Lorentz-Lorenz relation which is given by equation (2.47) of chapter 2. The values of $\bar{\alpha}$ obtained for the five nematic compounds for various wavelengths are presented in table 8 below.

Table 8: Values of isotropic polarizability $\bar{\alpha}$ (in units of $10^{-24}cm^3$) for the five compounds calculated using Lorentz-Lorenz relation.

Compound	Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3)		
	$5461A^0$	$5780A^0$	$5893A^0$
Hexanoate	44.21	43.43	43.25
Heptanoate	45.52	44.76	44.32
Undecyclenate	51.60	50.86	50.63
PBPA	41.43	41.03	40.91
BBPA	43.37	42.94	42.81

4.2.2. Calculation of $\bar{\alpha}$ using bond polarizability data.

Isotropic polarizabilities of the five compounds were also calculated from the data on bond polarizabilities using the principle of additivity of bond polarizabilities (Subramhanyam, 1975; Mukhebi, 1995).

The bond polarizabilities associated with various bonds are found to be reasonably constant for differnt organic compounds and bond polarizability data for $5893A^0$ for various bonds have been reported by Le Fevre (1972) and Subramhanyam *et al* (1975) and these data are given in Appendix II of this thesis. The calculation of isotropic polarizability $\bar{\alpha}$ using the principle of additivity of bond polarizabilities is based on the structural formulae of the

compounds which are shown in Figure 6 of chapter 3. The technique is described below.

According to Subramhanyam and Mukhebi (Mukhebi, 1995), the values of $\bar{\alpha}$ calculated using the principle of additivity of bond polarizabilities are found to be too low as compared with values obtained from refractive index data. This, according to them, is expected because of the conjugated nature of bonds in these molecules. Hence it is assumed that the bonds of the conjugated region, that is, the bonds between and immediately on either side of the two benzene rings have bond polarizabilities equal to those of their equivalent double bonds. This assumption is amply and satisfactorily justified by Mukhebi *et al* (Mukhebi, 1995).

As shown in figure 6 the molecules are made up of two benzene rings linked by three bonds and with the end groups R_1 and R_2 at the outer ends of the rings. For the first three compounds namely hexanoate, heptanoate and undecyclenate, the two benzene rings are joined by an N=N bond while for the last two compounds namely PBPA and BBPA the rings are joined by a C=N bond. For each of the benzene rings mean polarizability value is assumed to be equal to 8.974×10^{-24} cm^3. For all other bonds the actual mean polarizabiility values which are shown in Appendix II are used. The value of $\bar{\alpha}$ for the whole molecule is then the sum of the contributions of the individual bonds and those of the benzene rings. Typical calculations for hexanoate and PBPA are shown in tables 9 and 10 below respectively.

Table 9: Calculation of $\bar{\alpha}$ (in units of 10^{-24} cm^3) for hexanoate using the principle of additivity of bond polarizabilities.

Central rigid portion, C		Left end chain, R_1		Right end chain, R_2	
Bond or Group	$\bar{\alpha}$	Bond	$\bar{\alpha}$	Bond	$\bar{\alpha}$
2(C=O)	2.666	C-O	0.603	C-O	0.603
2(C_6H_4)rings	17.948	2(C-H)	1.346	C=O	1.333
2(C=N)	2.858	C-C	0.497	5(C-C)	2.485
N=N	2.343	3(C-H)	2.019	11(C-H)	7.403
$(\bar{\alpha})_C = 25.815$		$(\bar{\alpha})_{R1} = 4.465$		$(\bar{\alpha})_{R2} = 11.824$	

Therefore, $\bar{\alpha}$ for the whole molecule of hexanoate is the sum of the contributions of the central rigid portion and the end chains.

$$\bar{\alpha} = (25.815 + 4.465 + 11.824) \times 10^{-24} \text{ cm}^3 = 42.10 \times 10^{-24} \text{ cm}^3$$

Table 10: Calculation of $\bar{\alpha}$ (in units of 10^{-24} cm^3) for PBPA using the principle of additivity of bond polarizabilities.

Central rigid portion, C		Left end chain, R_1		Right end chain, R_2	
Bond or Group	$\bar{\alpha}$	Bond	$\bar{\alpha}$	Bond	$\bar{\alpha}$
C=O	1.333	7(C-H)	4.711	11(C-H)	7.403
2(C_6H_4)rings	17.948	2(C-C)	0.994	(C-C)	1.988
2(C=C)	3.360	C=O	0.603		
C-H	0.673				
2(C=N)	2.858				
$(\bar{\alpha})_C = 26.172$		$(\bar{\alpha})_{R1} = 6.308$		$(\bar{\alpha})_{R2} = 9.391$	

Therefore, $\bar{\alpha}$ for the whole molecule of PBPA is the sum of the contributions of the central rigid portion and the end chains.

$$\bar{\alpha} = (26.172 + 6.308 + 9.391) \times 10^{-24} \text{ cm}^3 = 41.87 \times 10^{-24} \text{ cm}^3$$

Following a similar procedure, values of $\bar{\alpha}$ were obtained for the other three compounds namely: heptanoate, undecyclenate and BBPA. Table 11 below shows the calculated values of $\bar{\alpha}$ for all the five compounds.

Table 11: Values of $\bar{\alpha}$ (in units of 10^{-24} cm^3) for the five compounds calculated using the principle of additivity of bond polarizabilities.

Compound	Polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3)			
	Central rigid portion, $(\bar{\alpha})_C$	Left end chain $(\bar{\alpha})_{R1}$	Right end chain, $(\bar{\alpha})_{R2}$	Whole molecule $(\bar{\alpha})_{total}$
Hexanoate	25.815	4.465	11.824	42.10
Heptanoate	25.815	4.465	13.667	43.95
Undecyclenate	25.815	4.465	220.876	51.16
PBPA	26.172	6.308	9.391	41.87
BBPA	26.172	8.151	9.391	43.71

4.2.3. Calculation of $\bar{\alpha}$ from Born's relation.

As mentioned ealier, the calculation of $\bar{\alpha}$ using Vuks' approach is based on Born's relation which is given by equation (2.27) of chapter **2**. From the available refractive index data given in tables **4** to **8** of Ap[pendix **I** and the measured values of the densities shown in tables **3** to **7** of chapter **3**, values of $\bar{\alpha}$ were calculated using Born's relation for each of the five compounds and for the wavelengths for which the birefringence data were available. The results are presented in tables **12**, **13**, **14**, **15** and **16** below.

Table 12: Isotropic polarizability α (in units of 10^{-24} cm^3) in the nematic phase of hexanoate.

Molecular weight = 340.42 gm

$(t_c - t)^0C$	Density, ρ (gm/cm^3)	Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3)			
		5461A⁰	**5780A⁰**	**5893A⁰**	**6563A⁰**
4.0	1.051	44.31	43.54	43.44	N/A
8.0	1.055	44.23	43.57	43.44	N/A
12.5	1.059	44.23	43.50	43.32	42.46
19.5	1.065	44.20	43.50	43.32	42.44
24.0	1.069	44.17	43.50	43.24	42.41
32.0	1.076	44.15	43.47	43.35	42.42
37.0	1.080	44.17	43.45	43.26	42.42
48.5	1.090	44.15	43.44	43.24	42.34
52.5	1.093	44.18	43.39	43.29	42.41

Table 13: Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3) in the nematic phase of heptanoate. (Molecular weight = 354.45 gm).

$(t_c - t)^0C$	Density, ρ (gm/cm^3)	Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3)		
		5461A°	**5780A°**	**5893A°**
4.0	1.046	45.63	44.86	44.49
6.0	1.048	45.62	44.86	44.69
9.0	1.051	45.58	44.85	44.65
13.0	1.055	45.52	44.85	44.61
19.0	1.060	45.53	44.82	44.59
21.5	1.062	45.54	44.83	44.58
25.0	1.065	45.51	44.83	44.57
28.0	1.067	45.57	44.84	44.36
34.0	1.072	45.52	44.82	44.58
39.0	1.076	45.56	44.79	44.62

Table 14: Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3) in the nematic phase of Undecyclenate. (Molecular weight = 408.54 gm).

$(t_c - t)^0C$	Density, ρ (gm/cm^3)	Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3)		
		5461A°	**5780A°**	**5893A°**
2.0	1.042	51.83	51.01	50.76
6.0	1.046	51.66	50.96	50.64
9.5	1.050	51.65	50.93	50.62
14.5	1.055	51.61	50.94	50.66
20.5	1.062	51.53	50.88	50.63
25.0	1.067	51.54	50.83	50.58
30.0	1.072	51.50	50.81	50.61
35.0	1.078	51.47	50.76	50.51
40.0	1.083	51.45	50.71	50.51
44.0	1.086	51.51	50.75	50.48

Table 15: Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3) in the nematic phase of PBPA.

(Molecular weight = 309.45 gm).

$(t_c - t)^0C$	Density, ρ (gm/cm^3)	Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3)			
		4358A°	**5461A°**	**5780A°**	**5893A°**
4.6	1.001	N/A	41.55	41.06	41.01
6.8	1.004	44.26	41.58	41.15	41.04
10.2	1.007	44.30	41.58	41.19	41.07
15.6	1.011	44.30	41.55	41.15	41.04
22.6	1.016	44.26	41.51	41.11	40.99
27.3	1.019	44.24	41.48	41.09	41.00
30.6	1.022	44.18	41.43	41.02	40.92
34.6	1.025	44.15	41.40	41.02	40.90
37.6	1.027	44.11	41.40	40.96	40.87
42.3	1.030	44.11	41.42	40.96	40.87

Table 16: Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3) in the nematic phase of BBPA.

(Molecular weight = 323.48 gm).

$(t_c - t)^0C$	Density, ρ (gm/cm^3)	Isotropic polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3)			
		4358A°	**5461A°**	**5780A°**	**5893A°**
3.2	0.985	N/A	N/A	43.01	42.89
6.0	0.988	46.14	43.40	42.97	42.84
10.9	0.993	46.08	43.36	42.91	42.76
13.5	0.996	45.99	43.29	42.88	42.73
18.0	0.999	46.02	43.26	42.85	42.70
22.5	1.003	45.97	43.20	42.82	42.67
25.9	1.005	45.99	43.19	42.80	42.65
31.4	1.010	45.92	43.09	42.68	42.58
35.0	1.013	45.81	43.05	42.64	42.54

4.3. CALCULATION OF EFFECTIVE AVERAGE POLARIZABILITIES α_e AND α_o IN THE NEMATIC PHASE.

4.3.1. Calculation of α_e and α_o using Neugebauer's approach.

The relevant equations in this approach are equations (2.46) and (2.47) of chapter 2. In order to solve for α_e and α_o, we let the expression;

$$\frac{n_e^2 + 2}{n_e^2 - 1} + 2\left(\frac{n_o^2 + 2}{n_o - 1}\right)$$

in equation (2.46) to be represented by 'x' and the expression $(n_l^2-1)/(n_l^2+2)$ in equation (2.47) be represented by 'y'. Thus, Neugebauer's relations (equation 2.46 & 2.47) may then be written as;

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \left(\frac{4\pi N_{LC}}{3}\right) x \qquad (4.1)$$

and

$$\frac{\alpha_e + 2\alpha_o}{3} = \left(\frac{3}{4\pi N_L}\right) y \qquad (4.2)$$

Multiplying equations (4.1) and (4.2) together yields;

$$\left(\frac{1}{\alpha_e} + \frac{2}{\alpha_o}\right)\left(\frac{\alpha_e + 2\alpha_o}{3}\right) = \left(\frac{N_{LC}}{N_L}\right) xy \qquad (4.3)$$

All symbols have the same meanings as defined in chapter 2. Simplifying equation (4.3) leads tothe expression;

$$2a^2 - (3s - 5)a + 2 = 0 \qquad (4.4)$$

where 'a' = (α_e/α_o) and 's' = (N_{LC}/N_L)xy. Equation (4.4) is quadratic in 'a' and its solutions

are given by;

$$a = \frac{(3s - 5) \pm \sqrt{(3s - 5)^2 - 16}}{4} \qquad (4.5)$$

Since $(\alpha_e / \alpha_o) > 1$ for nematic LCs and in particular the five compounds, then values of 'a' greater than 1 are choosen in equation (4.5) above.

Substituting for $\alpha_e = a\alpha_o$ in equation (4.2) above gives;

$$\alpha_o = \frac{9My}{4\pi N_A \rho_L (a + 2)} \qquad (4.6)$$

Thus, substituting the values of 'a'>1 obtained from equation (4.5) in equation (4.6) gives the values of α_o. The corresponding values of α_e were then calculated from the expression $\alpha_e = a\alpha_o$ and hence isotropic polarizability $\bar{\alpha}$ was calculated using the equation $\bar{\alpha} = (\alpha_e + 2\alpha_o)/3$.

4.3.2. Calculation of α_e and α_o using Vuk's approach.

In this approach, the effective average polarizabilities α_e and α_o were calculated from equations (2.23) and (2.24) respectively of chapter **2**. Isotropic polarizability $\bar{\alpha}$ was then calculated using expression $\bar{\alpha} = (\alpha_e + 2\alpha_o)/3$.

The values of α_e, α_o and $\bar{\alpha}$ calculated from the two approaches, for the five compounds at various temperatures and for different wavelengths are presented in tables **17**, **18**, **19**, **20** and **21** below. The subscripts N and V in α_e, α_o and $\bar{\alpha}$ indicates that they were calculated from Neugebauer's and Vuks' approach respectively. Table **22** below shows the values of $\bar{\alpha}$ calculated from the various approaches namely Lorentz- Lorenz relations, Born's relation, Bond polarizability technique, Neugebauer's and Vuks' approaches for 5893A° for the five compounds for the sake of comparison and discussion.

Tables 17a,17b,17c: Values of $\bar{\alpha}$, α_e and α_o (units of $10^{-24}cm^3$) in the nematic phase of hexanoate for 5461A^0, 5780A^0 and 5893A^0 respectively.

Table 17a : λ = 5461A^0

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.0	38.99	54.51	44.16	37.40	58.09	44.30
8.0	38.30	55.89	44.16	36.71	59.28	44.23
12.5	37.80	56.88	44.16	36.17	60.24	44.20
19.5	37.25	57.99	44.16	35.53	61.50	44.18
24.0	36.96	58.56	44.16	35.17	62.15	44.16
28.5	36.72	59.04	44.16	34.97	61.94	43.96
32.0	36.55	59.37	44.16	34.66	63.11	44.15
37.0	36.29	59.89	44.16	34.39	63.64	44.14
44.5	36.03	60.41	44.16	34.00	64.54	44.18
48.5	35.87	60.75	44.16	33.82	64.79	44.14

Table 17b : λ = 5780A^0

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.0	38.46	53.40	43.44	37.06	56.46	43.53
8.0	37.98	54.37	43.44	36.49	57.68	43.55
12.5	37.52	55.28	43.44	36.96	58.56	43.50
19.5	37.01	56.29	43.44	35.41	59.72	43.51
24.0	36.70	56.92	43.44	35.05	60.38	43.49
28.5	36.47	57.38	43.44	34.77	60.92	43.48
32.0	36.32	57.68	43.44	34.55	61.27	43.46
37.0	36.06	58.19	43.44	34.28	61.73	43.43
44.5	35.80	58.72	43.44	33.89	62.64	43.47
48.5	35.63	59.06	43.44	33.72	62.82	43.42

Table 17c:

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.0	38.47	52.84	43.26	37.02	56.23	43.42
8.0	37.92	53.93	43.26	36.49	57.12	43.37
12.5	37.44	54.89	43.26	35.96	58.01	43.31
19.5	36.86	56.05	43.26	35.54	59.11	43.26
24.0	36.58	56.61	43.26	34.98	59.77	43.25
28.5	36.34	57.10	43.26	34.69	60.40	43.26
32.0	36.17	57.43	43.26	34.48	60.75	43.23
37.0	35.92	57.94	43.26	34.20	61.29	43.23
44.5	35.71	58.35	43.26	33.89	62.10	43.29
48.5	35.54	58.70	43.26	33.72	62.27	43.24

Tables 18a, 18b, 18c: Values of $\bar{\alpha}$, α_e and α_o (units of $10^{-24}cm^3$) in the nematic phase of heptanoate for 5461A^0, 5780A^0 and 5893A^0 respectively.

Table 18a : $\lambda = 5461A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.0	40.68	55.22	45.53	39.36	58.18	45.63
6.0	40.21	56.17	45.53	38.80	59.25	45.62
9.0	39.68	56.23	45.53	38.30	60.14	45.58
13.0	39.28	58.03	45.53	37.75	61.07	45.52
19.0	38.77	59.04	45.53	37.21	62.16	45.53
21.5	38.63	59.33	45.53	37.01	62.59	45.54
25.0	38.42	59.75	45.53	36.69	63.16	45.51
28.0	38.28	60.03	45.53	36.47	63.76	45.57
34.0	37.99	60.60	45.53	36.15	64.27	42.52
39.0	37.78	61.03	45.53	35.84	65.00	45.56

Table 18b : $\lambda = 5780A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.0	40.29	53.74	44.77	38.97	56.65	44.86
6.0	39.85	54.62	44.77	38.59	57.40	44.86
9.0	39.44	55.43	44.77	38.08	58.39	44.85
13.0	39.05	56.21	44.77	37.59	59.37	44.85
19.0	38.56	57.19	44.77	36.98	60.50	44.82
21.5	38.41	57.50	44.77	36.78	60.93	44.83
25.0	38.17	57.98	44.77	36.54	61.39	44.83
28.0	38.06	59.19	44.77	36.35	61.82	44.84
34.0	37.73	58.85	44.77	36.01	62.42	44.82
39.0	37.52	59.27	44.77	35.73	62.91	44.79

Table 18c : $\lambda = 5893A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.0	40.14	53.46	44.58	38.95	55.56	44.49
6.0	39.81	54.11	44.58	38.49	57.10	44.69
9.0	39.30	55.13	44.58	37.98	58.00	44.65
13.0	38.86	56.02	44.58	37.51	58.82	44.61
19.0	38.40	56.94	44.58	36.91	59.95	44.59
21.5	38.22	57.29	44.58	36.72	60.29	44.58
25.0	38.02	57.69	44.58	36.48	60.76	44.57
28.0	37.89	57.97	44.58	36.36	60.30	44.34
34.0	37.64	58.47	44.58	35.94	61.88	44.58
39.0	37.48	58.78	44.58	35.70	62.59	44.66

Tables 19a, 19b, 19c: Values of $\bar{\alpha}$, α_e and α_o (in units of $10^{-24}cm^3$) in the nematic phase of undecyclenate for 5461A^0, 5780A^0 and 5893A^0 respectively.

