CHAPTER 1

INTRODUCTION

1.1   Liquid Crystals

During the process of melting, certain organic crystals pass through one or more turbid, fluid phases, before they transform to a clear isotropic liquid. This was first discovered by Reinitzer in 1888.[1] Such intermediate phases possess liquid like properties such as viscosity and surface tension. At the same lime, they exhibit many crystalline properties, i.e. , optical birefringence, dielectric and diamagnetic anisotropies, etc. As their physical properties are intermediate between those of crystals and liquids, such phases are called liquid crystala or mesophases,

The molecular ordering in liquid crystals differs from normal crystals, in which there is long range 3-dimensional positional ordering, and from isotropic liquid in which no long range correlations of any nature exist. The ordering in liquid crystals is only partial and it may be positional., orientational or both.

Two major categories of liquid crystals are known. Thermotropic liquid crystals are those in which the

mesophase is brought about by the action of heat on the crystalline solid. Lyotropic mesophases are obtained, on the other hand, by dissolving the material in suitable solvents. When the concentration exceeds a critical value, the solute molecules tend to become aligned, thus giving rise to the mesophases. This thesis is concerned only with thermotropic liquid crystals.

Based on the nature of the molecular ordering they exhibit, liquid crystals have been divided[2] into three major classes: nematics, cholesterics and smectics.

(a) Nematic liquid crystals: Nematics are characterized by a high degree of long range orientational ordering, but they possess no long range translational ordering. The long axes of the molecules have a tendency to align themselves parallel to each other (Fig. 1.la). The unit vector, $\hat{n}$, along the average direction of alignment is called the director. Experiments show that $\hat{n}$ and $-\hat{n}$ are equivalent and hence $\hat{n}$ is apolar. The nematic phase is optically uniaxial and strongly birefringent.

(b) Cholesteric liquid crystals: Cholesteric liquid crystals are nematic type of liquid crystals with the difference that the molecules are optically active. The director, $\hat{n}(n_x, n_y, n_z)$ as a consequence, follows a helix (Fig. 1.1b) of the farm

$$n_x = \cos(q_0 z + \varphi)$$
$$n_y = \sin(q_0 z + \varphi)$$
$$n_z = 0$$

where a is the direction of the axis of the helix and φ is a phase angle. Phe structure is periodic with a spatial period $L = \pi/q_0$ When L corresponds to the wave-length of visible light, they are found to reflect the light strongly in a Bragg like manner.

(c) <u>Smectic liquid crystals</u>. The smectic mesophase has a layered structure. The interlayer coupling is weak enough to allow the layers to slide past each other, thus giving rise to the fluidity. The various possible molecular arrangements within a layer give rise to the different smectic modifications.

In the smectic A phase, the molecules within each layer have a long range orientational ordering, but no long range positional ordering (Big. 1.1c). The director is parallel to the layer normal. There is an infinite fold symmetry axis normal to the layers and this leads to the uniaxial character of this phase.

