CHAPTER 1

INTRODUCTION

1.1 Liquid Crystals

Liquid crystals represent states of matter intermediate between the crystalline solid and the isotropic liquid. While possessing liquid-like properties such as viscosity and surface tension, they are strongly anisotropic and exhibit many crystalline properties such as optical birefringence, elasticity, etc.

The first observations of liquid crystalline behaviour, also called mesomorphism, were made by Reinitzer[1] and Lehmann.[2] Several thousands of organic compounds are now known to form liquid crystals (mesophases).

Till recently, only long rod-like molecules, with a high degree of geometrical anisotropy, were known to exhibit mesomorphism. However, in 1977 Chandrasekhar et al[3] showed that disc-like molecules can also exhibit liquid crystalline behaviour.

Liquid crystals can be classified into two categories - thermotropic and lyotropic. In thermotropic mesomorphism, the crystalline solid transforms to one or more mesophases solely by the action of heat. Lyotropic mesophases are obtained, on the other hand, by dissolving the material in certain solvents. This study deals only with thermotropic liquid crystals.

The nature of molecular ordering in liquid crystals differs from that in crystalline solids. The latter is characterised by long range three dimensional positional ordering. In liquid crystals there may be no long range positional ordering at all, or it may be restricted to one or two dimensions; in addition, there is long range orientational ordering of the molecules. In contrast, isotropic liquids exhibit no long range order of any kind. Based on the nature of molecular ordering exhibited, liquid crystals have been divided[4] into three types - nematic, cholesteric and smectic.

(a) Nematic liquid crystals

These are characterised by a high degree of long range orientational order, but no long range translational order. The long axes of the molecules tend to align themselves parallel to each other (figure 1.1a). The average direction of alignment may be characterised by the unit vector $\hat{n}$, called the director. The nematic phase is optically uniaxial and strongly birefringent.

(b) Cholesteric liquid crystals

These are essentially of the nematic type except that they are composed of optically active molecules. Hence the director acquires a twist about an axis normal to its plane and the resulting structure has a spatial periodicity.

(c) Smectic liquid crystals

Smectic mesophases are characterised by a layered arrangement of the molecules. Their fluidity is due to weak interlayer coupling which allows any two layers to slide over each other. Various molecular arrangements, with differing degree of ordering, are possible within each layer and this gives rise to different smectic modifications.

In the smectic A phase, the molecules possess a long range orientational order within each layer, but no long range positional order (figure 1.1b). The director $\hat{n}$ is normal to the layer plane and the phase is optically uniaxial.

The smectic C phase is very similar to the smectic A phase except that the molecules within each layer are tilted with respect to the layer normal (figure 1.1c). The tilt angle is often temperature dependent.[5] The phase is optically biaxial.

FIGURE 1.1

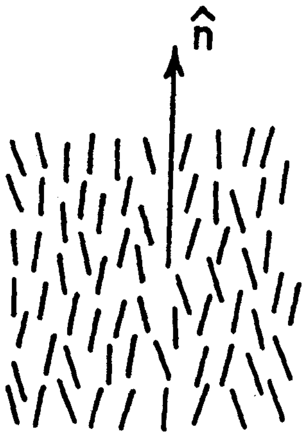
Schematic representation of molecular

order in some liquid crystals

(a) Nematic (b) Smectic A (c) Smectic C

$\hat{n}$ denotes the director.

(a)



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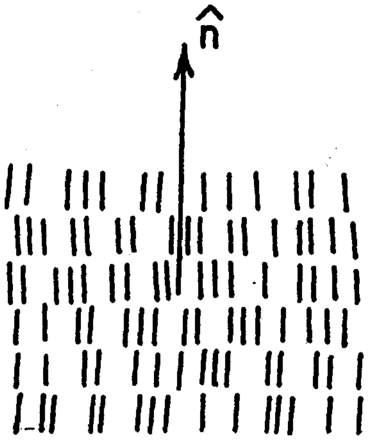

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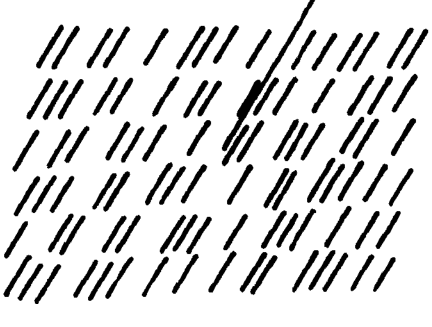

Two distinct types of smectic B phase are now known.[6,7] In one of them the molecules are stacked in 'hexatic' layers MOB in-plane oh@&?* range positional correlation and long range three dimensional six-fold 'bond-orientational' order. In the other, the molecules are arranged upright in a three dimensional crystal, hexagonal lattice.