Table 19a : $\lambda = 5461A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
2.0	47.22	60.37	51.60	45.65	64.19	51.83
6.0	45.92	62.99	51.61	44.42	66.14	51.66
9.5	45.27	64.29	51.61	43.76	67.42	51.65
14.5	44.59	65.64	51.61	43.05	68.73	51.61
20.5	44.04	66.74	51.61	42.36	69.86	51.53
25.0	43.76	67.30	51.61	42.05	70.53	51.54
30.0	43.35	68.12	51.61	41.57	71.36	51.50
35.0	43.04	68.74	51.61	41.23	71.94	51.47
40.0	42.78	69.26	51.61	40.86	72.63	51.45
44.0	42.66	69.50	51.61	40.66	73.21	51.51

Table 19b : $\lambda = 5780A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
2.0	46.51	59.58	50.87	45.17	62.70	51.01
6.0	45.55	61.51	50.87	44.09	64.71	50.96
9.5	44.96	62.69	50.87	43.45	65.88	50.93
14.5	44.41	63.78	50.87	42.82	67.17	50.94
20.5	43.81	64.99	50.87	42.22	68.18	50.88
25.0	43.45	65.65	50.86	41.85	68.79	50.83
30.0	43.14	66.32	50.87	41.46	69.49	50.81
35.0	42.81	66.99	50.87	41.14	70.00	50.76
40.0	42.53	67.55	50.87	40.77	70.59	50.75
44.0	42.32	67.96	50.87	40.58	71.08	50.75

Table 19c : $\lambda = 5893A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
2.0	46.41	59.11	50.64	45.06	62.15	50.76
6.0	45.25	61.43	50.64	44.02	63.86	50.63
9.5	44.70	62.54	50.64	43.37	65.14	50.62
14.5	44.06	63.81	50.64	42.73	66.52	50.66
20.5	43.65	64.63	50.64	42.12	67.64	50.63
25.0	43.35	65.23	50.64	41.75	68.25	50.58
30.0	43.04	65.85	50.64	41.45	68.93	50.61
35.0	42.70	66.51	50.64	41.04	69.46	50.51
40.0	42.49	66.95	50.64	40.75	70.03	50.51
44.0	42.27	67.39	50.64	40.50	70.46	50.48

Tables 20a, 20b, 20c, 20d: Values of $\bar{\alpha}$, α_e and α_o (in units of $10^{-24}cm^3$) in the nematic phase of PBPA for $4358A^0$, $5461A^0$, $5780A^0$ and $5893A^0$ respectively.

Table 20a : $\lambda = 4358A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
6.8	39.69	52.61	44.00	37.87	57.04	44.26
10.2	39.16	53.68	44.00	37.19	58.51	44.30
15.6	38.53	54.93	44.00	36.48	59.92	44.29
22.6	37.98	56.03	44.00	35.90	60.98	44.26
27.3	37.69	56.60	44.00	35.58	61.56	44.24
30.6	37.43	57.14	44.00	35.37	61.79	44.18
34.6	37.21	57.57	44.00	35.14	62.18	44.15
37.6	37.03	57.94	44.00	34.97	62.39	44.11
42.3	36.83	58.32	44.00	34.73	62.86	44.11

Table 20b : $\lambda = 5461A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.6	38.33	47.67	41.44	37.19	50.28	41.55
6.8	37.96	48.42	41.44	36.67	51.40	41.58
10.2	37.45	49.44	41.44	36.10	52.54	41.58
15.6	36.94	50.45	41.44	35.57	53.53	41.55
22.6	36.47	51.43	41.44	35.08	54.36	41.51
27.3	36.15	52.03	41.44	34.77	54.87	41.47
30.6	35.98	52.38	41.44	34.64	55.03	41.43
34.6	35.75	52.83	41.44	34.42	55.38	41.40
37.6	35.67	52.99	41.44	34.32	55.56	41.40
42.3	35.57	53.18	41.44	34.15	55.94	41.42

Table 20c : $\lambda = 5780A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.6	37.86	47.39	41.04	36.99	49.21	41.06
6.8	37.71	47.68	41.04	36.53	50.39	41.15
10.2	37.28	48.55	41.04	35.94	51.69	41.19
15.6	36.67	49.76	41.04	35.34	52.78	41.15
22.6	36.18	50.74	41.04	34.85	53.62	41.12
27.3	35.97	51.17	41.04	34.62	54.03	41.09
30.6	35.69	51.73	41.04	34.42	54.21	41.02
34.6	35.57	51.97	41.04	34.27	54.52	41.02
37.6	35.37	52.38	41.04	34.11	54.67	40.96
42.3	35.25	52.61	41.04	33.96	54.98	40.96

Table 20d : λ = 5893A^0

$(t_c - t)^0$C	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
4.6	37.96	46.83	40.92	36.93	49.15	41.01
6.8	37.60	47.56	40.92	36.42	50.28	41.04
10.2	37.24	48.29	40.92	35.91	51.40	41.07
15.6	36.63	49.51	40.92	35.31	52.49	41.04
22.6	36.13	50.49	40.92	34.82	53.33	40.99
27.3	35.95	50.86	40.92	34.58	53.82	41.00
30.6	35.66	51.43	40.92	34.38	54.00	40.92
34.6	35.52	51.72	40.92	34.24	54.23	40.90
37.6	35.34	52.08	40.92	34.07	54.46	40.87
42.3	35.22	52.31	40.92	33.92	54.77	40.87

Tables 21a, 21b, 21c, 21d: Values of $\bar{\alpha}$, α_e and α_o (in units of 10^{-24}cm^3) in the nematic phase of PBPA for 4358A^0, 5461A^0, 5780A^0 and 5893A^o respectively.

Table 21a : λ = 4358A^0

$(t_c - t)^0$C	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
6.0	41.06	55.98	46.03	39.53	59.35	46.14
10.9	40.10	57.90	46.03	38.47	61.30	46.08
13.5	39.69	58.73	46.04	37.99	61.97	45.99
18.0	39.27	59.55	46.03	37.55	62.95	46.02
22.5	38.92	60.26	46.03	37.17	63.58	45.97
25.9	38.78	60. 53	46.03	36.96	64.07	46.99
31.4	38.25	61.61	46.04	36.62	64.52	45.92
35.0	38.02	62.06	46.03	36.26	64.91	45.81

Table 21b : $\lambda = 5461A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
6.0	39.36	51.41	43.38	38.34	53.53	43.40
10.9	38.57	52.99	43.38	37.45	55.19	43.36
13.5	38.13	53.88	43.38	37.05	55.77	43.29
18.0	37.76	54.61	43.38	36.64	56.51	43.26
22.5	37.46	55.22	43.38	36.36	56.89	43.20
25.9	37.29	55.55	43.38	36.17	57.22	43.19
31.4	36.92	56.30	43.38	35.86	57.54	43.09
35.0	36.76	56.63	43.38	35.72	57.71	43.05

Table 21c : $\lambda = 5780A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
3.2	39.76	49.33	42.95	38.77	51.48	42.01
6.0	39.07	50.71	42.95	38.09	52.72	42.97
10.9	38.24	52.36	42.95	37.21	54.30	42.91
13.5	37.92	52.99	42.95	36.89	54.86	42.88
18.0	37.56	53.73	42.95	36.47	55.61	42.85
22.5	37.28	54.29	42.95	36.19	56.08	42.82
25.9	37.11	54.62	42.95	36.00	56.41	42.80
31.4	36.71	55.42	42.95	35.70	56.65	42.68
35.0	36.55	55.75	42.95	35.55	56.81	42.64

Table 21d : $\lambda = 5893A^0$

$(t_c - t)^0C$	Polarizabilities (in units of 10^{-24} cm^3)					
	Neugebauer's approach			Vuks' approach		
	$(\alpha_o)_N$	$(\alpha_e)_N$	$(\bar{\alpha})_N$	$(\alpha_o)_V$	$(\alpha_e)_V$	$(\bar{\alpha})_V$
3.2	39.63	49.20	42.82	38.65	51.36	42.89
6.0	38.94	50.58	42.82	37.96	52.60	42.84
10.9	38.26	51.95	42.82	37.19	53.91	42.76
13.5	37.83	52.80	42.82	36.86	54.46	42.73
18.0	37.47	53.53	42.82	36.45	55.21	42.70
22.5	37.19	54.09	42.82	36.16	55.68	42.67
25.9	37.03	54.42	42.82	35.97	56.01	42.65
31.4	36.68	55.12	42.82	35.65	56.43	42.58
35.0	36.62	55.44	42.82	35.51	56.59	42.54

Tables 22: Values of $\bar{\alpha}$ (in units of $10^{-24}cm^3$) for $5893A^o$ for the five compounds calculated from various methods.

Compound	Polarizability $\bar{\alpha}$ (in units of 10^{-24} cm^3)				
	L-L's relation*	Neugebaur's approach	Born's relation+	Vuks' approach+	Bond polariza-bility techn.
Hexanoate	43.25	43.25	43.28	43.28	42.10
Heptanoate	44.32	44.32	44.58	44.58	43.95
Undecyclenate	50.63	50.63	50.60	50.60	51.16
PBPA	40.91	40.91	40.97	40.97	41.87
BBPA	42.81	42.81	42.71	42.71	43.71

+ Value of $\bar{\alpha}$ is the average value for all the temperatures.

* Lorentz-Lorenz relation.

4.4. DISCUSSION CONCERNING $\bar{\alpha}$ CALCULATED USING THE VARIOUS METHODS AND THE RELATIVE MERITS OF NEUGEBAUER'S AND VUKS' APPROACHES

4.4.1. Born's relation and Lorentz - Lorenz relation.

Before presenting the discussion, it is improtant to state that $\bar{\alpha}$ value for a given compound at a given wavelength should be independent of temperature. In the calculation of α_e and α_o at various temperatures in the crystalline phase using Neugebauer's approach, use is made of the α value obtained from Lorentz-Lorenz relation. Therefore, as is evident from tables **17**, **18**, **19**, **20** and **21** above, $\bar{\alpha}$ value obtained from Neugebauer's approach is a constant over all temperatures for a given wavelength and for a given compound. Also the α value obtained from Born's relation is the same as that obtained from Vuks' approach for each of the five compounds (see table **22** above). This is because, as shown in Appendix **IV** Born's relation follows automatically from Vuks' formulae owing to the very nature of the assumptions made therein.

Thus , it would appear from the same table that it is immaterial whether one uses Lorentz-Lorenz relation or Born's relation to calculate $\bar{\alpha}$ as the two resulting values are practically the same. However, this observation is deceptive. The isotropic polarizability $\bar{\alpha}$ is a property of a compound in its liquid phase and hence depends only on the refractive index n_l and the concentration N_l of the compound in its liquid phase. Consequently, it should not be calculated from α_e and α_o as is done in Born's relation. Therefore, the application of Lorentz-Lorenz relation which makes use of the density and refractive index values in the liquid phase of the compound appears more meaningful, physically plausible and broad based. This is clearly a merit of Neugebauer's approach over Vuks' as Neugebauer's approach uses the same value of $\bar{\alpha}$ for all the temperatures in the liquid crystalline phase (see tables **17** to **22**).

From the same tables, it is also evident that $\bar{\alpha}$ value calculated from Vuks' approach shows a steady decrease. Since this discrepancy is a common feature for all the five compounds, it can not be attributed to any inaccuracy in the experimental measurement of refractive indices and densities of the compounds. This steady decrease in $\bar{\alpha}$ values calculated from Vuks' approach in contrast to the constancy of $\bar{\alpha}$ values obtained using Neugebauer's approach is clearly a drawback of Vuks' approach.

Born's relation can also be written as

$$N\,\bar{\alpha} = \bar{\chi} = \frac{3}{4\pi}\left(\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right) \qquad (4.8)$$

where $\bar{\chi}$ is the mean susceptibility of the molecule.

There are two merits of writting Born's relation in this form. One is that the mean susceptibility can be calculated even if the density and refractive index data in the isotropic phase are not available. Secondly, as the electronic structure of the molecules do not alter with change of phase of the organic compounds, Born's relation in this form can be used to verify that the mean susceptibility does not alter with change of phase or of temperature. Owing to these two merits of Born's relation, it may be argued that Vuks' approach which is based on Born's relation has an edge over Neugebauer's approach in this regard. However, such an argiment can also be proved to be baseless because Born's relation can also be derived from Neugebauer's relations without making any drastic assumptions (see Appendix **V**).

Thus, even from the above point of view, Neugebauer's approach has an edge over Vuks' approach. In fact Neugebauer's approach clearly shows that Born's relation is less relevant for use in such calculations as compared to Lorentz-Lorenz relation.

4.5. CALCULATION OF OPTICAL ANISOTROPY, $\Delta\alpha$.

4.5.1. Introduction.

Optical anisotropy is the difference between $\alpha_{\parallel}$ the polarizability parallel and $\alpha_{\perp}$ the polarizability perpendicular to the molecular axis. The importance and significance of $\Delta\alpha$ cannot be overemphasized and though it may not be necessary at this stage to narrate the scope and utility of $\Delta\alpha$, it is important to indicate that $\Delta\alpha$ is directly related to the orientational order parameter 'S' of liquid crystal compounds particularly in the nematic phase. This relationship between '$\Delta\alpha$' and 'S' will be discussed in the subsequent section.

It is therefore necessary to determine $\Delta\alpha$ for all the five compounds as the intention is to calculate the orientational order parameter of the compounds at various temperatures and for different wavelengths eventually. The most reliable method for the calculation of $\Delta\alpha$ is the direct method based on the birefringence and density data of the compounds. The details of this method of calculation of $\Delta\alpha$ are discussed in the next section.

4.5.2. Calculation of $\Delta\alpha$ from density and refractive index data in the crystalline phase.

It is possible to calculate $\Delta\alpha$ directly from the index and density data in the crystalline phase using Neugebauer's and Vuks' approaches. In this case use is made of the values of the indices n_g, n_m and n_p and the measured values of the crystal density ρ_c of a given compound to directly calculate the polarizabilities $\alpha_{\parallel}, \alpha_{\perp}$ and hence optical anisotropy $\Delta\alpha$ using expressions associated with each of the two approaches. The details of these calculations are discussed in the following subsections.

4.5.2.1. Calculation of $\Delta\alpha$ using Neugebauer's approach.

The relevant expressions are equations (2.53) and (2.55) of chapter **2**. By substituting the respective values of the indices n_g, n_m, n_p and n_l from tables **1** to **8** of Appendix **I** and the densities ρ_c and ρ_l from **2** to **7** of chapter **3**, the above two equations were solved simultaneously to obtain the values of $(\alpha_l)_N$ and $(\alpha_\perp)_N$ and hence $(\Delta\alpha)_N$ [$= (\alpha_l)_N - (\alpha_\perp)_N$]for various wavelengths and for each of the three compounds whose index data in the crystalline phase are available. The calculated values of $(\Delta\alpha)_N$ for the three compounds : hexanoate , heptanoate and undecyclenate are presented in tables **23**, **24** and **25** below.

4.5.2.2. Calculation of $\Delta\alpha$ using Vuks' approach.

The relevant expressions are equations (2.21) and (2.2) of chapter **2**. By direct substitution of the values of the indices n_g, n_m and n_p from tables **1** and **3** of Appendix 1 and crystalline density ρ_c from table **1** of chapter **3**, the values of $(\alpha_l)_V$ and $(\alpha_\perp)_V$ and hence $(\Delta\alpha)_v$ [$= (\alpha_l)_v - (\alpha_\perp)_v$] were calculated for various wavelengths and for each of the three compounds above. The results are presented in tables **23**, **24** and **25** below.

Table 23: $\alpha_{\parallel}$, $\alpha_{\perp}$ **and** $\Delta\alpha$ **values (in units of** 10^{-24} cm^3**) calculated from the density and refractive index data in the crystalline phase of hexanoate.**

Wavelength (A^0)	Polarizabilities (in units of 10^{-24} cm^3)					
	$(\alpha_{\parallel})_N$	$(\alpha_{\perp})_N$	$(\Delta\alpha)_N$	$(\alpha_{\parallel})_V$	$(\alpha_{\perp})_V$	$(\Delta\alpha)_v$
5461	66.75	32.87	33.88	73.33	29.66	43.67
5780	64.87	32.72	32.15	71.27	29.68	41.59
5893	64.59	32.59	32.00	70.53	29.65	40.88
$(\Delta\alpha)_{NMR}$*			31.78			39.79

Table 24: $\alpha_{\parallel}$, $\alpha_{\perp}$ **and** $\Delta\alpha$ **values (in units of** 10^{-24} cm^3**) calculated from the density and refractive index data in the crystalline phase of undecyclenate.**

Wavelength (A^0)	Polarizabilities (in units of 10^{-24} cm^3)					
	$(\alpha_{\parallel})_N$	$(\alpha_{\perp})_N$	$(\Delta\alpha)_N$	$(\alpha_{\parallel})_V$	$(\alpha_{\perp})_V$	$(\Delta\alpha)_v$
5461	77.13	38.84	38.29	80.52	36.38	44.14
5780	75.06	38.77	36.29	77.59	36.44	44.15
5893	74.51	38.71	35.80	76.98	36.44	40.54
$(\Delta\alpha)_{NMR}$*			35.10			42.86

* the average value of $(\Delta\alpha)$ values calculated from NMR data. The details of the calculations are discussed in section **4.5.3.** below.

Table 25: $\alpha_{\parallel}$, $\alpha_{\perp}$ **and** $\Delta\alpha$ **values (in units of** 10^{-24} cm^3**) calculated from the density and refractive index data in the crystalline phase of heptanoate.**

Wavelength (A^0)	Polarizabilities (in units of 10^{-24} cm^3)					
	$(\alpha_{\parallel})_N$	$(\alpha_{\perp})_N$	$(\Delta\alpha)_N$	$(\alpha_{\parallel})_V$	$(\alpha_{\perp})_V$	$(\Delta\alpha)_v$
5461	67.80	34.39	33.41	72.84	31.57	41.27
5780	65.66	34.33	31.33	70.20	31.75	38.45
5893	65.11	34.32	30.79	69.60	31.79	37.81

As the refractive index in the crystalline phase of the last two compounds, PBPA and BBPA were not available, it was not possible to calculate $\alpha_{\parallel}$, $\alpha_{\perp}$ and $\Delta\alpha$ values for these two

compounds directly as in the case of the first three compounds. However, alternative methods for the calculation of $\Delta\alpha$ for these two compounds were explored. The same method was later applied for the first three compounds as well. One such method is the use of 'S' values from any other source such as Nuclear Magnetic Resonance (NMR) Spectroscopy. The details of calculation of $\Delta\alpha$ using 'S' data from NMR and the results of the calculation are presented in the next section.