The smectic C phase is similar to the smectic A except that the molecules within the layers are tilted with respect to the layer normal (Fig. 1.1d). This phase is optically biaxial. The angle of tilt may remain constant or it may
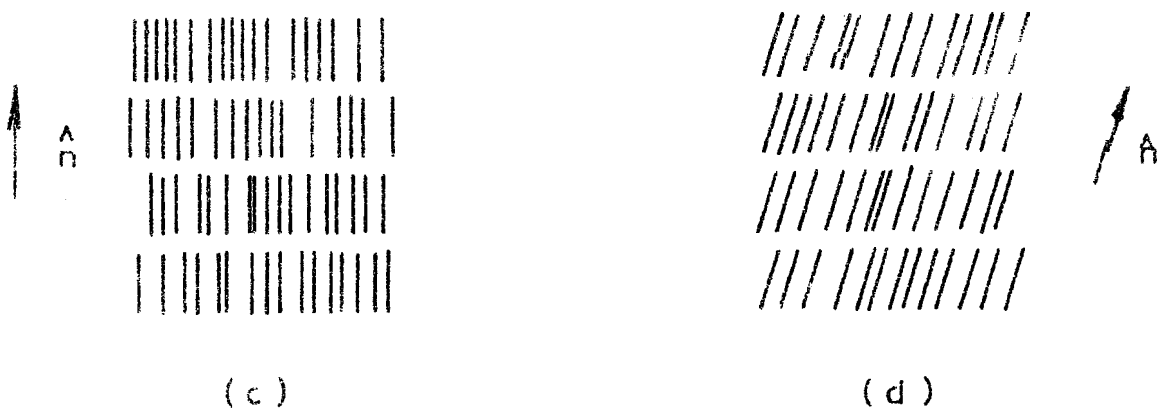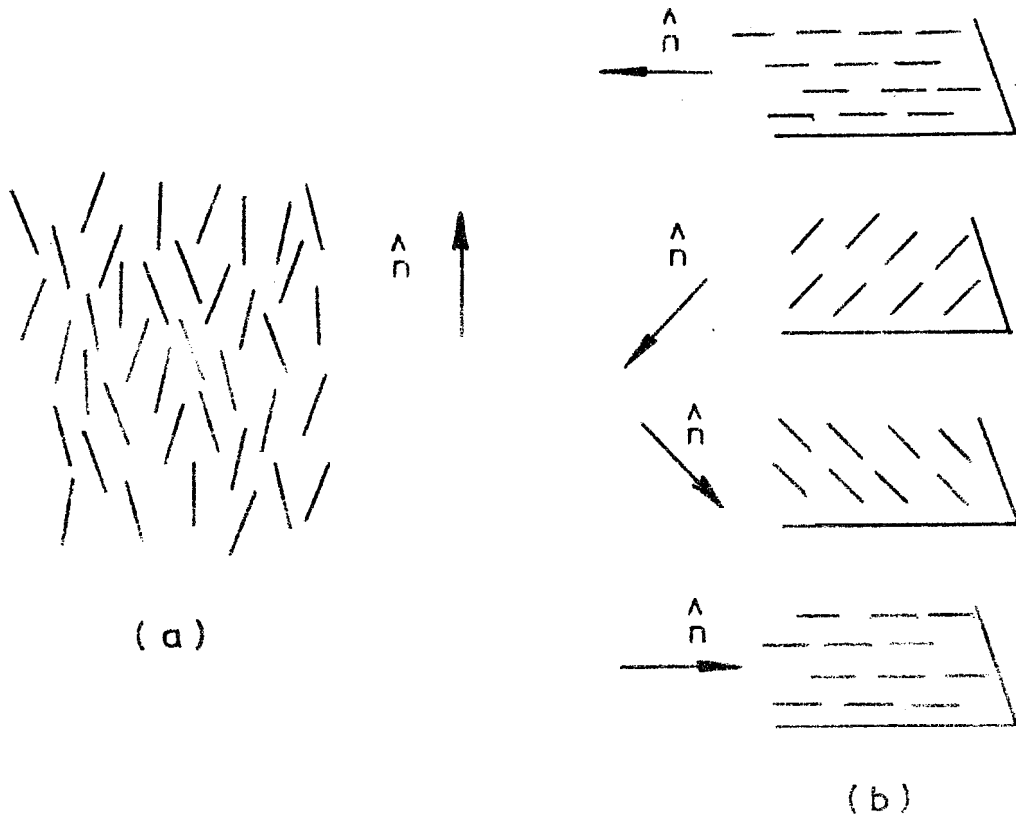
Figure 1.1

Schematic representation of the molecular order in some liquid
crystals. (a) Nematic (b) Cholesteric (c) Smectic A
(d) Smectic B.

vary with temperature.[3,4]

In the smectic B and H phases, the molecules are arranged in a hexagonal lattice within the layers. Hence, these layers possess a *two* dimensional positional ordering. In the B phase, the director is parallel to the layer normal, whereas in the H phase it is tilted.