The smectic H phase has a three dimensional monoclinic crystalline order.[6,7] There are two types of this; a > b in one and a < b in the other.

In addition to these three, several other smectic modifications have been identified.

Mesophases which occur during both heating and cooling are said to be enantiotropic while those appearing only on cooling are said to be monotropic.

When a liquid crystalline sample is contained between two glass plates, a large number of domains will be formed. Each domain is well ordered within itself and can be characterised by its own director. However, the directors of different domains will all be random. The domains can be aligned in a common direction by various techniques including the application of electric and magnetic fields. Special treatment of the glass plates also results in such preferential alignment. If the molecules are aligned parallel to the container walls the alignment is said to be 'homogeneous' (figure 1.2a). If the molecules are aligned perpendicular to the walls the alignment is said to be 'homeotropic' (figure 1.2b).

The coexistence of characteristics common to both solids and liquids in mesophases gives rise to a variety of interesting physical properties.[8] In the present study we are primarily concerned with the application of some techniques of vibrational spectroscopy to the study of a few thermotropic liquid crystals of rod-like molecules.

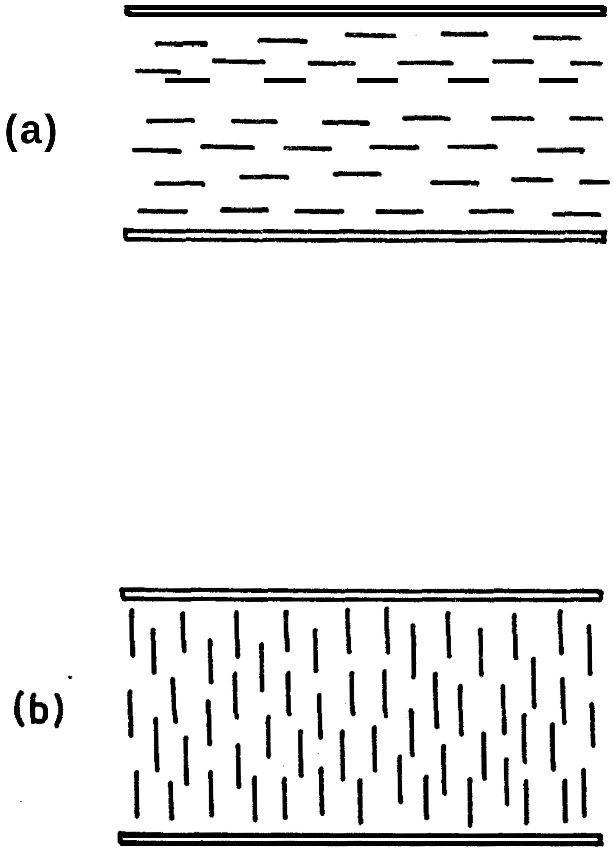

FIGURE 1.2

Schematic representation of molecular alignment be [illegible] e [illegible] of windows. (a) Homogeneous alignment (b) Homeotropic alignment.

1.2 Vibrational Spectra of Liquid Crystals

The vibrational spectra of molecules in general extend over the range 4000 - 10 cm^{-1}. This can be broadly divided into two regions:

i) 4000 to ~200 cm^{-1}, the region of internal modes, where the vibrations are mostly intramolecular in origin, and

ii) Below ~200 cm^{-1}, the region of external (lattice) modes, where intermolecular vibrations are predominant.

Infrared and Raman spectroscopy are the two major techniques which have been employed very extensively to probe these two regions. These techniques are complementary to one another. Infrared-active modes arise due to changes in molecular dipole moment while Raman-active modes arise due to changes in molecular polarisability. The two are mutually exclusive if the molecule has a centre of symmetry as is the case with many simple molecules. However, the complex organic molecules which give rise to mesomorphism possess almost no symmetry elements, so all vibrational modes are allowed in both infrared and Raman spectra. For the same reason, the interpretation of the spectra also becomes extremely difficult.

This situation in respect of complex molecules is altered to some extent by the local symmetry they often possess within specific groups of atoms. These 'group frequencies', identifiable through systematic studies of a large number of chemically related species, are often useful in interpreting vibration spectra and in obtaining structural information about the molecule. However, there is still the serious complication caused by overlapping bands to contend with. The probability of band overlap is high since the number of vibrational modes (3N-6), in a molecule containing N atoms, is very large for mesomorphic compounds.