4.5.3 Calculation of $\Delta\alpha$ using 'S' data from NMR studies,

By definition, orientational order parameter 'S' is related to the polarizabilities in the nematic and crystalline phases by the expression:

$$S = \frac{(\alpha_e - \alpha_o)}{(\alpha_{\parallel} - \alpha_{\perp})} = \frac{(\alpha_e - \alpha_o)}{\Delta\alpha} \qquad (4.8)$$

which gives $\Delta\alpha$ as;

$$\Delta\alpha = \frac{(\alpha_e - \alpha_o)}{S} \qquad (4.9)$$

If values of 'S' are available from other sources such as NMR studies and Raman band analysis they may be used to calculate $\Delta\alpha$. For the two approaches; Vuks' and Neugebauer's the expressions are;

$$(\Delta\alpha)_{N,V} = \frac{(\alpha_e - \alpha_o)_{N,V}}{S_{NMR}} \qquad (4.10)$$

where the subscripts N and V indicate that the respective quantities were calculated using Neugebauer's and Vuks' approaches respectively. S_{NMR} is the values of 'S' obtained from NMR studies. Since $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_v$ are different at a given temperature, then $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ are also different.

Watkins and Johnson (1981) have reported the values of 'S' at various temperatures

for two of the compounds namely hexanoate and undecyclenate using NMR spectroscopy. The data are presented in tables 1 and 2 of Appendix IV. By substituting these data in equation (4.10) above, values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ were calculated for these compounds and the results are presented in tables 26 and 27 below.

Table 26: $(\Delta\alpha)$ values (in units of 10^{-24} cm ^{3}) for hexanoate for 5893A^0

$(t_c-t)^0C$	S_{NMR}	$(\alpha_e-\alpha_o)_N$	$(\Delta\alpha)_N$	$(\alpha_e-\alpha_o)_V$	$(\Delta\alpha)_V$
4.0	0.471	14.37	30.51	19.22	40.80
8.0	0.500	16.00	32.00	20.63	41.27
12.5	0.540	17.45	32.31	22.04	40.82
19.5	0.600	19.18	32.00	23.77	39.61
24.0	0.620	20.03	32.31	24.79	39.98
28.5	0.650	20.76	31.94	25.70	39.54
32.0	0.665	21.26	31.97	26.27	39.51
37.0	0.690	22.02	31.93	27.09	39.26
44.5	0.720	22.64	31.44	28.21	39.18
48.5	0.740	23.16	31.30	28.56	38.59

Table 27: $(\Delta\alpha)$ values (in units of 10^{-24} cm ^{3}) for undecyclenate for 5893A^0

$(t_c-t)^0C$	S_{NMR}	$(\alpha_e-\alpha_o)_N$	$(\Delta\alpha)_N$	$(\alpha_e-\alpha_o)_V$	$(\Delta\alpha)_V$
2.0	0.370	12.70	34.32	17.09	46.19
6.0	0.450	16.17	35.93	19.84	44.09
9.5	0.505	17.84	35.33	21.79	43.11
14.5	0.553	19.74	35.70	23.91	43.02
20.5	0.600	20.98	34.97	25.54	42.57
25.0	0.630	21.87	34.71	26.50	42.06
30.0	0.653	22.82	34.93	27.46	42.09
35.0	0.680	23.80	35.00	28.43	41.80
40.0	0.700	24.46	34.94	29.27	41.82
44.0	0.715	25.12	35.13	29.96	41.90

The average values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ are 31.78 x 10^{-24} cm^3 and 39.79 x 10^{-24} cm^3 respectively while those of undecyclenate are 35.10 x 10^{-24} cm^3 and 42.86 x 10^{-24} cm^3 respectively. These are the average values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ which have been shown in tables **23** and **24** above for comparison purposes.

As 'S' data from NMR studies were not available for heptanoate, PBPA and BBPA, the method discussed in section **4.5.3** for calculating $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ could not be used for these three compounds. However, "S' data from NMR studies are available for MBBA which is homologous with PBPA and BBPA (see figure **6** of chapter **3**). The refractive index and density data for MBBA have been reported by Germain (1980). These data were used to calculate $(\alpha_e-\alpha_o)_N$ and $(\alpha_e-\alpha_o)_V$ using the method described in section **4.3.1** and **4.3.2** of this chapter. In addition, 'S' data from NMR studies of MBBA have also been reported at some temperatures (Rose, 1983) at which values of $(\alpha_e-\alpha_o)_N$ and $(\alpha_e-\alpha_o)_V$ have been calculated for this compound.

Using these data and 'S' data from NMR, values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ for MBBA were evaluated using equations (4.15) and (4.16) of this chapter. The results are presented along with 'S' data from NMR studies in table **28** below. In later sections a discussion has been presented on how these values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ of MBBA were used to calculate $(\Delta\alpha)$ values of PBPA and BBPA.

Table 28: $\Delta\alpha$ values (in units of 10^{-24} cm^3) of MBBA for 5893A^0 calculated using S_{NMR} data.

$(t_c-t)^0C$	Rose's S_{NMR} values	Neugebauer's approach		Vuks' approach	
		$(\alpha_e-\alpha_o)_N$	$(\Delta\alpha)_N$	$(\alpha_e-\alpha_o)_V$	$(\Delta\alpha)_V$
11.0	0.552	11.63	22.28	13.62	26.09
14.0	0.544	12.15	22.33	14.40	26.47
17.0	0.561	12.46	22.21	15.03	26.79
20.0	0.571	12.87	22.54	15.58	27.28

Another method for the calculation of $(\Delta\alpha)$ values of these compounds is based on the structural formulae of the compounds. The details of this method are discussed in section **4.5.4** below.

4.5.4. Calculation of $\Delta\alpha$ using bond polarizability technique.

4.5.4.1. Introduction.

The bond polarizability technique was developed by Subramhanyam and Mukhebi (Mukhebi, 1995) and it is useful when neither the data on "S' factors nor refractive index in the crystalline phase are available. The procedure, which is discussed below, is based on the knowledge of the bond lengths and the bond polarizabilities of the various bonds constituting a molecule.

In order to evaluate α_l, the polarizability parallel to the molecular axis, it is assumed that the molecular axis is along the line joining the centres of the two aromatic rings and that it is rigid. Figure 9 below shows a sketch (not drawn to scale) of the molecular structure of hexanoate as a typical example of the planar trans-conformational configuration, showing the molecular axis and the various angles on which the calculation of α_l, $\alpha_\perp$ and hence $\Delta\alpha$ were based.

Based on this configuration and the assumption made above, the effective polarizability $(\alpha_l)_{eff.}$ parallel to the molecular axis due to each bond is then given by;

$$(\alpha_{\parallel})_{eff} = \alpha_l \cos^2\theta + \alpha_t \sin^2\theta \qquad (4.11)$$

where θ is the angle the bond makes with the molecular axis, α_l and α_t are respectively the longitudinal and transverse components of $\bar{\alpha}$ the isotropic polarizability for each of the bonds.

For C-H bonds in whatever region of the molecule, the effective bond polarizability $(\alpha_l)_{eff}$ is assumed to be equal to its isotropic bond polarizability along all directions with respect to the molecular axis. However, for the aromatic benzene rings $(C_6H_4)_{ring}$, $(\alpha_l)_{ring}$ is calculated from the expression;

$$(\alpha_{\parallel})_{ring} = \alpha_1 \cos^2\theta_1 + \alpha_2 \cos^2\theta_2 + \alpha_3 \cos^2\theta_3 \qquad (4.12)$$

where α_1 and α_2 are the principal polarizabilities of the ring along the two directions perpendicular to one another in the plane of the ring and α_3 is the principal polarizability perpendicular to the plane of the ring. θ_1, θ_2 and θ_3 are respectively the angles made by the principal polarizability directions with the molecular axis. The values of α_1, α_2 and α_3 are 10.670, 11.110 and 5.142 respectively (Rao *et al*, 1970). Further, it is assumed that both rings lie in the plane of the molecule and therefore $\theta_3 = 90^0$ and thus the third term in equation (4.12)

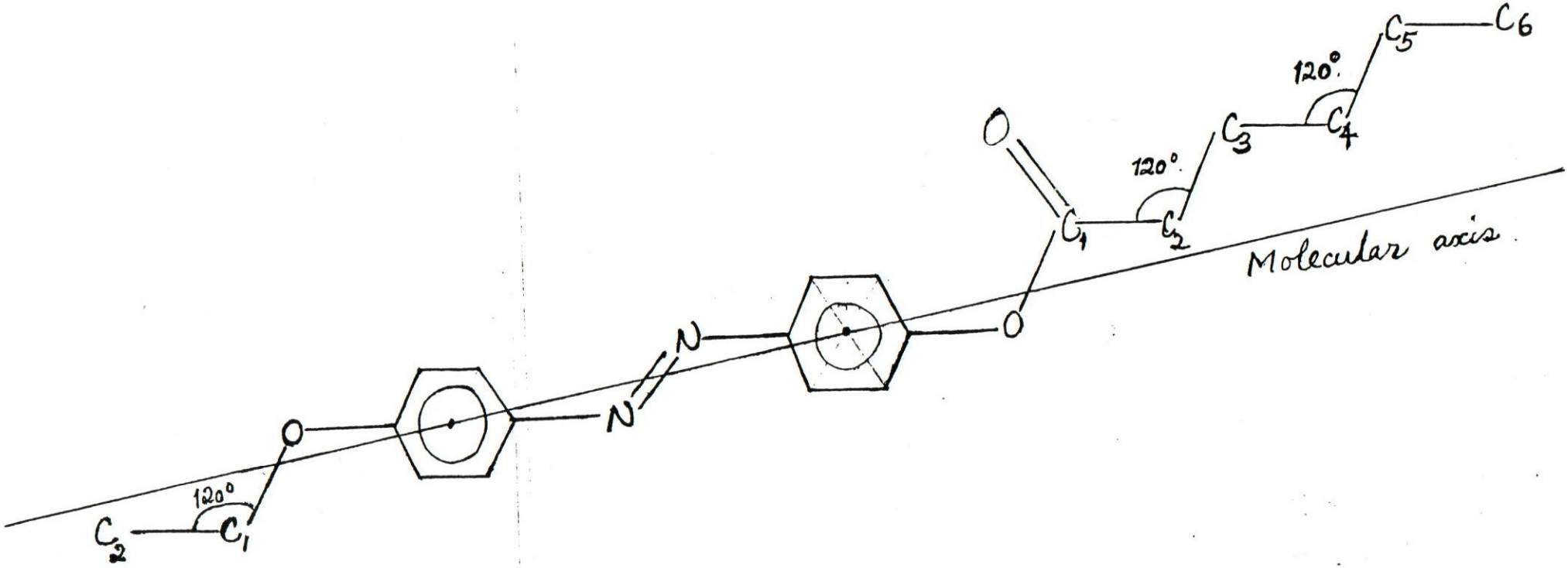


Figure 9: Structure of p-(p-ethoxyphenylazo) phenylhexanoate. The addition of an even-numbered carbon atom in the preferred trans-conformation is along the major molecular axis. This is not the case for an odd-numbered carbon atom.

vanishes. This assumption is justified because the calculation is based on a planar trans-conformation of the structure (see figure 9 above). Equation (4.12) then reduces to;

$$(\alpha_{\parallel})_{ring} = \alpha_1 \cos^2\theta_1 + \alpha_2 \cos^2\theta_2 \qquad (4.13)$$

The structures of the nematic homologues are composed of three namely;

(i) the left end chain,

(ii) the central rigid portion including the bonds in the conjugated region. This region is made up of the two benzene rings, all the bonds between them and those immediately on either side of the benzene rings and

(iii) the right end chain.

The molecular structures of these homologues have not been determined. For simplicity and uniformity, bond angles are assumed to be 120^0 except for the bonds involving tetrahedral linkages. Standard values of bond lengths and polarizabilities are shown in appendix **II**. The angles made by the bonds with the molecular axis for each homologue were determined by drawing to scale a large diagram of the molecule. Owing to the three different portions making up each molecule, the calculation of α_l for each portion is discussed below under two separate headings.

4.5.4.2. Calculation of $(\alpha_l)_{eff}$ for the end chains.

For the C-H bonds in the chains and in the conjugated region, $(\alpha_l)_{eff}$ is assumed to be equal to the isotropic polarizability. For all other bonds in the left and right end chains, $(\alpha_l)_{eff}$ is calculated using equation (4.11) of this chapter.

4.5.4.3. Calculation of $(\alpha_l)_{eff}$ for the central rigid portion.

The effective polarizability $(\alpha_l)_{ring}$ for each aromatic ring is calculated using equation (4.13) above. However, for bonds in the conjugated region, other than C-H bonds, α_t in equation (4.12) above is assumed to be equal to zero. Since $\alpha_l + 2\alpha_t = 3\alpha$, equation (4.12) reduces to;

$$(\alpha_{\parallel})_{eff} = 3\bar{\alpha}\cos^2\theta \qquad (4.14)$$

where α is the isotropic polarizability of the equivalent double bond. The justification for the

assumption that α_t is zero for the bonds in the conjugated region was given by Subramhanyam (Subramhanyam, 1977).

4.5.4.4. Calculation of $\alpha_\perp$ and $\Delta\alpha$.

$\alpha_\parallel$ and $\alpha_\perp$ are related to the isotropic polarizability $\bar{\alpha}$ by the expression $\bar{\alpha} = (\alpha_\parallel + 2\alpha_\perp)/3$ which gives;

$$\alpha_\perp = \frac{(3\bar{\alpha} - \alpha_\parallel)}{2} \qquad (4.15)$$

The values of $\bar{\alpha}$ have already been calculated for all homologues (see table **8** of chapter **4**). Using these values and those of $\alpha_\parallel$ evaluated from bond polarizability technique, the corresponding values of $\alpha_\perp$ were calculated for each compound. Optical anisotropy $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ was thus evaluated for each of the five compounds including valerate which is homologous with the first three compounds and MBBA which is homologous with the last two compounds. The results of these calculations are presented in table **29** below. The details of the calculations for individual compounds are not given because the general procedure has been described in detail. The purpose of calculating $\Delta\alpha$ by this procedure and of presenting the calculated values of $\Delta\alpha$ for valerate and MBBA will be discussed in later sections.

4.6. Discussion concerning the calculated values of $\alpha_\parallel$, $\alpha_\perp$ and $\Delta\alpha$.

The calculated values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ at various temperatures for 5893A^0 for hexanoate, undecyclenate and MBBA, based on 'S' data from NMR studies are given in tables **26**, **27** and **28** above respectively. Irrespective of the approach used, values of $\Delta\alpha$ should be constant over all temperatures for a given wavelength and compound. As can be seen from these tables, constancy of $\Delta\alpha$ values is much better for Neugebauer's approach. This is true because $(\Delta\alpha)_N$ values show slight positive and negative deviations from the mean value with increase in $(t_c\text{-}t)$ whereas $(\Delta\alpha)_V$ values steadily decreases for hexanoate and undecyclenate and steadily increases for MBBA as $(t_c\text{-}t)$ increases.

Table 29: Values $\bar{\alpha}$, $\alpha_{\parallel}$, $\alpha_{\perp}$ and $\Delta\alpha$ (in units of 10^{-24} cm^3) for the five homologues, MBBA and Valerate calculated using the bond polarizability technique.

Compound	Polarizabilities (in units of 10^{-24} cm^3)			
	$\bar{\alpha}$	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$
Hexanoate	42.10	57.69	34.31	23.38
Heptanoate	43.95	59.36	36.24	23.13
Undecyclenate	51.16	66.96	43.74	23.22
PBPA	41.87	59.86	32.88	26.98
BBPA	43.71	62.15	34.49	27.66
MBBA	36.34	53.37	27.83	25.54
Valerate	40.26	55.39	32.70	22.69

Secondly, the $(\Delta\bar{\alpha})_N$ values calculated directly from Neugebauer's approach for the largest wavelength available (5893A^0) for hexanoate and undecyclenate are 32.00 x 10^{-24} cm^3 and 35.80 x 10^{-24} cm^3 respectively whereas the corresponding values calculated from 'S' data from NMR are 31.78 x 10^{-24} cm^3 and 35.10 x 10^{-24} cm^3 respectively. The agreement between the two sets of values is within two percent for each compound. The $(\Delta\alpha)_V$ values for the two compounds from Vuks' approach are respectively 40.88 x 10^{-24} cm^3 and 40.54 x 10^{-24} cm^3 whereas the corresponding values from 'S' data from NMR are 39.79 x 10^{-24} cm^3 and 42.86 x 10^{-24} cm^3 respectively. Thus, the disagreement is much more in Vuks' than in Neugebauer's approach.

Concerning $(\Delta\alpha)$ values calculated from the bond polarizability technique, it can be seen from column **5** of table **29** that at least for the first three compounds , the values are very different from the corresponding values calculated from the direct and the NMR-based approaches. However, the difference is not so pronounced for MBBA as is evident from table **21**. In fact Maghanga (1995) calculated $(\Delta\alpha)$ values using the bond polarizability technique for a number of nematic compounds and compared these values with those obtained using the direct approach, i.e., from refractive index data in the crystalline phase. Mukhebi (1995) made a similar study for smectic liquid crystalline compounds. From their results, it emerged that agreement is excellent in some cases but unsatisfactory in other cases. This enigmatic behaviour must be ascribed most probably to deviations from the perfect parallelism in the arrangement of molecules in the crystalline phase. A satisfactory theory is yet to be worked

out. However, whether the arrangement is perfectly parallel or not, the contribution from the end chains to $\Delta\alpha$ should be independent of the degree of perfection in alignment.

Therefore, though the absolute values of $\Delta\alpha$ obtained from the bond polarizability technique may not be accurate, the difference in $\Delta\alpha$ values at least between members of a homologous series, i.e., arising due to the changes in the composition of the end chains only should be accurate. In fact as will be discussed in subsequent sections, this is the utility of table **29**.

4.7. Calculation of orientational order parameter 'S'.

4.7.1. Introduction.

The importance and significance of orientational order parameter need not be over emphasized. The order parameter is a constant at a given temperature and for a given compound whatever the approach from which it is calculated. Thus, if S_N and S_V are the order parameters calculated from Neugebauer's and Vuks' approaches respectively, then they should be equal at a given temperature and for a given compound, in its liquid crystalline phase. If the two are not equal, then the question is; which of the two, S_N or S_V, is more reliable?. What are the criteria for assessing the merits of one over the other?. This is in fact the subject matter of the discussion in this section. At the outset, values of S_N and S_V were calculated using the expression;

$$S_{N,V} = \frac{(\alpha_e - \alpha_o)_{N,V}}{(\Delta\alpha)_{N,V}} \qquad (4.16)$$

for each of the five compounds at different temperatures in the liquid crystalline phase. Initially, calculations were made for $\lambda = 5893A^0$ only. The values of $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_v$ at various temperatures are already known for all the compounds viz. tables **17** to **21** of this chapter. The data next needed were the values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ for each of the compounds. In the following subsections, a discussion of how these values were obtained for each of the compounds is presented.