Other smectic modifications, labeled E, F, G, etc. have been discovered in recent years. Their detailed structure is yet *to* be understood completely.

Some materials exhibit only one mesophase between the solid and Isotropic phases, while some others exhibit more than one. The latter type are said to be polymeso- morphic. Mesophases which occur during both heating and *cooling* are known as enantiotropic, while those that appear only on cooling are termed monotropic.

An essential requirement for the formation of mesophases is that the shape of the molecules should be highly anisotropic. Nematic and smectic behaviour is generally observed in materials having the schematic structure

$$--\left[\underset{}{\bigcirc}\ \ Y\ \right]_n -\bigcirc - Z$$
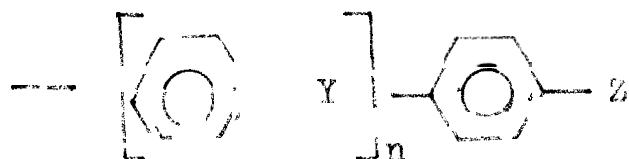
where X and Z are end groups, typically alkyl, alkoxy,

cyano, etc. and Y is a linkage group which is typically azo, azoxy, azomethine, ester, etc. and n = 0,1,2. In some oases, as in 4'-n-alkyl-4-cyanobiphenyls, no linkage group may be present at all. Cholesteric liquid crystals are usually obtained from optically active derivatives of cholesterol.

When a liquid crystalline sample is contained between two untreated glass plates of a cell, a large number of domains can be observed. Each domain is well ordered within itself, but the directors of the different domains are arranged in a random manner. The domains can be aligned in a common direction using relatively low electric and magnetic fields. It is also possible to accomplish this through appropriate treatment of She substrate surfaces. Depending on whether the molecules are parallel or perpendicular to the walls, of the cell, the alignment is referred to as 'homogeneous' or 'homoeotropic' respectively (Pig. 1.2).

The anisotropic nature of the mesophases gives rise to several interesting physical properties such as curvature elasticity, anisotropic viscosity, etc., but we shall not he concerned with those aspects of the subject. They have been dealt with extensively in a number of recent reviews and monographs.[5] We shall confine our attention in this thesis primarily to the applications of infrared techniques to the study of thermotropic liquid crystals.

(a) HOMOGENEOUS
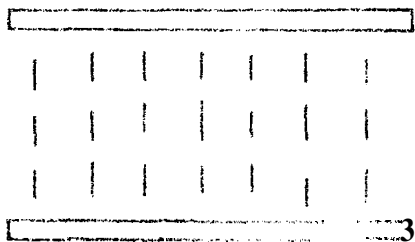
(b) HOMEOTROPIC

<u>Figure 1.2</u>

Schematic representations of (a) homogeneous
alignment (b) homeotropic alignment.

1.2   Vibrational Spectra of Liquid Crystals

The degrees of freedom available to the molecules in the different types of mesophases has been a topic sf considerable interest both from the experimental and theoretical standpoint. Experiments show that in the uniaxial nematic and smectic A phases, the molecules rotate nearly freely about their long axes,[6-8,12] Theoretical models of the more ordered smectic C and smectic H phases presume that in these phases such rotation is absent.[9-11] However recent experiments do not support this view[7,12,13]; in fact the neutron scattering experiments[13] seem to show that body reorientations of the molecules about their long axes can occur even in a smectic H phase with a correlation time $\sim 18 \times 10^{-12}$ sec. Also, the dynamics of the alkyl end chains of mesogenic molecules is another important factor in determining the nature of molecular ordering in liquid crystals. This has been demonstrated by recent experimental[14] and theoretical[15-17] work. In this respect, possible conformational changes that can occur in the end chains in the different mesophases as also at the crystal-liquid crystal transition are of particular interest and several studies have been carried out in this direction,[18-22] Marked pretransition phenomena have also been reported in some cases in the behaviour of the crystalline solid in a temperature interval just

preceding the crystal-mesophase transition.[19,23-25]
These changes were attributed to the occurrence of
increased molecular motion which 'prepares' the crystal
for the transition to the mesophases.