Apart from selection rules and band frequencies, other spectral features which can yield useful information about molecular and structural characteristics of mesomorphic compounds are intensities, shapes and polarisation of the vibrational bands. They are generally temperature and phase dependent and can often be correlated with the nature of the crystal-mesophase transition, [illegible] ordering and [illegible] molecular interactions in mesophases, molecular conformational changes and the dynamics of molecular reorientations.[9-12]

Despite the considerable difficulties and uncertainties associated with the application of vibrational [illegible]scopic techniques to the study of liquid crystals, sustained effort in this field has not been lacking so far.[12] The greatest interest has been in the homologous para azoxyanisole (PAA) series an extensive study of whose infrared spectra was first carried out by Maier and Englert.[13] This work also included dichroic studies of homogeneously aligned nematic samples. Amer and Shen[14] studied the Raman spectra of four members of the PAA series in the region covering both external and internal modes. Bulkin and coworkers[15-17] made extensive studies of both the Raman and far-infrared spectra of PAA. N-(p-methoxybenzylidene)-p'-butylaniline (MBBA) was also the subject of extensive investigations.[18-21] A significant finding from these studies is the occurrence of marked pretransitional effects at the crystal-nematic phase transition. They signify a decrease in order in the crystalline phase as the crystal-nematic transition is approached.

In the internal modes region, vibrations of the hydrocarbon tail have received great attention.[10,22] By studying the PAA homologous series, Schnur[23] has identified the interesting accordion-mode of the end chain. Several studies have focussed on possible conformational changes in the end chains in different mesophases as also at the crystal-nematic transition.[23-26]

Measurements of infrared dichroism have been used to determine the order parameter $\langle P_2(\cos\theta)\rangle$ of mesophases.[27-29] Of considerably greater difficulty is the measurement of polarisation of Raman bands in the mesophases. Nevertheless, they have been attempted with success and considerable interest.[30,31]

This thesis deals mainly with several experimental studies, both qualitative and quantitative, on the vibration spectra of the different phases of a number of liquid crystalline materials.

The principal instruments employed in the experimental studies reported in this work are a Polytec FIR-30 Far-infrared Fourier Spectrometer, a Cary-81 Raman Spectrometer with modified external optics employing a Spectra-Physics He-Ne Laser as source, a Leitz double beam prism spectrometer and a Perkin-Elmer DSC-2 Differential Scanning Calorimeter. Broad details of these instruments and the experimental techniques employed are discussed in chapter 2.

The complex molecular structure of most liquid crystals makes it likely that their far-infared absorption might arise from overlapping contributions both due to intramolecular motion and the permanent dipole moment of the molecules. Experimentally, it can be quite difficult to discriminate between these factors and assess their relative importance solely from the spectra of unrelated mesogens. A systematic study of several homologues within a given series, as a function of end chain length, should lead to a better understanding of the spectra and their dependence on the molecular structure. While this approach is evident in past investigations of several properties of liquid crystals, including their Raman and near-infrared spectra, the far-infrared studies so far have only dealt with specific mesogens without any attempt to correlate the spectral changes within a series with the corresponding molecular structure.

In chapter 3, we present the results of a far-infrared study of the first seven members (C_1 - C_7) of the well known homologous PAA series in the range 30-210 cm^{-1}. The various factors that can possibly contribute to the far-infrared absorption in the fluid phases of these mesogens are considered. It is found that Poley absorption[32] may be the dominant factor in C_4 – C_7, but it cannot account for the distinct changes associated with the central band in C_1 – C_3. The observed decrease in the intensity and the shift in the peak position of this band on going from C_1 to C_2 strongly suggest that this band originates from the torsion of the end alkoxy groups about the phenyl-oxygen bonds. This assignment is also consistent with (i) the virtual disappearance of the central band in C_4 – C_7, (ii) the dichroic behaviour of the band in C_1 in the homogeneously aligned nematic phase, and (iii) the considerably reduced intensity of absorption in the liquid phase of the related mesomorphic compound p,p'-azoxytoluene. We conclude that in the composite absorption profiles due to a superposition of the Poley and torsional bands, the latter contribution becomes increasingly important for the lower homologues of this series.