4.7.2. Calculation of S_N and S_V values for hexanoate and undecyclenate.

The values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ are already known for all the wavelengths; $5461A^0$, $5780A^0$ and $5893A^0$ for these two compounds (see tables **23** and **24** above). They were

calculated directly from Neugebauer's and Vuks' approaches using the index and density data in the crystalline and liquid phases of these two compounds. As these values are in good agreement with those calculated on the basis of NMR data, they were used for the calculation of S_N and S_V values. Values of $(\Delta\alpha)_N$ for hexanoate and undecyclenate for 5893A^0 are 32.00 x 10^{-24} cm^3 and 35.80 x 10^{-24} cm^3 respectively while $(\Delta\alpha)_v$ values are 40.88 x 10^{-24} cm^3 and 40.54 x 10^{-24} cm^3 respectively. The values of $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_v$ for 5893A^0 for these two compounds were obtained from tables **17c** and **19c** respectively. Hence S_N and S_V values were calculated from equation (4.16) of this chapter. The calculated values of S_N and $S_{\bar{V}}$ for 5893A^0 at various temperatures are presented in tables **31** and **33** below.

4.7.3. Calculation of S_N and S_V values for heptanoate.

Heptanoate differs from hexanoate by an additional CH_2 group. Therefore, the difference in $\Delta\alpha$ values of the two compounds should be very small. However, as can be seen from tables **23** and **25**, the $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ values for heptanoate calculated from the index and density data in the crystalline and liquid phases are significantly smaller than those of hexanoate calculated using the same approach. The actual differences between the corresponding values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ for hexanoate and heptanoate are 1.21x 10^{-24} cm^3 and 3.07 x 10^{-24} cm^3 respectively for 5893A^0. However, the difference in $\Delta\alpha$ values of these two compounds calculated from the bond polarizability technique is much smaller as is evident from table **29** above. In fact, the actual difference is 0.25 x 10^{-24} cm^3. It is this smaller difference that is taken to be more accurate and hence is used to obtain $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ values of heptanoate. This is done by subtracting this difference from the corresponding values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ for heptanoate. Hence, $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ values for heptanoate for 5893A^0 are obtained as (32.00 - 0.25) x 10^{-24} cm^3 which is equal to 31.75 x 10^{-24} cm^3 and (40.88 - 0.25) x 10^{-24} cm^3 which is equal to 40.63 x 10^{-24} cm^3 respectively. These are the values that have been used to calculate the 'S' factors S_N and S_V for heptanoate. The values of $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_v$ for heptanoate for 5893A0 were obtained from table **18c** of this chapter. Hence, S_N and S_V values were calculated from equation (4.16) of this chapter for 5893A^0 at various temperatures and are presented in table **32** below.

4.7.4. Calculation of S_N and S_V values for PBPA and BBPA.

The refractive index and the density data in the crystalline phases of PBPA and BBPA are not available. Therefore, $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ values for these two compounds could not be calculated from the direct approach as in the case of hexanoate, heptanoate and undecyclenate. However, the refractive index and density data in the liquid crystalline phase of MBBA, which is homologous with PBPA and BBPA have been reported by Germain (Germain, 1980) for 5893A^0. In addition, 'S' data from NMR studies of the same compound are available in literature (Rose *et al* , 1983). These refractive index and density data were then used to calculate values of $(\alpha_e - \alpha_o)_N$, $(\alpha_e - \alpha_o)_v$ and hence $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ for MBBA using the expression;

$$(\Delta\alpha)_{N,V} = \frac{(\alpha_e - \alpha_o)_{N,V}}{S_{NMR}} \qquad (4.17)$$

where S_{NMR} refers to the values of 'S' obtained from NMR spectra of MBBA. The calculated values of $(\alpha_e - \alpha_o)_N$, $(\alpha_e - \alpha_o)_v$, $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ along with S_{NMR} factors of MBBA are presented in table **28** above.

From the same table it is clear that the calculated values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ from S_{NMR} data of MBBA in the range 10^0C to 20^0c are fairly constant. However, constancy is better for $(\Delta\alpha)_N$ values than for $(\Delta\alpha)_v$ values. The average values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ for MBBA are 22.34×10^{-24} cm^3 and 26.66×10^{-24} cm^3 respectively. As can be seen from figure **6** of chapter **3**, the central rigid portions of all the three compounds MBBA, PBPA and BBPA are the same. However, PBPA has an additional CH_2 group in the right end chain and two additional CH_2 groups in the left end chain as compared to MBBA while BBPA has an additional CH_2 group in the right end chain and three additional CH_2 groups in the left end chain as compared to MBBA. It is assumed that the contribution of the central rigid portions of the molecules of MBBA, PBPA and BBPA to their optical anisotropy values is the same. However, the optical anisotropy values for each of these three compounds are different due to the varying contributions of the respective end chains.

From table **29** above, $\Delta\alpha$ value for PBPA differs from that of MBBA by $1.44 \times 10^{-24}cm^3$. Adding this difference to the average values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ of MBBA gives the corresponding values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ for PBPA as 23.78×10^{-24} cm^3 and 28.10×10^{-24}

cm^3 respectively. Similarly, $(\Delta\alpha)_N$ and $(\Delta\alpha)_v$ values for BBPA are obtained as 24.46×10^{-24} cm^3 and 28.78×10^{-24} cm^3 respectively. These are the values that were used to calculate the 'S' factors S_N and S_V for PBPA and BBPA. The values of $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_v$ for $5893A^0$ for these compounds were obtained from tables **20** and **21** respectively. Hence, S_N and S_V values were calculated for $5893A^0$ at various temperatures using equation (4.16) of this chapter and are presented in tables **34** and **35** below.

4.7.5. Calculation of S_N and S_V values for $5461A^0$ and $5780A^0$.

The values of S_N and S_V that were calculated in sections **4.7.2, 4.7.3** and **4.7.4** above at various temperatures in the liquid crystalline phases of all the five compounds are for $5893A^0$. In what follows a discussion of how S_N and S_V values for other two wavelengths $5461A^0$ and $5780A^0$ were calculated is presented.

First, it is assumed that the values of S_N and S_V for $5893A^0$ obtained for the lowest temperature in the liquid crystalline phase are the same as for $5461A^0$ and $5780A^0$ at the same temperature. This assumption is valid because 'S' factors obtained at a given temperature and for a given compound for various wavelengths should all be equal, that is, independent of the wavelength. This is particularly true for temperatures just beyond the K-N transition point. Using these values of 'S' and the values of $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_V$ at that temperature, the values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ for $5461A^0$ and $5780A^0$ were calculated. As an illustration of how these calculations of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ were done for each of the five compounds, a typical example of the calculation in the case of hexanoate is presented below.

For hexanoate, S_N and S_V values for $5893A^0$ at $(t_c - t) = 48.5^0C$ are 0.724 and 0.698 respectively (from table **31**). The corresponding values of $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_V$ for $5461A^0$ at 48.5^0C are 24.88×10^{-24} cm^3 and 30.97 x 10-24 cm^3 respectively (see table **17a** above of this chapter). Thus the values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ for $5461A^0$ are $[(24.88 \times 10^{-24})/0.724] = 34.36 \times 10^{-24}$ cm^3 and $[(30.97 \times 10^{-24})/0.698] = 44.37 \times 10^{-24}$ cm^3 respectively. Similarly, the values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ for $5780A^0$ were obtained as 32.36×10^{-24} cm^3 and 41.69×10^{-24} cm^3 respectively. By following a similar procedure, $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ values were calculated for the remaining four compounds namely heptanoate, undecyclenate, PBPA and BBPA and the results are tabulated for all the three wavelengths and for all the five compounds in table **30** below. These are the values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ that have been used for the calculation of orientational order parameter in the next sections. The values of $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_V$ for $5461A^0$ and $5780A^0$ were obtained from tables **17a** and **17b** for

hexanoate, **18a** and **18b** for heptanoate, **19a** and **19b** for undecyclenate, **20b** and **20c** for PBPA and finally from **21b** and **21c** for BBPA. Using equation (4.21) of this chapter S_N and S_V values were calculated at various temperatures for the two wavelengths 5461A^0 and 5780A^0 for each of the five compounds. The calculated values of S_N and S_V are presented in tables **31**, **32**, **33**, **34** and **35** below along with those for 5893A^0.

Table 30. Values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ calculated for the wavelengths; 5461A^0, 5780A^0, 5893A^0 for all the five compounds.

Compound	Polarizabilities (in units of 10^{-24} cm^3)					
	5461A^0		5780A^0		5893A^0	
	$(\Delta\alpha)_N$	$(\Delta\alpha)_V$	$(\Delta\alpha)_N$	$(\Delta\alpha)_V$	$(\Delta\alpha)_N$	$(\Delta\alpha)_V$
Hexanoate	34.36	44.37	32.36	41.69	32.00	40.88
Heptanoate	34.65	44.05	32.41	41.06	31.75	40.63
Undecyclenate	38.23	44.05	36.52	41.27	35.80	40.54
PBPA	24.49	29.37	24.14	28.33	23.78	28.10
BBPA	25.84	30.04	24.97	29.04	24.46	28.78

Table 31: 'S' factors S_N and S_V for various wavelengths and at various temperatures in the nematic phase of hexanoate.

$(t_c - t)^0$C	5461A^0		5780A^0		5893A^0	
	S_N	S_V	S_N	S_V	S_N	S_V
4.0	0.4520	0.466	0.462	0.465	0.449	0.470
8.0	0.512	0.509	0.506	0.508	0.500	0.505
12.5	0.555	0.542	0.549	0.542	0.545	0.549
19.5	0.604	0.585	0.596	0.583	0.600	0.581
24.0	0.629	0.608	0.625	0.608	0.626	0.606
28.5	0.650	0.608	0.646	0.627	0.649	0.629
32.0	0.664	0.641	0.660	0.641	0.664	0.643
37.0	0.687	0.659	0.684	0.658	0.688	0 663
44.5	0.710	0.688	0.708	0.689	0.708	0.690
48.5	0.724	0.698	0.724	0.698	0.724	0.698

Table 32: Orientational order parameter S_N and S_V for various wavelengths and at various temperatures in the nematic phase of heptanoate.

$(t_c - t)$ ^0C	5461A^0		5780A^0		5893A^0	
	S_N	S_V	S_N	S_V	S_N	S_V
4.0	0.420	0.427	0.415	0.431	0.420	0.409
6.0	0.461	0.464	0.456	0.458	0.450	0.458
9.0	0.478	0.496	0.493	0.495	0.499	0.493
13.0	0.541	0.529	0.529	0.530	0.540	0.524
19.0	0.585	0.566	0.575	0.573	0.584	0.567
21.5	0.597	0.581	0.589	0.588	0.601	0.580
25.0	0.616	0.601	0.611	0.605	0.620	0.598
34.0	0.628	0.620	0.621	0.620	0.632	0.589
34.0	0.653	0.638	0.652	0.643	0.656	0.638
39.0	0.671	0.662	0.671	0.662	0.671	0.662

Table 33: Order parameters, S_N and S_V for various wavelengths and at various temperatures in the nematic phase of undecyclenate.

$(t_c - t)$ ^0C	5461A^0		5780A^0		5893A^0	
	S_N	S_V	S_N	S_V	S_N	S_V
2.0	0.344	0.421	0.358	0.425	0.355	0.422
6.0	0.447	0.493	0.437	0.500	0.452	0.489
9.5	0.498	0.537	0.485	0.543	0.498	0.537
14.5	0.551	0.583	0.530	0.590	0.552	0.587
20.5	0.594	0.624	0.580	0.629	0.586	0.630
25.0	0.616	0.647	0.609	0.653	0.611	0.654
30.0	0.648	0.676	0.635	0.679	0.637	0.678
35.0	0.672	0.697	0.662	0.699	0.665	0.701
40.0	0.693	0.721	0.685	0.723	0.683	0.722
44.0	0.702	0.739	0.702	0.739	0.702	0.739

Table 34: Order parameters S_N and S_V for various wavelengths and at various temperatures in the nematic phase of PBPA.

$(t_c - t)$ ^0C	$5461A^0$		$5780A^0$		$5893A^0$	
	S_N	S_V	S_N	S_V	S_N	S_V
4.6	0.381	0.446	0.395	0.431	0.373	0.435
6.8	0.427	0.502	0.413	0.489	0.419	0.493
10.2	0.489	0.560	0.467	0.556	0.465	0.551
15.6	0.552	0.612	0.542	0.616	0.542	0.611
22.6	0.611	0.656	0.603	0.663	0.604	0.659
27.3	0.648	0.684	0.630	0.685	0.627	0.685
30.6	0.670	0.694	0.664	0.699	0.663	0.698
34.6	0.697	0.714	0.679	0.715	0.681	0.711
37.6	0.707	0.723	0.705	0.726	0.704	0.726
42.3	0.719	0.742	0.719	0.724	0.719	0.742

Table 35: Order parameters S_N and S_V for various wavelengths and at various temperatures in the nematic phase of BBPA.

$(t_c - t)$ ^0C	$5461A^0$		$5780A^0$		$5893A^0$	
	S_N	S_V	S_N	S_V	S_N	S_V
3.2	N/A	N/A	0.383	0.438	0.391	0.442
6.0	0.466	0.506	0.466	0.504	0.476	0.509
10.9	0.558	0.591	0.565	0.588	0.560	0.581
13.5	0.610	0.623	0.604	0.619	0.612	0.612
18.0	0.652	0.661	0.648	0.659	0.657	0.652
22.5	0.687	0.683	0.681	0.685	0.691	0.678
25.9	0.707	0.701	0.701	0.703	0.711	0.696
31.4	0.750	0.722	0.749	0.721	0.754	0.722
35.0	0.769	0.732	0.769	0.732	0.769	0.732

For the sake of comparison and dis cussion of the relative merits of the two approaches, it is essential to compare the calculated values of S_N and S_V with 'S' data from

NMR at least for those compounds for which S_{NMR} data are available. S_{NMR} data are available only for hexanoate and undecyclenate (Watkin *et al*, 1981). These values of S_N, S_V for 5893A^0 and S_{NMR} data for these two compounds are given in tables **36** and **37** below.

Table 36: Order parameters S_N, S_V and S_{NMR} for 5893A^0 for hexanoate.

$(t_c - t)\ ^0C$	S_{NMR}	S_N	S_V
4.0	0.471	0.449	0.470
8.0	0.500	0.500	0.505
12.5	0.540	0.545	0.540
19.5	0.600	0.600	0.581
24.0	0.620	0.626	0.606
28.5	0.650	0.649	0.629
32.0	0.665	0.664	0.643
37.0	0.690	0.688	0.663
44.5	0.705	0.708	0.690
48.5	0.720	0.724	0.698

Table 37: Order parameters S_N, S_V and S_{NMR} for 5893A^0 for undecyclenate.

$(t_c - t)\ ^0C$	S_{NMR}	S_N	S_V
2.0	0.370	0.355	0.422
6.0	0.450	0.452	0.489
9.5	0.505	0.498	0.537
14.5	0.553	0.552	0.587
20.5	0.600	0.586	0.630
25.0	0.608	0.611	0.654
30.0	0.630	0.637	0.678
35.0	0.653	0.665	0.701
40.0	0.680	0.683	0.722
44.0	0.700	0.702	0.739

4.7.6. Calculation of orientational order parameter for valerate.

Refractive index and density data in the liquid crystalline and liquid phases of valerate have been reported by Subramhanyam *et al* (1978) for different wavelengths. These data are given in table 1 of Appendix **III**. These data have been used to calculate $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_V$ values for valerate for the three wavelengths: 5461A^0, 5780A^0 and 5893A^0 and the results are presented in table **38** below.

Table 38: Polarizability anisotropies $(\alpha_e - \alpha_o)_N$ and $(\alpha_e - \alpha_o)_V$ (in units of 10^{-24} cm^3) calculated from index and density data in the nematic phase of valerate.

$(t_c - t)$ ^{0}C	5461A^0		5780A^0		5893A^0	
	$(\alpha_e - \alpha_o)_N$	$(\alpha_e - \alpha_o)_V$	$(\alpha_e - \alpha_o)_N$	$(\alpha_e - \alpha_o)_V$	$(\alpha_e - \alpha_o)_N$	$(\alpha_e - \alpha_o)_V$
1.0	12.61	18.09	12.34	16.51	11.97	15.98
2.0	13.98	N/A	13.74	N/A	13.29	N/A
4.0	15.07	20.95	14.51	19.10	14.42	18.76
10.0	17.42	23.40	16.72	21.64	16.35	21.12
15.5	19.04	25.11	18.30	23.37	17.87	22.94
23.5	20.31	26.72	19.54	24.99	19.11	24.56
30.0	21.26	27.70	20.45	25.99	20.03	25.55
35.5	21.92	28.46	20.90	26.76	20.67	26.32
41.0	22.26	29.11	21.38	27.49	21.05	26.89
48.0	22.80	29.72	21.95	28.01	21.53	27.59

In order to calculate 'S' factors, S_N and S_V for valerate, the values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ for the same compound had to determined. These values were calculated by adopting the same procedure as the one used in the case of PBPA and BBPA since refractive index and density data in the crystalline phase of this compound were not available. Valerate is homologous with hexanoate but has one CH_2 group less in its right end chain than hexanoate. Thus by correcting appropriately the value of $(\Delta\alpha)$ for hexanoate, $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ values for valerate were obtained. From table **29**, $(\Delta\alpha)$ value for valerate is less than that of hexanoate by 0.685×10^{-24} cm^3. By subtracting this difference from $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ values of hexanoate, $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ values for valerate were obtained as $(32.00 - 0.685) \times 10^{-24}$ cm^3 = 31.315×10^{-24} cm^3 and $(40.880 - 0.685) \times 10^{-24}$ cm^3 = 40.195×10^{-24} cm^3 respectively

for 5893A^0.

The 'S' factors, S_N and S_V at various temperatures in the nematic phase of valerate for 5893A^0 were obtained by substituting the calculated values of $(\alpha_e - \alpha_o)_N$, $(\alpha_e - \alpha_o)_V$, $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ calculated above in equation (4.21) of this chapter. Assuming that the values of S_N and S_V for 5893A^0 at the lowest temperature (=80^0 C) are the same as for 5461A^0 and 5780A^0 at the same temperature, $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ values for these two wavelengths were evaluated using equation (4.21). The resulting values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ are 33.140 x 10^{-24} cm^3 and 43.324 x 10^{-24} cm^3 for 5461A^0 and 5780A^0 respectively. Using these values of $(\Delta\alpha)_N$ and $(\Delta\alpha)_V$ for 5461A^0 and 5780A^0, the 'S' factors, S_N and S_V, at various temperatures in the nematic phase of valerate were evaluated for these two wavelengths. Table **39** below, shows these values of S_N and S_V for the three wavelengths 5461A^0, 5780A^0 and 5893A^0. Also shown in column **8** of the same table are values of 'S' for this compound determined by Subramhanyam *et al* (1978) using Raman spectroscopy for the sake of comparison.