From the foregoing remarks it is evident that the
study of intra and intermolecular vibrations in the
different phases of mesogens is of considerable importance.
The vibrational spectra of several liquid crystals have
been studied from this view point using infrared and Raman
spectroscopic methods,[26-28] but as liquid crystalline
systems are rather complex, the answers to many of the
problems touched upon in the preceding paragraph are by
no means unequivocal. The present study was undertaken
with a view to throwing further light on some of these and
other related problems. We begin with a brief review of
the underlying principles of vibrational spectroscopy.
According to classical theory, a modulated component of
the dipole moment of a physical system will lead to the
emission or absorption of radiation. If the initial state
of the system is described by the wave function ψ_i and
the final state by ψ_f , then absorption or re-emission
of radiation can occur during this transition only if the
matrix element

$$\langle \psi_f | \mu | \psi_i \rangle \neq 0 \quad ,$$

here μ is the **dipole moment** of the system. Only the
creation ox annihilation of a single photon is involved
in this process.   On the other hand, Raman scattering
is the inelastic scattering of photons by excitations in
any medium. An incident photon is destroyed in tbia case,
and a scattered photon merges with a different energy,
the difference in energy corresponding to a characteristic
quantum of excitation of the system, For such a process
to occur, the appropriate condition is that

$$\langle \Psi_f \,|\, \alpha \,|\, \Psi_i \rangle \neq 0 \quad ,$$

where α is the polarizability tensor of the system.
Classically, Raman scattering can occur only when a time-
varying component of the polarizability tensor exists in
the system. The physical origins of infrared absorption
and Raman scattering being different, the two spectra often
yield complementary information. In particular, for systems
which possess a centre of inversion, the two spectra are
mutually exclusive and both are needed to obtain a more
complete picture of the vibrational spectrum.[29]

A free polyatomic, geometrically non-linear molecule
containing N atoms would possess 3N-6 intramolecular normal
modes. Based on the symmetry of the molecule, group theory
enables one *to* classify these normal modes according to the
different irreducible representations of the point group of

the molecule. Such a classification is also useful in predicting the number of infrared and Raman active modes. Specifically, if at least one component of the dipole moment transforms according to the irreducible representation of a given normal mode, that mode will be active in the in infrared spectrum. Similarly, the mode will be Raman active only if its representation is contained in the reduction of the representation corresponding to that of the polarizability tensor.[29]

In the case of complex organic molecules, the large number of atoms and the low symmetry of the molecules can complicate the interpretation of the spectra. However, systematic studies on a large number of chemically related systems have led to the identification of 'group frequencies', i.e., the frequencies corresponding to the vibrations of specific pairs or groups of atoms. Such data are often useful in interpreting a given spectrum and in obtaining structural information about the molecule. The group vibrations which involve pairs of atoms or small groups of them, normally occur in the high frequency region, between 650 cm^{-1} and 3500 cm^{-1}. Hence, this region is often referred to as the 'fingerprint' region of the spectrum. The group vibrations of still larger clusters of atoms, as exist in mesogenic molecules, may be observed at much lower frequencies. While relying on group frequencies to

interpret the spectra of complex molecules, due caution must be exercised as the group vibrations may not necessarily correspond to the normal modes sf the molecule.