Chapter 4 deals with a far-infrared and Raman study of the different phases of the smectogen, ethyl-*p*-azoxybenzoate (EPAB). It has two crystalline polymorphs,[33] designated solid I and solid II, that are stable respectively above and below 375 K. Their far-infrared spectra show marked changes in the range 30-160 cm^{-1}. Further, a comparison of the far-infrared spectra in the range 30-210 cm^{-1} shows that the spectrum of solid I resembles that of the isotropic phase, while that of the smectic phase is highly broadened. These results are discussed in terms of the structure, molecular conformation and packing obtaining in the different phases. In the region of the internal modes, the same Raman frequencies are observed in both crystalline polymorphs although relative intensity changes occur for several bands. From a comparison of the Raman band shapes corresponding to the N-O and N=N band stretching vibrations in solid II and solid I, we conclude that in the latter case the reorientations of the azoxy group occur at a rate too slow to affect the vibrational relaxation of these modes.

In chapter 5, we present evidence based on calorimetric, optical texture and infrared spectral studies which strongly indicate that p,p'-di-n-pentyloxy-azoxybenzene exhibit a highly ordered enantiotropic phase below its nematic phase. Hitherto, this phase, observed in the temperature range 341.5 K - 349.5 K on the heating cycle, was believed to be a solid phase. We also examine the nature of the molecular dynamics which might give rise to this mesophase and show that configurational melting[34] of the alkyl end-chains can largely account for the observed enthalpy of the solid-smectic transition.

An experimental determination of the two orientational order parameters $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$, given by

$$\langle P_2(\cos\theta)\rangle = \int_{-1}^{+1} P_2(\cos\theta) f(\cos\theta) d(\cos\theta)$$

and

$$\langle P_4(\cos\theta)\rangle = \int_{-1}^{+1} P_4(\cos\theta)f(\cos\theta)d(\cos\theta)$$

$f(\cos\theta)$ is the molecular orientation distribution function, is of considerable interest from the standpoint of the statistical theories of molecular order in liquid crystals.[35] While the variation of $\langle P_2(\cos\theta)\rangle$ with both temperature and molecular structure has been studied extensively, little is known about the behaviour of $\langle P_4(\cos\theta)\rangle$. Polarised Raman scattering from both homogeneously and homeotropically aligned liquid crystalline emerged as a major technique for the simultaneous determination of the absolute values of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$.[30] A puzzling result emerging from these measurements is that $\langle P_4(\cos\theta)\rangle$ is negative in some cases, especially wl — a temperature range close to the nematic-isotropic transition.

In chapter 6 we report the results of a combined

Raman and infrared study of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ in the liquid crystalline phases of heptylcyanobiphenyl (7CB) and octyloxycyanobiphenyl (8 OCB) employing the strong, isolated $-C\equiv N$ stretching vibration which lies along the molecular axis in all compounds of the cyanobiphenyl series. The $\langle P_2(\cos\theta)\rangle$ values determined independently by these two techniques compare well with each other and with previous birefringence measurements.[36]

We compare the $\langle P_4(\cos\theta)\rangle$ values of 7CB and 8 OCB with those of the structurally related mesogen pentylcyanobiphenyl (5CB), determined previously.[31] These three mesogens have identical cyanobiphenyl rigid cores, but differ in their alkyl end-chain length. We find a clear decrease in the $\langle P_4(\cos\theta)\rangle$ values with increasing end-chain length. This suggests that molecular flexibility is an important factor in lowering the $\langle P_4(\cos\theta)\rangle$ values well below the predictions based on the mean field theories.

In Appendix A we present a summary of the theoretical background concerning the Raman measurements of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$. The procedure and computation program used to calculate these from the Raman depolarization ratios are given in Appendix B.

Most of the results discussed in this thesis have been published in the following papers:

1. Submillimeter wave absorption in a homologous series of liquid crystals (S.Venugopalan and S.N.Prasad), J.Chem.Phys. 71(12), 5293 (1979).
2. Polymorphism of the smectogen ethyl-p-azoxybenzoate: Far-infrared and Raman study (S.Venugopalan and S.N.Prasad), J.Chem.Phys. 72(7), 4153 (1980).
3. Anomalous smectic mesomorphism of 4,4'-di-n-pentyloxyazoxybenzene (S.N.Prasad, S.Venugopalan and J.Billard), Mol.Cryst.Liquid Cryst.Letters, 49, 271 (1979).
4. Orientational statistics in 8 OCB - Raman and Infrared study (S.N.Prasad and S.Venugopalan) - Proc.Int.Liq.Crystals Conference, Bangalore 1979, Ed.S.Chandrasekhar, Heyden, London (1980) p.381.

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