Table 39: Values of 'S' factors, S_N and S_V, calculated for 5461A^0, 5780A^0 and 5893A^0 with values of 'S' obtained from Raman spectroscopy for 5893A^0 and at various temperatures in the nematic phase of valerate.

$(t_c - t)$ ^{0}C	5461A ^{0}		5780A ^{0}		5893A ^{0}		S_{Raman} for 5893A^0
	S_N	S_V	S_N	S_V	S_N	S_V	
1.0	0.381	0.418	0.386	0.404	0.382	0.398	0.389
2.0	0.422	N/A	0.431	N/A	0.424	N/A	0.431
4.0	0.455	0.484	0.455	0.468	0.460	0.467	0.468
10.0	0.526	0.540	0.524	0.530	0.522	0.525	0.531
15.5	0.575	0.580	0.574	0.572	0.571	0.571	0.580
23.5	0.613	0.617	0.612	0.612	0.610	0.611	0.620
30.0	0.642	0.639	0.641	0.636	0.640	0.636	0.650
35.5	0.661	0.657	0.655	0.655	0.660	0.655	0.670
41.0	0.672	0.672	0.670	0.673	0.672	0.669	0.683
48.0	0.688	0.686	0.688	0.686	0.688	0.686	0.698

4.7.7. Graphical plots of orientational order parameter for the various compounds.

In order to discuss the results more clearly and arrive at significant conclusions, plots of orientational order parameters S_N and S_V versus $(t_c - t)^0C$ for all the five compounds and valerate have been made. The graphical representation was done for only one wavelength, $5893A^0$ as the trend is supposed to be the same for other wavelengths. Figure $\mathbf{E_1}$ below shows the plot of S_N, S_V and S_{NMR} versus $(t_c - t)$ for hexanoate while $\mathbf{E_2}$ shows similar plots for undecyclenate. Figure $\mathbf{E_3}$ show plots of S_N, S_V and S_{Raman} versus $(t_c - t)$ for valerate on the same axes. Figure $\mathbf{E_4}$ shows plots of S_N versus $(t_c - t)$ for hexanoate, heptanoate, undecyclenate and valerate on the same axes while E_5 is a plot of S_V versus $(t_c - t)$ for the same compounds. Plots of S_N, S_V versus $(t_c - t)$ for PBPA and BBPA are shown in figures $\mathbf{E_6}$ and $\mathbf{E_7}$ respectively. Plots of S_N versus $(t_c - t)$ for PBPA and BBPA are shown in figure $\mathbf{E_8}$ while $\mathbf{E_9}$ show plots of S_V versus $(t_c - t)$ for the same compounds.

4.8. DISCUSSION CONCERNING CALCULATED VALUES OF ORIENTATIONAL ORDER PARAMETERS, S_N AND S_V.

4.8.1. Constancy of S_N and S_V values over various wavelengths.

It is well known that orientational order parameter 'S' increases with an increase in temperature but remains a constant at a given temperature irrespective of the wavelength, that is, it is temperature dependent but it is independent of wavelength as long as temperature is constant.

It can be seen from tables **31, 32, 33, 34** and **35** that S_N values for different wavelengths, at a given temperature, $(t_c - t)$, are in agreement to within 1-2 percent of their mean value. A similar observation can be made regarding S_V values. From this point of view, both approaches are equally good. While the values of S_N and S_V for a given compound at a given temperature in the liquid crystalline phase of each of the five compounds are different as can be seen from tables **31** to **32**, this difference is less significant in the case of hexanoate, heptanoate and undecyclenate but more pronounced in the case of PBPA and BBPA. The question therefore is; which of the two, S_N or S_V is more reliable? . To answer this question, it is imperative to compare S_N and S_v values with those obtained from other standard methods such as NMR and Raman spectroscopy.

Figure E_1: Order parameter S_{NMR} (solid line), S_V (Open circles, O) and S_N (crosses, x) versus (t_c-t) for hexanoate for 5893A^0.

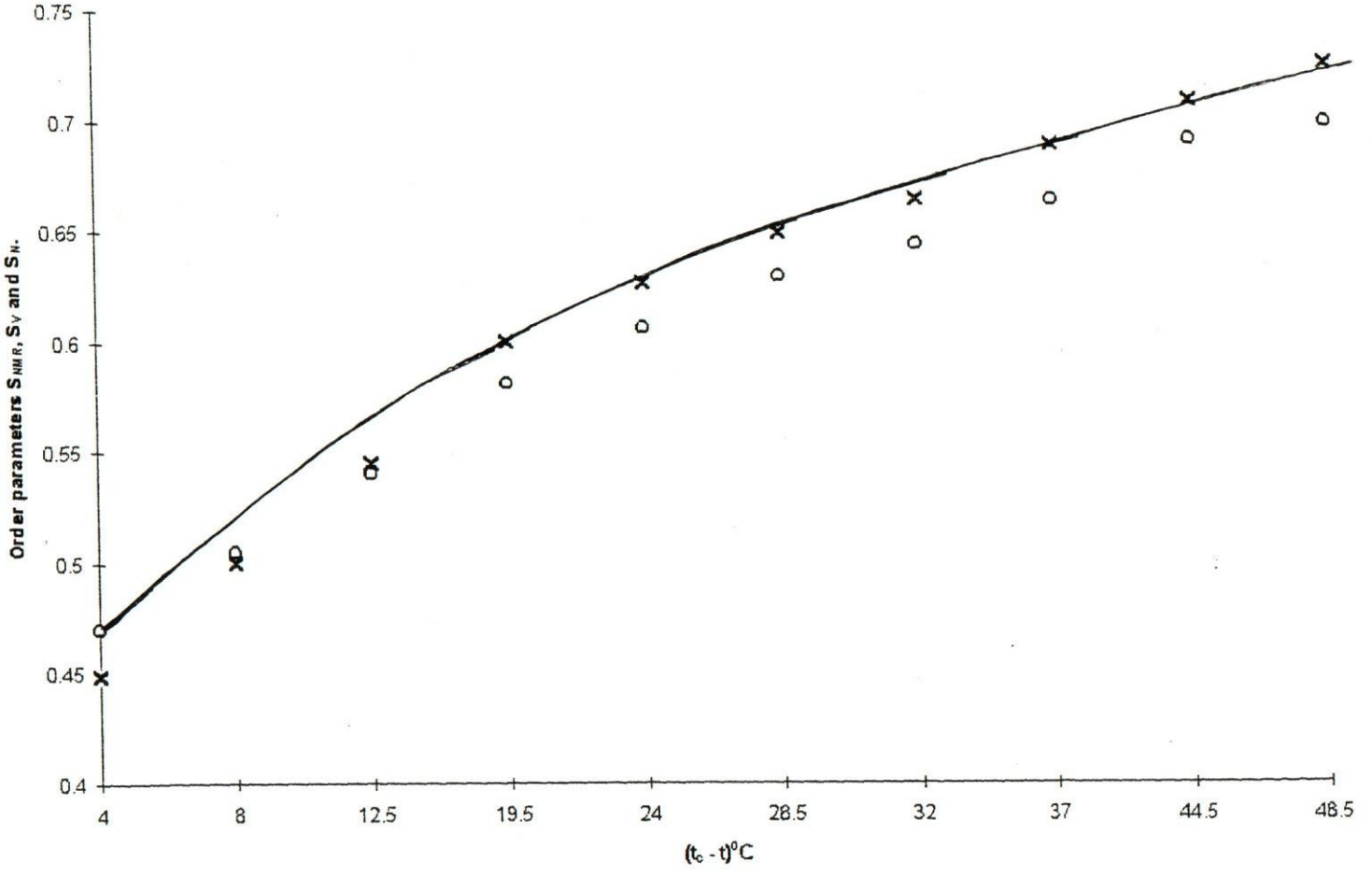


Figure E_2: Order parameters S_{NMR} (solid line), S_V (open circles), and S_N (crosses, x) for undecyclenate for 5893A^0.

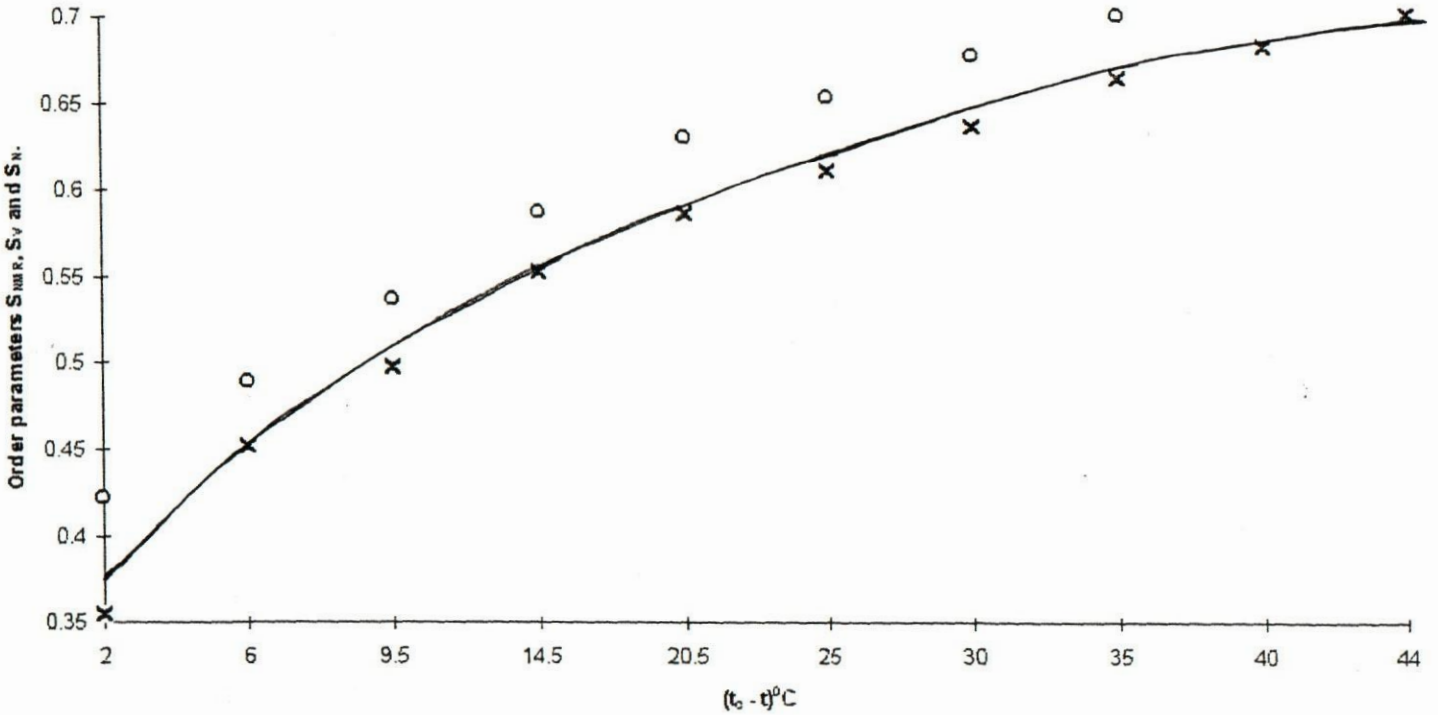


Figure E_3: Order parameters S_{Raman} (solid line), S_V (open circles, O) and S_N (crosses, x) versus (t_c-t) for valerate for 5893A^0.

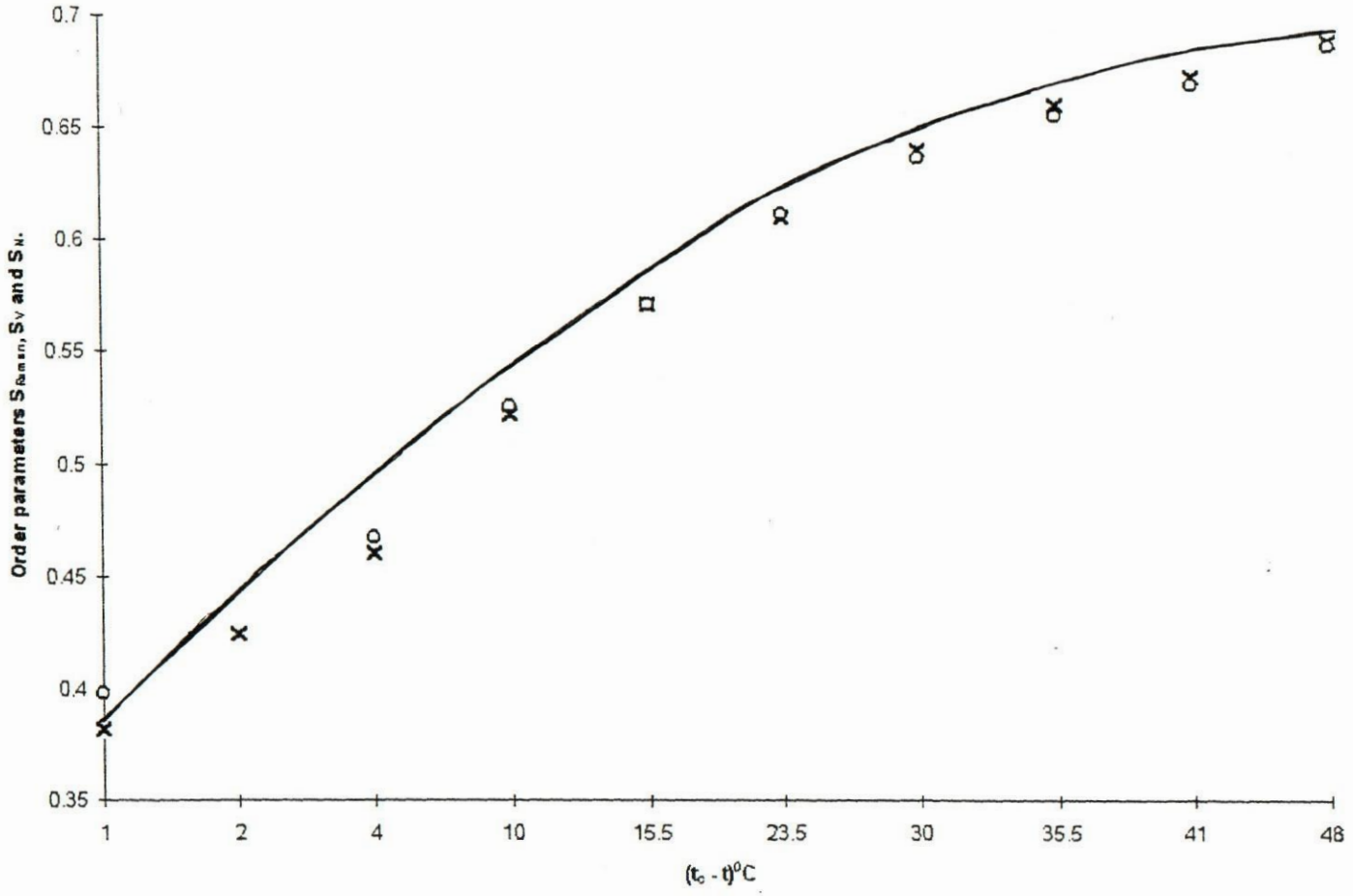


Figure E_4: Order paramterer S_N versus (t_c-t) for hexanoate (squares), heptanoate (crosses), undecyclenate (triangles) and valerate (open circles) for 5893A^0.

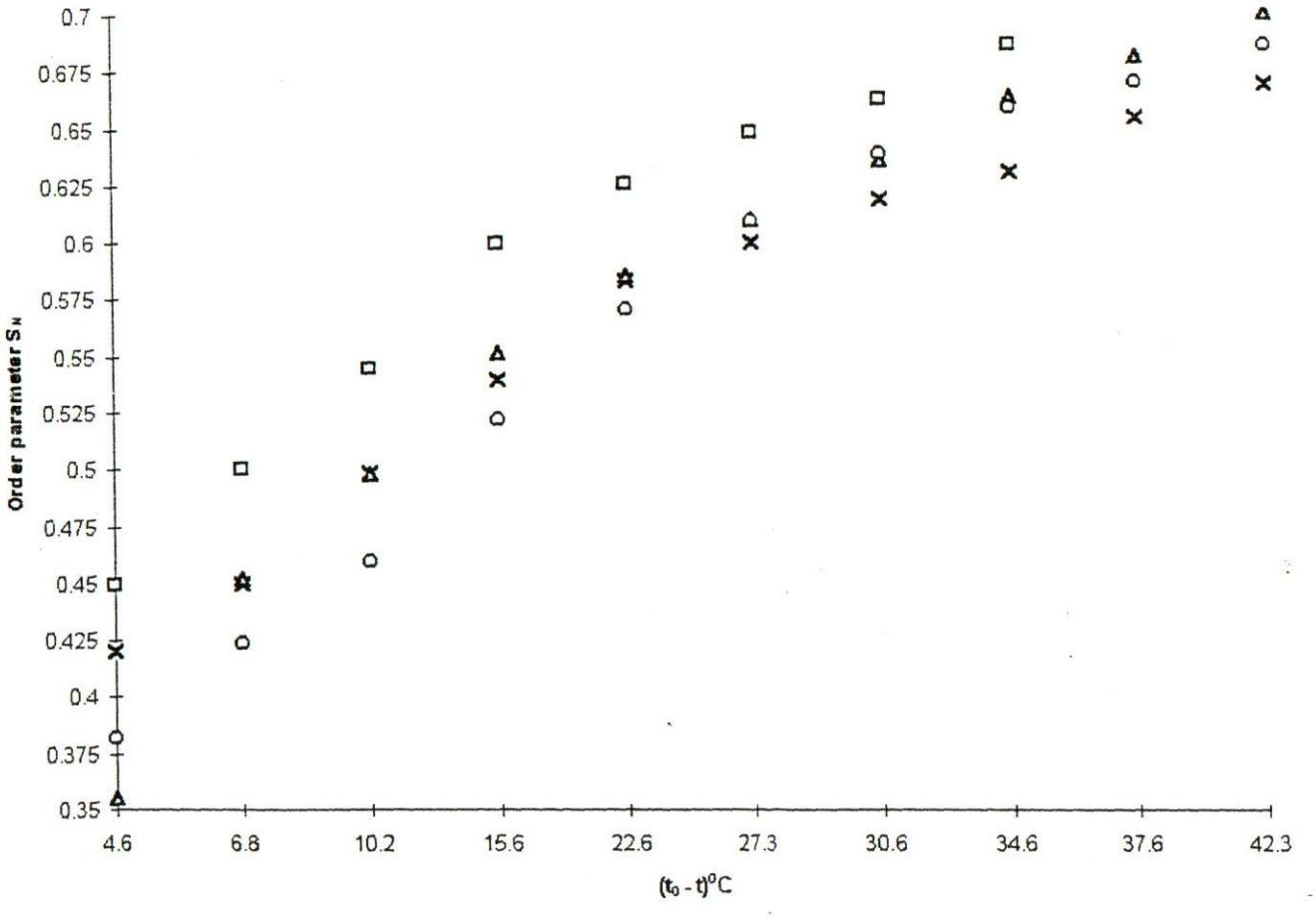


Figure E_5: Order parameter S_V versus (t_c-t) for hexanoate (square) ; heptanoate (crosses); undecyclenate (triangles) and valerate (open circles) for 5893A^0.