Detailed studies of low frequency intermolecular vibrational modes in mesogens has been attempted only since the last Len years. The progress made in this direction is undoubtedly due to the increased availability of improved experimental techniques and spectrometers. Historically, infrared spectra were difficult to obtain in the region below ~ 250 cm^{-1}, mainly due to the lack of strong sources of radiation and sensitive detectors. The use of dispersive spectrometers in this region only aggravates the problem as they are inherently wasteful of radiation and hence yield spectra with poor signal-to-noise ratio. The development of commercial fas-infrared Fourier spectrometers during the last 10 years has contributed vastly to the relative ease and accuracy with which far-infrared spectra can be obtained now-a-days. All the low frequency infrared spectra reported in this thesis were measured using the Yolytec far-infrared Fourier spectrometer. Near-infrared spectra axe relatively easy to obtain with conventional dispersive instruments and a Leitz double-beam spectrograph was used to obtain such spectra. The details of these instruments and the experimental techniques employed during the work reported in this thesis are discussed in chapter 2.

Organic **materials often exhibit solid state**
polymorphism **and this is true of many mesogens too.**[30-34]
However, these transitions acquire, particular importance!
i n mesogenic materials because the changes in the solid phase
may reflect an anticipation of the formation of the mesophase.
X-ray structural data on the solid phases of p-azoxyanisole
(PAA) and p-azoxyphenetole (PAP) show that *tho* molecules
are arranged with their long axes nearly parallel t o each
other in an imbricated structure*[35] Such an arrangement
in a less ordered fashion, with. the molecules acquiring
translational freedom along their long axes, could lead
to the formation of the nematic phase. Recent studies on
cholesteryl esters show that slightly below the transition
to the mesophase, *the* crystalline order decreases markedly
in directions normal Lo the long axes of the molecules.[23]
This was interpreted as an anticipation of the transition
to the mesophase which, of course, exhibits complete
disorder in directions normal to the long axes of the
molecules. From neutron scattering and infrared studies
of the solid phases of PAA and p-methoxybenzylidene-p'-n-
butylaniline (MBBA), the existence of a 'soft solid' region
below the nematic transition temperature has also been
suggested.[24,32,36]

A crystalline solid exhibits characteristic external
or lattice modes which arise due to the coupled rigid body

rotations and translations sf the molecules within a unit cell. These modes, which are of low frequency, are therefore sensitive to the crystal structure. Hence, in the case of pre-transition effects in the solid phase, where the molecules are thought to acquire greater motional freedom, or in polymorphic transitions, where the crystal structure undergoes an abrupt change, it can be expected that these external modes should exhibit striking changes.

In chapter 3, we discuss the results of a study of the temperature dependence of the far-infrared and Raman spectra of the crystalline phase of n-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA). This study reveals the existence of a solid-solid transition 8°C below the solid-smectic A transition. We have confirmed this transition using differential scanning calorimetry. We have also studied the X-ray powder diffraction patterns of these two phases. These show that the crystal structures are different in the two phases. We also discuss the implications of this transition to the occurrence of the mesophase.

In a crystalline solid, wave vector conservation dictates that in a first order vibrational spectrum, only those modes can participate whose wave vector in nearly zero. Such optical modes lie close to the centre of the Brillouin zone of the crystal and are hence referred to as zone-centre modes. For these modes, the characteristic

atomic motions are in phase over a very large number of unit cells within the crystal. Thus, translation can be considered to be the identity element. In order to determine the number of vibrational modes in a first order spectrum and the irreducible representations *to* which they belong, it *is* hence sufficient; *to* consider only the point group symmetry of the crystal and examine the behaviour of the atoms within the primitive cell. This is easily accomplished using straightforward group-theoretical methods.[25,37,38] Further, when one is only concerned with the external modes, it is sufficient to regard the molecules as rigid units. Then the number and site symmetry of the molecules within the primitive cell is ,211 the information needed for determining group theoretically the number of external modes and the irreducible representations to which they belong. A group theoretical analysis of the external modes of CBOOA and terephthal-bis-butylaniline (TBBA) *kine* been carried out and this is discussed in Appendix A.

In chapter 4 we discuss the results of a near and far-infrared spectroscopic study of the phase transitions in CBOOA. We have obtained evidence for conformational changes in the alkyl end chain at the crystal-smectic A transition. We also present the results of a dichroism study in the near and far-infrared regions. *uentative*

assignments have also been made for many of the observed bands.