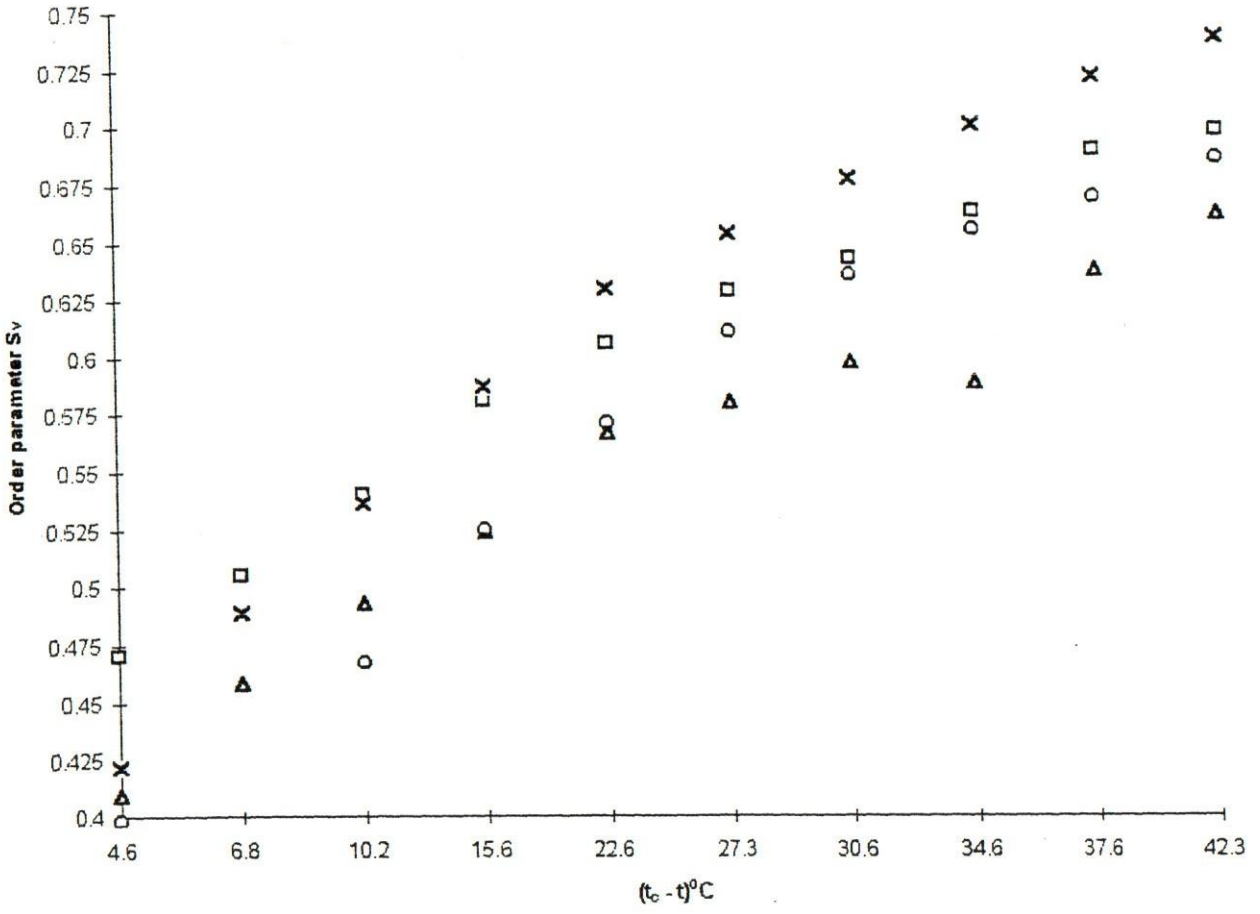


Figure E_6: Order parameters S_N (open circles); S_V (crosses) for PBPA for 5893A^0.

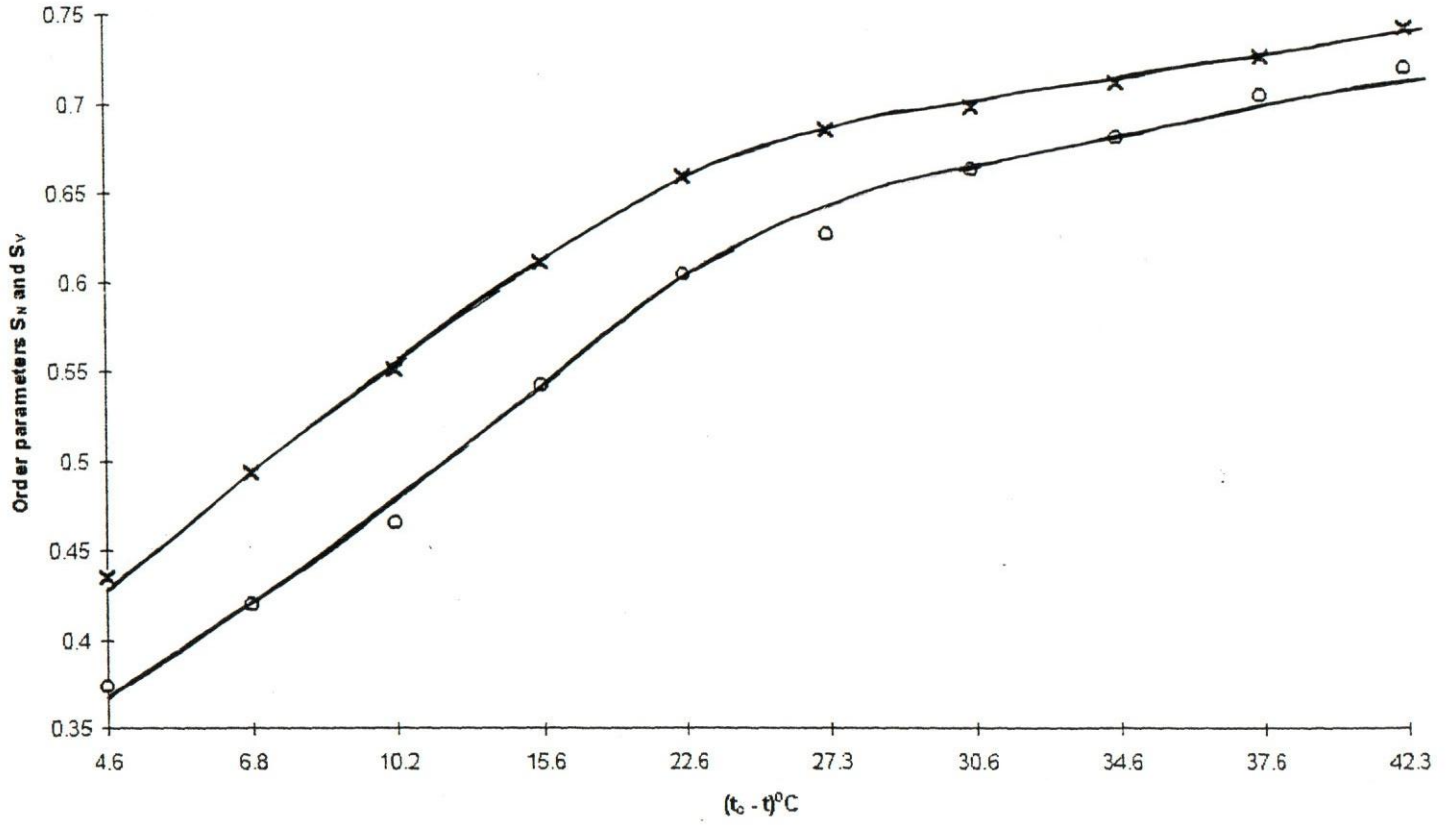


Figure E_7: Order parameters S_N (open circles) and S_V (crosses) versus (t_c-t) for PBPA for $5893A^0$.

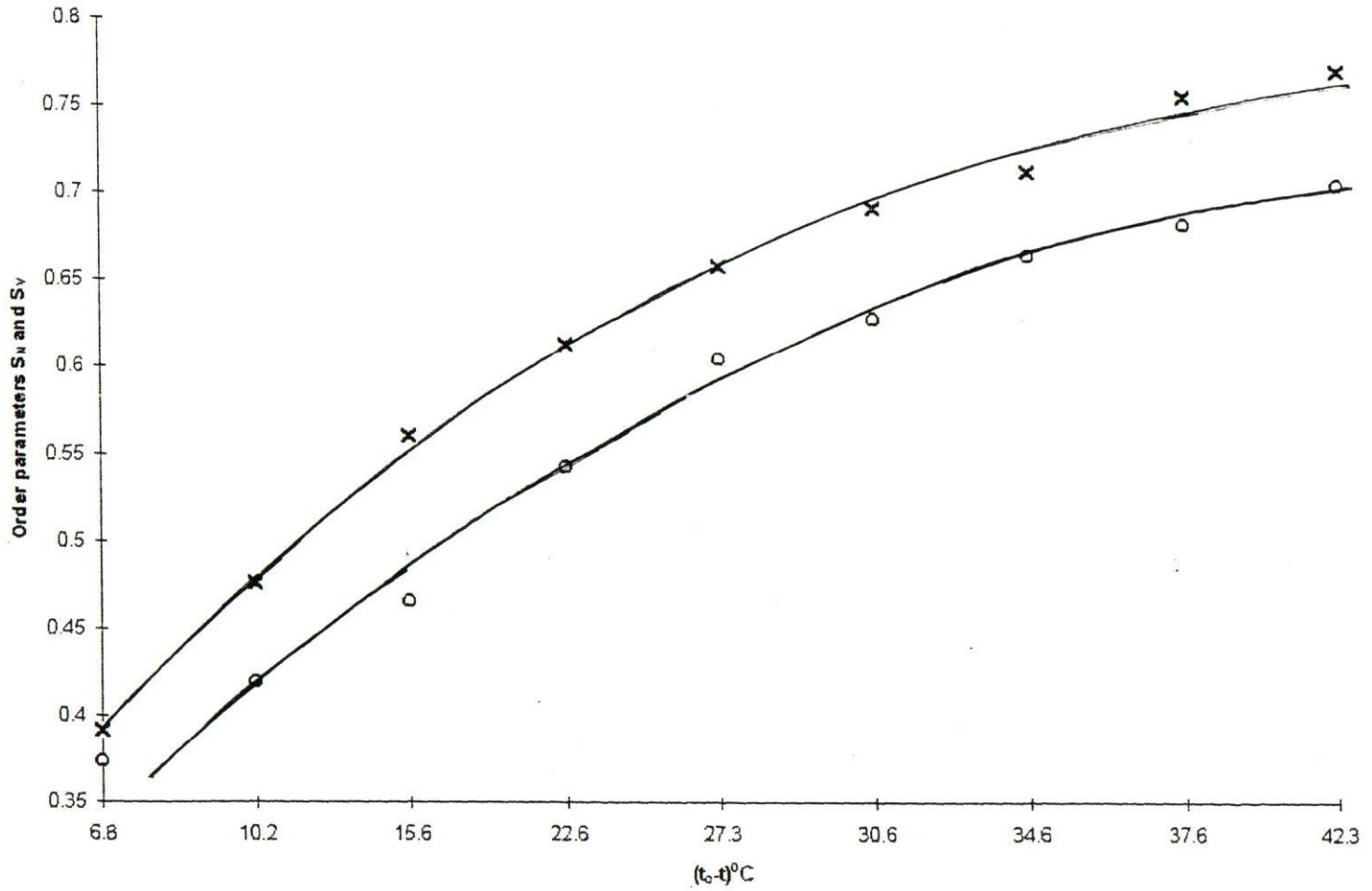


Figure E_8: Order parameter S_N VS (tc.t) for PBPA (open circles) and BBPA (crosses) for 5893A^0.

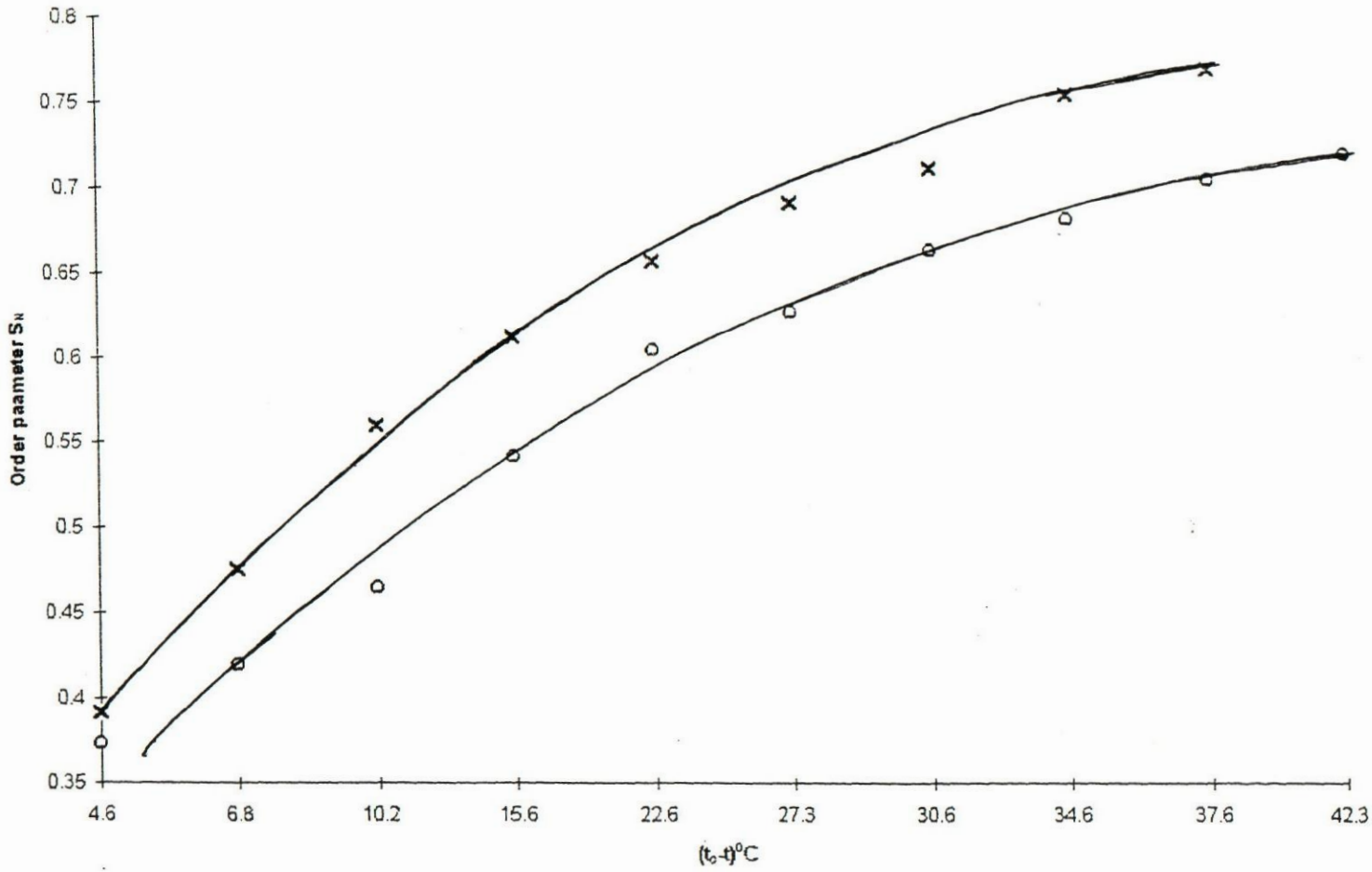
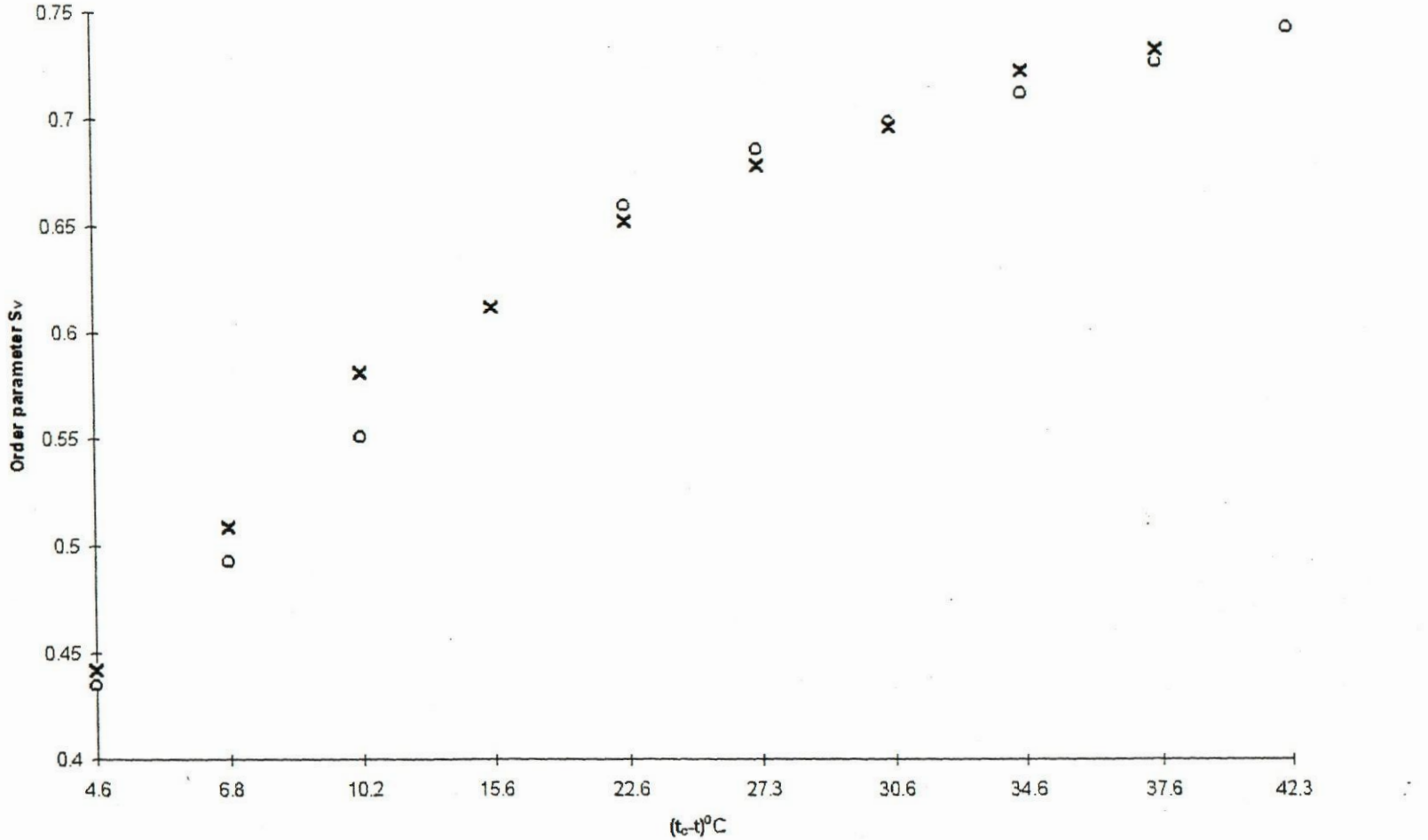


Figure E_9: Order parameter S_V versus (t_c-t) for PBPA (open circles) and BBPA (with crosses) for 5893A^0.



4.8.2. Comparison of S_N or S_V with corresponding values obtained from NMR and Raman spectra.

'S' data from NMR measurements are available only for hexanoate and undecyclenate. Thus, S_N, S_V and S_{NMR} values for these two compounds are shown in tables **36** and **37** respectively. From these two tables, it is clear that S_N and S_{NMR} values at the same temperature are in very fair agreement. However, that between S_V and S_{NMR} is not as satisfactory. This is further confirmed by the examination of Figures $\mathbf{E_1}$ and $\mathbf{E_2}$ which shows plots of S_N, S_V and S_{NMR} versus $(t_c - t)$ for hexanoate and undecyclenate respectively.

'S' data from Raman band analysis are available for valerate only. It is difficult to conclude from table **39**, where S_N, S_V and S_{Raman} values for valerate are given, whether agreement is better for S_N or S_V values. However, examination of Figure $\mathbf{E_3}$, which shows plots of S_{Raman}, S_N and S_V versus $(t_c - t)$ for valerate on the same axes indicates clearly that S_N values are in greater agreement with S_{Raman} values than S_V values.

Examination of figure $\mathbf{E_4}$ which shows plots of S_N vs. $(t_c - t)$ for hexanoate, heptanoate, undecyclenate and valerate on the same axes, reveals that the trend of variation is similar at least for hexanoate, heptanoate and undecyclenate as the three curves are approximately parallel to each other. A similar observation can be made from figure $\mathbf{E_5}$ which shows plots of S_V versus $(t_c - t)$ for the four compounds, on the same axes. However, it is evident from the two figures that for valerate, the trend of variation deviates slightly. Nonetheless, it may be concluded that for homologues with same central rigid portions but varying terminal chains, the trend of variation should be similar.

While the agreement between S_N and S_V values is tolerably satisfactory for hexanoate, heptanoate and undecyclenate it is poor for PBPA and BBPA as can be seen from the plots of S_N versus $(t_c - t)$ and S_N versus $(t_c - t)$ for PBPA in figure $\mathbf{E_6}$ and BBPA in figure $\mathbf{E_7}$. The same observation can also be made from tables **34** and **35**. From figure E_8 which shows plots of S_N versus $(t_c - t)$ for PBPA and BBPA on the same axes and figure $\mathbf{E_9}$ showing plots of S_V versus $(t_c - t)$ for the same compounds, it is evident that the trend of variation of S_N and S_V for the two compounds are similar.

4.9. CALCULATION OF LORENTZ FIELD FACTORS.

4.9.1. Calculation of Lorentz field factors $L_{\parallel}$ and $L_{\perp}$ in the crystalline phase.

From the index data in the crystalline phase n_p, n_m and n_g which are available for only three of the five compounds namely hexanoate, heptanoate and undecyclenate (tables **1**, **2** and **3** of Appendix **I**), it is possible to calculate the Lorentz field factors in the crystalline phase $L_{\parallel}$ and $L_{\perp}$ using the expressions.

$$L_{\parallel} = \frac{M}{4\pi N_A \rho_C \alpha_{\parallel}} - \frac{1}{(n_g^2 - 1)} \qquad (4.18)$$

and

$$L_{\perp} = \frac{1}{4\pi N_A \rho_C \alpha_{\perp}} - \frac{1}{(n_{\perp}^2 - 1)} \qquad (4.19)$$

where symbols have their usual meanings.

Alternatively, having obtained one of the factors, the other can be calculated using the relation

$$L_{\parallel} + 2L_{\perp} = 1 \qquad (4.20)$$

Field anisotropy is given by $(L_{\perp} - L_{\parallel})$. Calculations of these factors have been made for the three compounds; hexanoate, heptanoate and undecyclenate. For example, for hexanoate molecular weight, M = 340.42gm, density ρ_C = 1.21gm/cm^3, $\alpha_{\parallel}$ = 66.75 x 10^{-24} cm^3 and n_g = 2.066 for 5461A^0 and therefore,

$$L_{\parallel} = \frac{340.42}{4\pi N_A \ (1.21)(66.75 x 10^{-24})} - \frac{1}{(2.066)^2 - 1}$$

which gives $L_{\parallel}$ as 0.251 correct to 3 decimal places.

Using equation (4.18), $L_{\perp}$ is obtained as 0.375 and field anisotropy as 0.124. By following a similar procedure, calculations were made for the other two compounds and for

all the three wavelengths; 5461A^0, 5780A^0 and 5893A^0. The results are shown in table 40 below.

Table 40: Calculated values of $L_{\parallel}$, $L_{\perp}$ and $(L_{\perp} - L_{\parallel})$ for the three wavelengths along with the molecular lengths of hexanoate, heptanoate and undecyclenate.

Compound		Hexanoate	Heptanoate	Undecyclenate
Molecular length in A^0		20.90	21.63	26.26
5461A^0	$L_{\parallel}$	0.251	0.248	0.236
	$L_{\perp}$	0.375	0.376	0.382
	$(L_{\perp} - L_{\parallel})$	0.124	0.128	0.146
5780A^0	$L_{\parallel}$	0.255	0.250	0.236
	$L_{\perp}$	0.373	0.375	0.382
	$(L_{\perp} - L_{\parallel})$	0.118	0.125	0.146
5893A^0	$L_{\parallel}$	0.253	0.252	0.236
	$L_{\perp}$	0.374	0.374	0.382
	$(L_{\perp} - L_{\parallel})$	0.121	0.122	0.146

4.9.2. Calculation of Lorentz field factors L_e and L_o in the nematic phase.

From the index and density data in the liquid crystalline phase of the compounds, the Lorentz field factor L_o was calculated for all wavelengths and at various temperatures using Neugebauer's relations (Equation 2.44 of chapter **2**). The average value of $L_o[= (L_o)_{av}]$ was then calculated for all wavelengths at each temperature. Then using the relation $L_e + 2L_o = 1$ the corresponding average values of L_e, $[=(L_e)_{av}]$ was calculated at each temperature in the nematic phase of each of the five compounds. These values of $(L_o)_{av}$, $(L_e)_{av}$, and $(L_o - L_e)_{av}$ for all compounds at various temperatures in the nematic phase are presented in tables **41**, **42**, **43**, **44** and **45** below.

Table 41: Values of L_o, $(L_o)_{av}$., $(L_e)_{av}$ and $(L_o - L_e)_{av}$ at various temperatures in the nematic phase of hexanoate.

$(t_c - t)$ ^0C	Lorentz field factor, L_o			$(L_o)_{av}$	$(L_e)_{av}$	$(L_o - L_e)_{av}$
	5461A^0	5780A^0	5893A^0			
4.0	0.348	0.349	0.348	0.348	0.303	0.045
8.0	0.353	0.352	0.352	0.352	0.295	0.057
12.5	0.357	0.354	0.355	0.355	0.289	0.066
19.5	0.360	0.358	0.359	0.359	0.282	0.077
24.0	0.361	0.360	0.360	0.360	0.279	0.081
28.5	0.362	0.361	0.361	0.361	0.277	0.084
32.0	0.362	0.360	0.361	0.361	0.278	0.083
37.0	0.364	0.362	0.363	0.363	0.274	0.089
44.0	0.364	0.362	0.363	0.363	0.274	0.089
48.5	0.365	0.364	0.365	0.365	0.271	0.094

Table 42: Calculated values of L_o, $(L_o)_{av}$., $(L_e)_{av}$ and $(L_o - L_e)_{av}$ at various temperatures in the nematic phase of heptanoate.

$(t_c - t)$ ^0C	Lorentz field factor, L_o			$(L_o)_{av}$	$(L_e)_{av}$	$(L_o - L_e)_{av}$
	5461A^0	5780A^0	5893A^0			
4.0	0.350	0.346	0.347	0.348	0.305	0.043
6.0	0.352	0.351	0.348	0.350	0.299	0.051
9.0	0.356	0.352	0.352	0.353	0.293	0.060
13.0	0.356	0.354	0.355	0.355	0.290	0.065
19.0	0.360	0.355	0.356	0.357	0.286	0.071
21.5	0.360	0.356	0.357	0.358	0.285	0.073
25.0	0.359	0.358	0.358	0.358	0.283	0.075
28.0	0.360	0.357	0.360	0.359	0.282	0.077
34.0	0.361	0.360	0.359	0.360	0.280	0.080
39.0	0.361	0.360	0.359	0.360	0.280	0.080

Table 43: Calculated values of L_o, $(L_o)_{av}$, $(L_e)_{av}$ and $(L_o - L_e)_{av}$ at various temperatures in the nematic phase of undecyclenate.

$(t_c - t)\ ^0C$	Lorentz field factor, L_o			$(L_o)_{av}$	$(L_e)_{av}$	$(L_o - L_e)_{av}$
	$5461A^0$	$5780A^0$	$5893A^0$			
2.0	0.341	0.343	0.342	0.342	0.316	0.026
6.0	0.350	0.348	0.352	0.350	0.300	0.050
9.5	0.354	0.351	0.354	0.353	0.294	0.0 59
14.5	0.359	0.354	0.359	0.357	0.285	0.072
20.5	0.360	0.358	0.358	0.359	0.283	0.076
25.0	0.362	0.360	0.359	0.360	0.279	0.081
30.0	0.363	0.361	0.362	0.362	0.276	0.086
35.0	0.365	0.364	0.363	0.364	0.272	0.092
40.0	0.365	0.364	0.363	0.364	0.272	0.092
44.0	0.365	0.367	0.364	0.365	0.269	0.096

Table 44: Calculated values of L_o, $(L_o)_{av}$, $(L_e)_{av}$ and $(L_o - L_e)_{av}$ at various temperatures in the nematic phase of PBPA.

$(t_c - t)$	Values of L_o				$(L_o)_{av}$	$(L_e)_{av}$	$(L_o - L_e)_{av}$
^0C	$4358A^0$	$5461A^0$	$5780A^0$	$5893A^0$			
4.6	-	0.340	0.345	0.340	0.342	0.317	0.025
6.8	0.340	0.340	0.341	0.341	0.341	0.319	0.022
10.2	0.342	0.347	0.341	0.341	0.343	0.315	0.028
15.6	0.346	0.347	0.347	0.346	0.343	0.307	0.040
22.6	0.346	0.351	0.351	0.351	0.347	0.299	0.052
27.3	0.351	0.354	0.352	0.351	0.351	0.296	0.056
30.6	0.354	0.356	0.356	0.355	0.352	0.290	0.065
34.6	0.356	0.358	0.356	0.356	0.355	0.287	0.070
37.6	0.357	0.358	0.359	0.358	0.357	0.284	0.074
42.3	0.358	0.358	0.359	0.358	0.358	0.284	0.074

Table 45: Calculated values of L_o, $(L_o)_{av}$ $(L_e)_{av}$ and $(L_o - L_e)_{av}$ at various temperatures in the nematic phase of BBPA.

$(t_c - t)$ ^0C	Values of L_o				$(L_o)_{av}$	$(L_e)_{av}$	$(L_o - L_e)_{av}$
	4358A^0	5461A^0	5780A^0	5893A^0			
3.2	N/A	N/A	0.342	0.342	0.342	0.316	0.026
6.0	0.348	0.348	0.347	0.348	0.348	0.305	0.043
10.9	0.354	0.353	0.353	0.351	0.353	0.295	0.058
13.5	0.355	0.357	0.356	0.357	0.356	0.288	0.068
18.0	0.359	0.359	0.358	0.359	0.359	0.283	0.076
22.5	0.361	0.362	0.360	0.361	0.361	0.278	0.083
25.9	0.361	0.363	0.361	0.362	0.362	0.277	0.085
31.4	0.369	0.367	0.366	0.365	0.367	0.267	0.100
35.0	0.367	0.368	0.367	0.363	0.366	0.268	0.098

4.9.3. Discussion Concerning Lorentz field factors.

From the results shown in table **40**, it is clear that value of the field anisotropy $(L_\perp - L_\parallel)$ increases with the increase in molecular length. In other words, the greater the departure of the shape of the molecules from spherical symmetry, the greater the anisotropy in the Lorentz field factors. In display devices, the oriented samples are more sensitive to changes in the applied electric field. Since $(L_\perp - L_\parallel)$ is a measure of the sensitivity of a molecule, it follows that the compounds become more and more sensitive to changes in applied field with the increase in the length of the end chains. For a given compound $(L_\perp - L_\parallel)$ is greater than $(L_o - L_e)$, that is the field anisotropy is greater in the crystalline phase than in the liquid crystalline phase. This is naturally expected because as the sample passes from the crystalline to the liquid crystalline phase, it becomes less and less anisotropic. Lorentz field factors should depend only on the nature of molecular distribution and hence different sets of values of these factors calculated for different wavelengths using the index data should be found to be reasonably constant at each temperature. This is in fact the case with our results as can be seen from tables **41** to **42**, and this constancy of Lorentz field factors is a merit of Neugebauer's approach.

The field anisotropy (L_o- L_e) is a measure of a deviation from the spherically symmetric field at the site of the molecule. As can be seen from tables **41,** (L_o - L_e) increases with an increase in (t_c-t), that is, it decreases as temperature increases from the K-N transition point to the N-I transition temperature. This is expected because in the isotropic phase the field at the site of the molecule within a liquid crystal sample should be perfectly symmetric owing to the random orientation of the molecules whereas the deviation from spherical symmetry should be maximum in the crystalline phase owing to the perfectly parallel alignment of the molecules in the phase. Hence the decrease of (L_o - L_e) from the crystalline to the isotropic phase, which is confirmed by the results from Neugebauer's approach, is an indication of the validity of this approach.

As (L_o - L_e) values are practically the same at same relative temperatures for hexanoate, heptanoate and undecyclenate, it can be concluded that the field anisotropy, that is the deviation from the spherical symmetry of the field at the site of the molecule in a liquid crystal sample is practically the same for homologues with same central rigid portions in their molecules. As Vuks' approach is based on the isotropic polarizing field, i.e., spherically symmetric field at the site of the molecule, the field anisotropy does not arise at all as it assumes molecular distribution to be isotropic. The anisotropic molecular distribution is naturally expected in the liquid crystalline phase otherwise it cannot be birefringent. Thus Neugebauer's approach which is based on anisotropic polarization field should be more realistic and more practical than Vuks' approach.

CHAPTER 5

5.0. CONCLUDING REMARKS AND RECOMMENDATIONS

5.1. INTRODUCTION.

This section discusses briefly the highlights of the conclusions arrived at by a few earlier investigators concerning the relative merits of Neugebauer's and Vuks' approaches. Thus, the aspect of comparison between these two approaches is not entirely new. As early as 1971, Derzhanski and Petrov and Dunmur in 1972 had recognized that the original Vuks' formulae for the local field which is the basis of Vuks' approach (Equation **2.15** of chapter **2**) developed by Chandrasekhar et al has no theoretical justification. This according to them was essentially because the positional order of molecules in the crystalline and nematic phases is anisotropic. Hence the local field must also be anisotropic and consequently they took into account the anisotropic nature of the polarization field. However, as pointed out in chapter **2**, proper theoretical expressions for polarizabilities and other parameters were not given by them.

Horn (Horn, R. G.,1978) applied both Neugebauer's and Vuks' approaches for the calculation of the order parameter 'S' in the nematic phase of 5CB (cyanobiphenyl) and compared the results obtained from the two approaches. Similarly, Parneix and Chapoton (1977) employed the two approaches for the calculation of polarizabilities from the experimentally determined birefringence and density data of 4,4'-di-n-alkoxy azo-benzene. They compared the results obtained with the theoretically calculated values of polarizabilities based on tension additivity of bond polarizability components, cosidering the various conformations of the alkyl end chains of the compound. Both Horn and Parneix *et al* remarked that Neugebauer's approach gives better agreement with the theory.

Van Hecks *et al* (1978) calculated the polarizabilities and orientational order parameter of a nematogenic compound namely trans-4-ethoxy-4'-n- alkanoyloxyazobenzene using the two aproaches and reported that Neugebauer's approach is better suited than Vuks' approach for such calculations. None of these earlier investigastors made an elaborate investigation and comparative study. Hence, inspite of their remarks, investigators went on employing Vuks' approach for their calculations. Therefore, it was absolutely essential to make an elaborate comparative study of the two approaches, which has been done in this investigation.

5.2. AN ADDITIONAL FEATURE

In this section an additional feature which emerged from our calculations but was not presented in previous chapters is discussed.

From tables **17** to **21** of chapter **4**, it is clear that the numerical values of the effective polarizabilities α_e and α_o that were calculated on the basis of the two approaches are significantly different. However, the orientational order parameters calculated from either set of values using the expression $S=(\alpha_e-\alpha_o)/(\alpha_{||}-\alpha_\perp)$ agrees reasonably well in the case of a few compounds and disagrees in the case of a good number of compounds. In the case of a few nematic compounds for which values for orientational order parameter have been obtained from other techniques such as NMR splittings and Raman band analysis, it was found that orientational order parameter, S_N obtained from Neugebauer's approach is in much better agreement than the ones obtained from Vuks' approach. Further, the calculated values of α_e, α_o, $\alpha_{||}$ and $\alpha_\perp$ can be used to calculate the Lorentz field factors L_e, L_o, $L_{||}$ and $L_\perp$ respectively using equations (2.43) and (2.44) of chapter **2** and (4.18) and (4.19) of chapter **4**. These expressions are a consequence of Neugbauer's approach. However, Vuks' approach does not give such expresions for Lorentz field factors as it assumes an anisotropic polarization field.