The lineshape of vibrational bands and their accompanying changes at the different transitions exhibited by mesogens deserve a careful analysis. It is well known that such information can provide much insight into the dynamics of inter and intramolecular motion.[39] The nature of molecular motion is clearly influenced by the local ordering and environment of the molecules and this varies considerably within %he many different types of mesophases that are now known to exist. In recent years neutron scattering[13,24] and NMR[7] have emerged as especially powerful methods for such studies on mesogens. However, these techniques are quite often limited in their ability to probe, in detail, any molecular motion which occurs on a time scale faster than 10^{-11} sec. On the other hand, the infrared and Raman spectra of these systems are potentially capable of discerning molecular rotations or reorientations which occur at much higher frequencies. Despite this advantage, systematic and detailed studies on vibrational bandshapes of mesogens have remained quite scarce so far.[40,41] The rather rich vibrational spectra of mesogens and the consequent difficulty of making unambiguous assignments to the observed bands are perhaps the major reasons for this situation. Nevertheless, such investigations

would be interesting, especially in the case of poly-
mesomorphic materials. For this reason, we carried out
lineshape studies on an absorption band of TBBA and this
has enabled the determination of correlatiom times
characteristic of intramolecular reorientations in the
highly ordered smectic phases of this mesogen. These
results are discussed in chapter 5.

A useful measure of the long range orientational
ordering is the parameter, S, defined as

$$S = \langle P_2(\cos \theta) \rangle = \frac{1}{2}[3\langle \cos^2 \theta \rangle - 1]$$

where θ is the deviation of the long axis of the molecule
from the average direction of orientation and P_2 is *the*
second Legendre polynomial. The angular brackets denote
a statistical average over all molecules in the medium.
For perfect ordering S = 1 and for complete disorder S = 0.

It is of interest to consider the temperature
variation of S. This has been measured in nematic and
smectic A liquid crystals using a number of techniques.[42-52]
Most infrared studies performed hitherto to measure the
orientational order parameter have used homogeneously
aligned samples and polarized radiation. The need for
polarized radiation and the consequent reduction in available
energy are two of the inherent disadvantages of this method.

In contrast, a homeotropically aligned sample facilitates
the use of unpolarized radiation.[53] This method also
possesses other distinct advantages; consequently we have
it in all our measurements of the orientational ordering
in the smectic A and nematic phases of liquid crystals.
In chapter 6, we discuss this method and apply it to deter-
mine the orien-tatlorial ordering in CBOOA. The results of
our investigations are found to agree well with some of
the earlier studies of the orientational order parameter in
this material.

The temperature and entropy of the nematic-isotropic
transition as well as the order parameter at the transition
are known to exhibit an alternating behaviour as a homologous
series is ascended.[14] Recent theoretical work[15-17] has shown
that the nature of the conformations adopted by the hydro-
carbon end-chains in primarily responsible for this behaviour.
In chapter 7, we discuss the results of ow study of the
orientational order parameter in the smectic A and nematic
phases of soma members of the homologous seriea, trans-p-n-
alkoxy-α-methyl p'-cyanophenyl cinnamates (n-OMCPC). The
order parameter discontinuities at the smectic A-nematic
transition in some of the higher homologues sf this series
have also been measured and correlated with their thermo-
dynamic properties. Calorimetric evidence for tricritical
behaviour of the smectic A-nematic transition in mixtures

of these compounds are also presented in this chapter.

A novel differential technique has "been developed in the course of the present study for obtaining the dichroic spectra of uniaxial liquid crystals from a single spectral scan, using unpolarized radiation. The differential technique is equally applicable to the study of anisotropic solute molecules which can be aligned in a liquid crystalline solvent. These aspects of differential dichroic spectroscopy with illustrative results are presented in chapter 8.

Some of the results discussed in this thesis are reported in the following publications:

1. Far-Infrared and Raman Spectra of the Solid Phases of CBOOA (S. Venugopalan, J.R. Fernandes and G.V.Vani) – MOLECULAR CRYSTALS AND LIQUID CRYSTALS 31, 29–46 (1975).

2. Infrared Spectroscopic Study of Orientational Order and Phase Transformations in Liquid Crystalline CBOOA (J.R. Fernandes and S. Venugopalan) – MOLECULAR CRYSTALS AND LIQUID CRYSTALS 35, 113–134 (1976).

3. Far-Infrared Absorption in the Highly Ordered Smectic Phases of TBBA (S.Venugopalan, J.R.Fernandes and V. Surendranath) – MOLECULAR CRYSTALS AND LIQUID CRYSTALS 40, 149–161 (1977).

4. Differential Dichroic Spectroscopy in Liquid Crystals Using Unpolarized Radiation (J.R.Fernandes and S.Venugopalan) CHEMICAL PHYSICS LETTERS 53, 407 (1978).

5. Orientational Order and Tricritical Behaviour in the **trans-p-n-Alkoxy-α-Methyl p'-Cyanophenyl Cinnamate (n-OMCPC)** Series of Liquid Crystals (J.R.Fernandes and S. Venugopalan)(to be submitted).

References

1. F. Reinitzer, Montasch. Chem. $\underline{9}$, 421 (1888).

2. G. Friedel, Am. Physique $\underline{18}$, 273 (1922).

3. T.R. Taylor, S.L. Arora and J.L. Fergason,
   Phys. Rev. Lett. $\underline{25}$, 722 (1970).

4. R.A. Wise, D.H. Smith and J.W. Doane, Phys. Rev.
   $\underline{A7}$, 1366 (1973).

5. *See* for example: S. Chandrasekhar, Liquid Crystals
   (Cambridge University Press, Cambridge 1977);
   Reports Progr. Phys. 39, 613 (1976); P.G. de Gennes,
   The Physics of Liquid Crystals (Clarendon Press,
   Oxford, 1974).