Equation (2.43) of chapter **2** was used to calculate the L_e values for four wavelengths viz. 5461A^0, 5780A^0, 5893A^0 and 6563A^0 at same (t_c-t) for PBPA and hexanoate by substituting the values of α_e obtained from Vuks' aproach in the equation. Similar calculations have also made by substituting values of α_e from Neugebauer's approach. The resulting values of L_e obtained from the two approaches for both compounds are presented in table **46** below. As L_e depends on molecular distribution, the L_e values calculated for different wavelengths at any given (t_c-t) should be equal. The subscripts N and V in L_e, indicate that Neugebauer's and Vuks' polarizabilities respectively were used in its calculation.

An examination of Table **46** clearly shows that L_e values obtained from Neugebaner's polarizabilites are resonably constant at same (t_c-t) for a given compound whereas that is not the case for L_e values obtained from Vuk's polarizabilities. This is of course one of the limitations of Vuk's approach.

Table 46: Values of L_e for PBPA and hexanoate for various wavelengthscalculated using α_e values from Neugebauer's and Vuks' approaches.

Wavelength (A^0)	Values of Lorentz field factor L_e.			
	PBPA at $(t_c-t) = 6.8^0C$		Hexanoate at $(t_c-t) = 44.5^0C$	
	$(L_e)_V$	$(L_e)_N$	$(L_e)_V$	$(L_e)_N$
5461	0.305	0.319	0.283	0.274
5780	0.311	0.319	0.286	0.275
5893	0.312	0.318	0.287	0.275
6563	0.313	0.319	0.289	0.275

5.3. SUMMARY OF THE CONCLUSIONS

On the basis of the several calculations of the various parameters made in chapter **4** , certain significant conclusions were arrived at and are summarized below;

1. The mean polizability $\bar{\alpha}$ obtained from Neugebauer's approach is calculated using Lorentz - Lorenz expression (equation 2.47 of chapter **2**) which gives exactly the same value for $\bar{\alpha}$ at each temperature for a given compound and for a given wavelength whereas the calculation of $\bar{\alpha}$ in Vuk's approach is based on Born's relation (equation 2.2 of chapter **2**). The use of Born's relation does not give exactly the same values of $\bar{\alpha}$ at various temperature for a given compound and wavelength. However since constancy of $\bar{\alpha}$ values at various temperature for a given compound and wavelength is a must, then Neugebauer's approach has an edge over Vuk's approach in this respect.
2. Born's relation is of course a versatile relation as far as its utility is concerned and is derivable from Neugebauer's relations (See Appendix **V**). Infact Neugebauer's approach shows that Born's relation is a particular form of a more general Neugebauer's formula.
3. The effective polarizabilities α_e and α_o calculated using Neugebauer's approach are significantly different from those obtained from Vuk's approach. However, as shown in section **5.1** of this chapter, L_e and L_o values obtained from Neugebauer's approach are more realistic than those calculated from Vuk's approach.
4. The polarizabilities, $\alpha_{\parallel}$ and $\alpha_{\perp}$, parallel and perpendicular to the long axis of the molecule

calculated for Neugebauer's approach are more reliable than those from Vuk's approach. This is because optical anisotropy $(\alpha_{\parallel} - \alpha_{\perp})_V$ based on Neugebauer's approach is in better agreement with $(\alpha_{\parallel} - \alpha_{\perp})$ values obtained from NMR approach (Section **4.5.2** of chapter 4). Since NMR spectrosiopy is a standard techique it may be concluded that Neugebauer's values of optical anisotropy are certainly more reliable than Vuks' based values.

5. The orientational order parameter calculated from Neugabauer's approach using the expression $S = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$ is in better agreement with orientational order parameter obtained from NMR splittings and Raman band analysis (see section **4.7.5** of chapter 4: tables **36** and **37**).

6. The orientational order parameters calculated using either of the two approaches clearly shows that the trend of variation of S with temperature is similar for compounds with same central rigid core but varying end chains (see figures $\mathbf{E_4}$, $\mathbf{E_5}$, $\mathbf{E_8}$ and $\mathbf{E_9}$ of Chapter **4**). However, the deviations from this characteristic are more frequent for Vuks' based S factors than those obtained from Neugebauer's approach. Thus in this respect, Neugebauer's approach once again has an edge over Vuks' approach. Further, a detailed examination of tables **24** to **28** of chapter 4 shows that S factor for same $(t_c - t)$ decreases with increase in the chain length. A higher value of S being a measure of a higher degree of alignment of molecules, it may be concluded that the alignment in homologues become more and more random with increases in the length of the chain. From the point of view of display utility, its is clear that a higher and higher power is needed to align the molecules as the homologous series is ascended. Such a significant conclusion of course is a consequence of Neugebauer's approach.

7. The results depicted in tables **34** to **38** of chapter **4** indicate that $(L_o - L_e)$ increases with $(t_c - t)$, that is field anisotropy decreases as temperature within the mesomorphic range increases. This is expected because the degree of molecular order decreases as temperature in the nematic phase increases and since anisotrophy of the physical characteristics of LCs is due to the long-range order of the molecules, then it (field arisotrophy) should also decrease. Further a detaled examination of table **40** shows that field anistotropy $(L_{\perp} - L_I)$ in the crystalline phase increases with the length of the end chains. In the display devices, larger values of optical and field aristotropies means that the oriented samples are more and more sensitive to changes in

the applied eletric field. ($L_{\perp}$ -$L_{\parallel}$) being a measure of this sensitivity, then the compounds become more and more sensitive to changes in applied eletric fields with increase in chain length, that is as the homologous series is ascended. This is also a consequence of Neugebauer's approach.

8. Neugebauer's approach gives a relationship between Lorentz field aristrophy ($L_{\perp}$ -$L_{\parallel}$) and the orientational order parameter S and shows that S increases with the molecular length (see section **2.2.5** of chapter **2**). This is an experimental fact, which is again an outcome of Neugebauer's approach.

On the basis of the conclusions that have been discussed above it clear that Neugebauer's approach is more realistic, broadbased and well suited for elaborate studies on the nematic liquid crystals and for drawing significant conclusions regarding the various optical properties of nematic LC compounds.

5.4. RECOMMENDATIONS

Based on the conclusions that were arrived at above regarding the two approaches, namely Neugebauer's and Vuks' approaches and their relative merits, the following are a summary of the recommendations;

1. A comparative study of the two approaches and their relative merits be extended to more nematic homologues in order to arrive at more comprehensive conclusions. Whenever data on birefringence and density are available, such an extension is easier, otherwise experimental determinations of refractive indices and densities have to be taken up.
2. It is also important to extend such a study to the case of smectics and cholesterics in order to determine whether similar conclusions can be arrived at regarding the relative merits of the two approaches and the various optical parameters and their variation with temperature, chain length and so forth.
3. The case of nematic mixtures is very fascinating since a mixture of the two nematics with same central rigid portions or of a nematic and a cholesteric can drastically change the transition temperatures and mesomorphic ranges of liquid crystal compounds. In order to explore the possibility of choosing suitable LCs for the purpose of utility in display devices which includes a mixture of LCs, it is important to determine which approach is more suitable

for calculating the various optical parameters.

4. The most important recommendation concerns a third approach. As was pointed out in chapter 2, the merits and demerits of Guest Dye Dichroism technique for the calculation of orientational order parameter were not fully explored. Blinov *et al* (1985) gave a simple expression for the orientational order parameter which is given by equation (2.55) of chapter 2. As defined, $N^* = gN$ in which g is a correction factor and $N = D_e/D_o$ where D_e and D_o are optical densities for two polarization directions of light incident in a suitable nematic matrix. Blinov etal have calculated 'g', the correction factor by using the simple expression $g=n_e/n_o$. Dunmur (1971) modified the expression for g to;

$$g = \frac{n_e}{n_o}\left[\frac{1 + L_{xx}(n_o^2 - 1)}{1 + L_{zz}(n_e^2 - 1)}\right]$$

where L_{xx} and L_{zz} are the Lorentz field factors for which he has also obtained expressions. Even this expression by Dunmur has a number of limitations. It is therefore recommended that Neugebauer's approach be used to obtain a more general expression for 'g' which should involve not only a factor corresponding to the indices n_e and n_o but a more involved factor taking into account the anisotropy of the local field, the dye length and its exact molecular structure as well as the length and molecular structure of the nematic matrix in which the dye molecule is dissolved.

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APPENDICES

APPENDIX I

Table 1: Refractive index in the crystalline phase of hexanoate

Wavelength (A^0)	Refractive indices		
	n_p	n_m	n_g
5461	1.498	1.549	2.066
5780	1.493	1.546	2.036
5893	1.491	1.544	2.025

Table 2: Refractive index in the crystalline phase of heptanoate

Wavelength (A^0)	Refractive indices		
	n_p	n_m	n_g
5461	1.494	1.540	2.001
5780	1.493	1.537	1.966
5893	1.493	1.536	1.958

Table 3: Refractive index in the crystalline phase of undecyclenate

Wavelength (A^0)	Refractive indices		
	n_p	n_m	n_g
5461	1.466	1.522	1.931
5780	1.465	1.516	1.898
5893	1.465	1.514	1.891

Table 4: Refractive indices in the nematic and isotropic phases of hexanoate

$(t_c - t)^0C$	5461A^0		5780A^0		5893A^0		6563A^0	
	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
-0.5(isot)	1.600		1.587		1.584		1.570	
4.0	1.753	1.528	1.731	1.520	1.728	1.519	-	-
8.0	1.768	1.522	1.747	1.516	1.740	1.515	-	-
12.5	1.781	1.578	1.759	1.512	1.752	1.511	1.726	1.505
19.5	1.799	1.574	1.776	1.509	1.768	1.507	1.742	1.500
24.0	1.809	1.572	1.786	1.507	1.778	1.505	1.751	1.498
28.5	1.809	1.511	1.795	1.506	1.788	1.504	1.760	1.497
32.0	1.825	1.510	1.801	1.505	1.794	1.503	1.766	1.497
37.0	1.834	1.509	1.809	1.504	1.803	1.502	1.774	1.496
44.5	1.849	1.508	1.824	1.503	1.817	1.502	1.785	1.495
48.5	1.855	1.508	1.829	1.505	1.822	1.502	1.791	1.495

Table 5: Refractive indices in the nematic and isotropic phases of heptanoate

$(t_c - t)^0C$	5461A^0		5780A^0		5893A^0	
	n_e	n_o	n_e	n_o	n_e	n_o
-1.0(isotr)	1.589		1.577		1.570	
4.0	1.723	1.527	1.703	1.519	1.690	1.517
6.0	1.735	1.522	1.712	1.516	1.708	1.514
9.0	1.746	1.518	1.724	1.512	1.719	1.510
13.0	1.758	1.514	1.737	1.509	1.730	1.507
19.0	1.773	1.511	1.752	1.505	1.745	1.503
21.5	1.779	1.510	1.758	1.504	1.750	1.502
25.0	1.787	1.508	1.765	1.503	1.757	1.501
28.0	1.795	1.507	1.771	1.502	1.753	1.500
34.0	1.804	1.506	1.781	1.501	1.771	1.499
39.0	1.815	1.505	1.789	1.500	1.785	1.499

Table 6: Refractive indices in the nematic and isotropic phases of undecyclenate

$(t_c - t)^0C$	5461A^0		5780A^0		5893A^0	
	n_e	n_o	n_e	n_o	n_e	n_o
-0.5(isotr)	1.575		1.565		1.562	
2.0	1.691	1.524	1.674	1.516	1.668	1.514
6.0	1.710	1.514	1.694	1.508	1.685	1.506
9.5	1.724	1.510	1.707	1.504	1.699	1.502
14.5	1.739	1.506	1.722	1.501	1.715	1.499
20.5	1.754	1.503	1.736	1.499	1.730	1.497
25.0	1.764	1.505	1.745	1.498	1.739	1.496
30.0	1.775	1.501	1.755	1.497	1.749	1.496
35.0	1.785	1.501	1.764	1.497	1.753	1.495
40.0	1.795	1.500	1.773	1.496	1.767	1.495
44.0	1.803	1.500	1.780	1.496	1.773	1.494

Table 7: Refractive indices in the nematic and isotropic phases of PBPA

$(t_c - t)^0C$	4358A^0		5461A^0		5780A^0		5893A^0	
	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
-0.1 (isotr.)	1.630		1.585		1.578		1.576	
4.6	-	-	1.692	1.542	1.677	1.537	1.676	1.536
6.8	1.788	1.568	1.707	1.538	1.693	1.534	1.691	1.532
10.2	1.806	1.562	1.722	1.533	1.710	1.629	1.706	1.528
15.6	1.826	1.556	1.736	1.529	1.725	1.524	1.721	1.523
22.6	1.843	1.552	1.749	1.526	1.738	1.521	1.734	1.520
27.3	1.851	1.550	1.752	1.524	1.745	1.520	1.742	1.519
30.6	1.856	1.549	1.761	1.524	1.749	1.519	1.746	1.518
34.6	1.863	1.548	1.767	1.523	1.755	1.519	1.751	1.518
37.6	1.867	1.547	1.771	1.623	1.758	1.518	1.755	1.517
42.3	1.875	1.546	1.778	1.523	1.764	1.518	1.761	1.517

Table 8: Refractive indices in the nematic and isotropic phases of BBPA

$(t_c - t)^0C$	$4358A^0$		$5461A^0$		$5780A^0$		$5893A^0$	
	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
-0.2 (isotr.)	1.630		1.585		1.578		1.576	
3.2	-	-	-	-	1.665	1.528	1.665	1.526
6.0	1.769	1.555	1.691	1.527	1.680	1.522	1.678	1.520
10. 9	1.793	1.546	1.712	1.520	1.700	1.515	1.695	1.514
13.5	1.802	1.542	1.720	1.517	1.708	1.513	1.703	1.512
18.0	1.815	1.539	1.730	1.514	1.718	1.510	1.713	1.509
22.5	1.825	1.537	1.737	1.513	1.726	1.509	1.721	1.508
25.9	1.832	1.536	1.742	1.512	1.731	1.508	1.726	1.507
31.4	1.841	1.535	1.749	1.511	1.737	1.507	1.734	1.506
35.0	1.847	1.532	1.753	1.511	1.741	1.507	1.738	1.506

APPENDIX II

Bond lengths, Bond and Molecular polarizability data for 5893A0 for selected bonds and groups

Bond/group	Bond length (A^0)	Polarizabilities (in units of 10^{-24} cm^3)			Ref.+
		α_l	α_t	$\bar{\alpha}$	
C - H	1.54	0.82	0.60	0.673	1
C - C(arom.)	1.39	2.25	0.48	1.07	2
C = C	1.34	2.90	1.07	0.68	2
C(aro)-C(ali)	1.43	1.40	0.30	0.667	3
C = O	1.22	2.0	1.00	1.333	3
C - N	1.47	1.38	0.22	0.607	3
C - C	1.54	0.97	0.26	0.497	4
C - O	1.43	1.46	0.17	0.603	5
C = N	1.29	-	-	1.429	5
N = N	1.24	-	-	2.343	6
C_6H_6	-	12.31 (in plane)	6.35 (normal to plane)	10.32	7

+ References for these bond and molecular data.

1. Bunn and Dauberry, 1954
2. Denbigh, 1940 ; Bunn, 1961.
3. Le Fevre *et al*, 1972.
4. Condon and Odishaw, 1958.
5. Vogel *et al*, 1952
6. Rao *et al*, 1970.

APPENDIX III

Refractive index and density data in the nematic and isotropic phases of valerate

$(t_c - t)^0C$	Density ρ	5461A^0		5780A^0		5893A^0	
	(gm/cm^3)	n_e	n_o	n_e	n_o	n_e	n_o
- 0.8 (liquid)	1.053	1.604					
1.0	1.058	1.747	1.540	1.722	1.533	1.714	1.531
2.0	-	1.759	1.536	1.783	1.530	1.726	1.527
4.0	1.062	1.771	15.31	1.744	1.525	1.737	1.522
10.0	1.068	1.793	1.524	1.767	1.518	1.759	1.516
15.5	1.074	1.810	1.520	1.784	1.514	1.777	1.512
23.5	1.080	1.827	1.517	1.801	1.511	1.794	1.509
30.0	1.086	1.839	1.516	1.813	1.510	1.806	1.508
35.5	1.090	1.848	1.515	1.822	1.509	1.805	1.507
41.0	1.092	1.855	1.514	1.830	1.508	1.821	1.506
48.0	1.095	1.862	1.513	1.836	1.507	1.829	1.505

APPENDIX IV

Derivation of Born's relation from Vuks' approach.

In Vuks' approach the polarizabilities α_e and α_o are given by equations (2.23) and (2.24) respectively of chapter **2**. The isotropic polarizability is then given by $\alpha = (\alpha_e + 2\alpha_o)/3$.
On substituting for α_e and α_o from the two equations above, the isotropic polarizability is obtained as;

$$\bar{\alpha} = \frac{3M}{4\pi N_{LC}} \left[\frac{n_e^2 - 1 + 2n_o^2 - 2}{3(\bar{n}^2 + 2)}\right]$$

which may be written as;

$$\bar{\alpha} = \frac{3M}{4\pi N_{LC}} \left[\frac{\frac{n_e^2 + 2n_o^2}{3} - 1}{(\bar{n}^2 + 2)}\right]$$

But

$$\frac{(n_e^2 + 2n_o^2)}{3} = \bar{n}^2$$

Therefore;

$$\bar{\alpha} = \frac{3M}{4\pi N_{LC}} \left[\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right]$$

which is Born's relation.

APPENDIX V

Derivation of Born's relation from Neugebauer's approach.

The following relations are obtainable from Neugebauer's approach;

$$n_e^2 - 1 = 4\pi\chi_e(1 - 4\pi L_e\chi_e)^{-1}$$

$$n_o^2 - 1 = 4\pi\chi_o(1 - 4\pi L_o\chi_o)^{-1}$$

and

$$\bar{\chi} = \frac{(\chi_e + 2\chi_o)}{3}$$

Let;

$n_o^2 = \bar{n}^2 - u \quad \chi_e = \bar{\chi} + 2v \quad L_e = \frac{1}{3} - \frac{2w}{4\pi}$ where u, v and w are positive quantities.

From the definition of n^2 and the fact that $L_e + 2L_o = 1$ it follows that $n_e^2 = n^2 + 2u$, $\chi_o = \chi - v$ and $L_o = 1/3 + w/4\pi$. On substituting for the relevant quantities in either of the first two equations above and simplifying leads to the following expression;

$$\bar{\chi} = \frac{3}{4\pi}\left(\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2}\right)\left[1 - \frac{q}{3(\bar{n}^2 - 1)}\right]$$

where $q = -6uvw - 6uw\chi + 8\pi uv - 6(n^2 - 1)vw$.

In the Lorentz field approximation $L_e = L_o = 1/3$ and therefore $w = 0$ and hence Born's relation results. Even in the case of anisotropic internal field, the term $8\pi uv$ is approximately equals to the sum of the negative terms, so that q is practically zero.This can be verified for any compound and hence Born's relation results.