6. H. Lippmann and K.H. Weber, Ann. Phys. (Leipzig)
   $\underline{20}$, 265 (1957).

7. Z. Luz and S. Meiboom, J. Chem. Phys. $\underline{59}$, 275 (1973).

8. B. Deloche, J. Charvolin, L. Liebert and L. Strzelecki,
   J. de Phys. $\underline{36}$, Suppl. 3, C1-21 (1975).

9. W.L. McMillan, Phys. Rev. $\underline{A8}$, 1921 (1973).

10. R.J. Mayer and W.L. McMillan, Phys. Rev. $\underline{A9}$, 899 (1974).

11. R.G. Priest, J. de Phys. $\underline{36}$, 437 (1975).

12. Z. Luz, R.C. Hewitt and S. Meiboom, J. Chem. Phys. $\underline{dL}$,
    4758 (1974).

13. H. Hervet, F. Volino, A.J. Dianoux and R.E. Lechner,
    J. de Phys. $\underline{L35}$, 151 (1974).

14. A. Pines, D.J. Ruben and S. Allison, Phys.Rev.Lett. 33, 1002 (1974).

15. S. Marcelja, Solid State Commun. 13, 759 (1973).

16. S. Marcelja, J. Chem. Phys. 60, 3599 (1974).

17. D.A. Pink, J.Chem.Phys. 63, 2533 (1975).

18. D. Guillon, A. Mathis and A. Skoulios, J. de Phys. 36, 695 (1975).

19. P. Poldy, M. Dvolaitzky and C. Taupin, J. de Phys. 36, Suppl. 3, C1-27 (1975).

20. J.M. Schnur, Phys. Rev. Lett. 29, 1141 (1972).

21. J.M. Schnur, Mol. Cryst. Liquid Cryst. 23, 155 (1973).

22. D. Krishnamurti, K.S. Krishnamurthy and R.Shashidhar, Mol. Cryst. Liquid Cryst. 8, 339 (1969).

23. J.H. Wendorff and F.P. Price, Mol.Cryst.Liquid Cryst. 22, 85 (1973).

24. T. Riste and R. Pynn, Solid State Commun. 12, 409 (1973).

25. B.J. Bulkin, D. Grunbaum and A.V. Santoro, J.Chem.Phys. 51, 1602 (1969).

26. S. Chandrasekhar and N.V. Madhusudana, Appl.Spectrosc. Rev. 6, 189 (1972).

27. B.J. Bulkin, Advances in Liquid Crystals, EC. G.H.Brown (Academic Press, New York, 1976) Vol. TI, p. 199.

28. V.D. Neff, Liquid Crystals and Plastic Crystals Eds. G.W. Gray and P.A. Winsor (Ellis Harwood Ltd., U.K., 1974) Vol. 11, p.231.

29. S, Bhagavantam and T.Venkatarayadu, <u>Theory of Groups and its Application to Physical Problems</u> (Academic Press, New York, 1969).

30. J. Hayes, T. Waluga and J.A. Janik, Phys.Lett. <u>41A</u>, 2 (1972).

31. G.W. Smith, Mol. Cryst. Liquid Cryst. Lett. <u>34</u>, 87 (1976).

32. E. Sciesinska, J. Sciesinski, J. Twardowski and J.A. Mol. Cryst. Liquid , <u>27</u>, 125 (1974).

33. A.M. Fuller and C.E. Farr, Mol. Cryst. Liquid Cryst. <u>25</u>, 5 (1974).

34. J.M. Schnur, M. Hass and W.L. Adair, Phys.Lett. <u>41A</u>, 326 (1972).

35. J.D. Bernal and D. Crowfoot, Trans. Far. Soc. <u>29</u>, 1032 (1933).

36. R. Pynn, K. Otnes and T. Riste, Solid State Commun. <u>11</u>, 1365 (1972).

37. L. Couture and J.P. Mathieu, J.Phys.Radium. <u>10</u>, 145 (1949).

38. W.G. Fateley, F.R. Dollish, N.T.McDevitt and F.F.Bentley, <u>Infrared and Raman Selection Rules for Molecular and Lattice Vibrations. The Correlation Method</u>. (Wiley Interscience, New York, 1972).

39. R.G.Gordon, J.Chem.Phys. <u>43</u>, 1307 (1965).

40. S. Lugomer, Mol. Cryst. Liquid Cryst. <u>29</u>, 141 (1974).

41. N. Kirov and P. Simova, Spectrochim.Acta <u>29A</u>, 55 (1973).

42. P. Chatelain, Bull. Soc. Franc. Miner. Cryst. 78, 262 (1955).

43. S. Chandrasekhar and N.V. Madhusudana, J. de Phys. , Suppl. C4-24 (1969).

44. W.Maier and G. Englert, Z. Electrochem. 64, 689 (1960).

45. W. Maier and A. Saupe, Z. Physik.Chem. (NF) 6, 327 (1956).

46. A. Saupe and W. Maier, Z. Naturforschg. 16a, 816 (1961).

47. H. Gasparoux, F. Hardouin and M.F. Achard, Pramana Suppl. 1, 215 (1973).

48. R.D. Spence, H.A. Moses and P.L. Jain, J.Chem.Phys. 21, 380 (1953).

49. R.D. Spence, H.S. Gutowsky and C.H. Holm, J.Chem.Phys. 21, 1891 (1953).

50. J.W. Doane, R.S. Parker, b.Cvikl, D.L. Johnson and. D.L. Fishel, Phys. Rev. Lett. 28, 1694 (1972).

51. B. Cabane and W.G. Clark, Solid State Commun. 13, 129 (1973).

52. A. Carrington and G.R. Luckhurst, Mol.Phys. 8, 401 (1964).

53. H. Kelker, R. Hatz and G. Wirzing, Z.Anal Chem. 267, 161 (1973).