EXPERIMENTAL STUDIES ON THE OPTICAL PROPERTIES OF CHOLESTERIC LIQUID CRYSTALS

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for the degree of
DOCTOR OF PHILOSOPHY

by

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DECLARATION

I hereby declare that the thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title.

K A Suresh

K. A. SURESH

Certified
S. Chandrasekhar
27/1/77

CERTIFICATE

I certify that this thesis has been composed by Mr. K.A. Suresh based on investigations carried out by him at the Liquid Crystals Laboratory, Raman Research Institute, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or other similar title.

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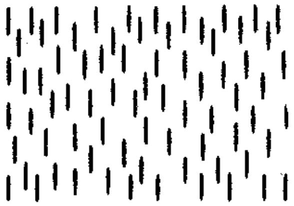
CONTENTS

PREFACE

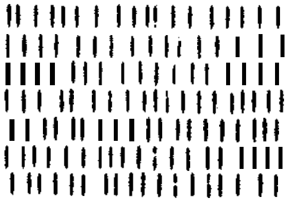
Liquid crystals are states of matter that are intermediate between the crystalline solid and the isotropic liquid. They are strongly anisotropic in some of their properties (for example, they are birefringent and diamagnetically anisotropic) and at the same time they have the ability to flow. Friedel (1922), after a careful study of the optical properties of the 'mesophases', classified them into three types: nematic, smectic and cholesteric.

1) The nematic liquid crystal has long range orientational order but no translational order (Figure 1a). A monodomain sample of a nematic is optically uniaxial, positive and strongly birefringent. The birefringence decreases gradually with rise of temperature and drops abruptly to zero at the nematic-isotropic transition temperature.

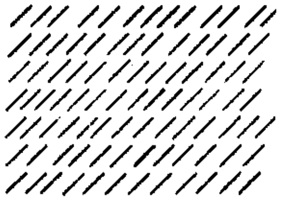
2) Smectic liquid crystals have stratified structures. Depending on the molecular arrangement within each layer, smectics are classified into smectic A, smectic B, smectic C, etc. In smectic A the long axis of the molecules are, on the average,



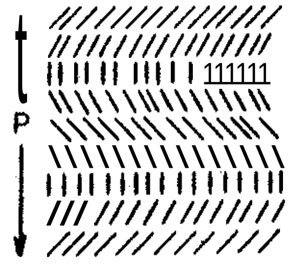
a NEMATIC



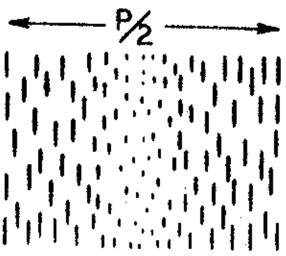
b SMECTIC A



c TILTED SMECTIC



d TWISTED SMECTIC



e CHOLESTERIC
(TWISTED NEMATIC)

Figure 1: The molecular arrangement in various mesophases.

normal to the layers with their centres distributed at random within each layer (Figure 1b). Smectic B resembles smectic A except that the molecules are hexagonally close packed in each layer. Smectic C is a tilted form of smectic A (Figure 1c). Recently it has been shown that smectic C may also occur in a twisted form, i.e., with a twist imposed on the structure about an axis normal to the layers (Figure 1d). The other smectic modifications, e.g., D, E, F, etc. have more complicated molecular structures which are not yet fully elucidated.

3) Cholesteric liquid crystals are also nematic type of liquid crystals, except that they are composed of optically active molecules. Thus, the structure has a spontaneous helical twist superimposed about an axis perpendicular to the preferred molecular direction (Figure 1e). For the purpose of optical calculations the structure may also be described as a pile of very thin birefringent layers, the principal axes of the successive Layers turned through a small angle. This spiral structure gives rise to some remarkable optical properties, When white light is incident on the surface of a plane texture preparation (in which the helical axis is normal to the glass surfaces),

selective reflection takes place over a small region of the spectrum, the wavelength of maximum reflection varying with angle of incidence in accordance with Bragg's law. At normal incidence, the reflected light is circularly polarised: one circular component is totally reflected over a spectral range of some 0.02 µm while the other passes through unchanged. Further in contrast to the case of reflection from normal dielectrics, the reflected wave has the same sense of circular polarisation as that of the incident wave. Along the helical axis, the medium exhibits optical rotatory power of the order of several thousands of degrees per millimetre. In the neighbourhood of the region of reflection, the rotatory dispersion is anomalous and the sign of the rotation opposite on opposite sides of the reflection band.

These properties are generally well understood theoretically and have been extensively studied experimentally. However, the experimental and theoretical studies have not been fully explored in certain special cases. This thesis describes investigations carried out on such problems. The work has led to some significant new results.

The first two chapters deal with studies in the regime of large pitch, much larger than the wavelength of light. These studies have established conclusively that the optical properties in this regime cannot be described adequately by a direct application of the standard de Vries equation as has been done by previous workers (Baessler *et al.* 1969, Teucher *et al.* 1971). The experiments were carried out on a mixture of right handed and left handed cholesterics. Such a mixture, referred to as a *compensated* mixture, adopts the helical structure of a cholesteric but the pitch is sensitive to composition and temperature. For a given composition, there is a temperature (say T_N) at which the pitch becomes infinity, i.e., structure goes over to the nematic state (Friedel, 1922). At temperatures above and below T_N the structure is cholesteric but of opposite handedness. The particular compensated cholesteric used in the present work was a 1.6:1 by weight mixture of cholesteryl chloride and cholesteryl myristate (CM), which has a nematic temperature $T_N \approx 48°C$. Some measurements of the rotatory power as a function of temperature/pitch for this mixture (but of composition 1.75: 1) have been reported previously by Baessler *et al.* (1969), who interpreted the observations on the basis of the de Vries equation,

$$\rho = -\frac{2\pi}{P} \frac{\alpha^2}{8\lambda'^2(1-\lambda'^2)} \qquad (1)$$

where ρ is the optical rotatory power, P is the pitch of the helix, $a = (\varepsilon_1 - \varepsilon_2)/2\varepsilon$, ε_1 and ε_2 are the principal dielectric constants of the untwisted structure, $\varepsilon = \frac{1}{2}(\varepsilon_1 + \varepsilon_2)$, $\lambda' = \frac{\lambda}{P\varepsilon^{\frac{1}{2}}}$ and λ is the wavelength in vacuum.

In chapter I we present systematic measurements of the rotatory power as a function of temperature/pitch for samples of thickness 3, 6.4 and 12.7 µm. These measurements were carried out using a slightly modified Winkel-Zeiss (Gottingen) Polarimeter. The experimental curves are shown in figure 2. It can be seen that the rotatory power (i.e., the optical rotation per unit thickness) as well as its variation with temperature/pitch is a function of the thickness of the sample. It is evident that this behaviour cannot be explained in terms of equation (1). According to this equation the rotatory power ρ should approach infinity as temperature T tends to T_N (or pitch tends to infinity) and should be independent of sample thickness, whereas experimentally ρ tends to zero in the vicinity of T_N and is very much dependent on the sample thickness. The experimental results are

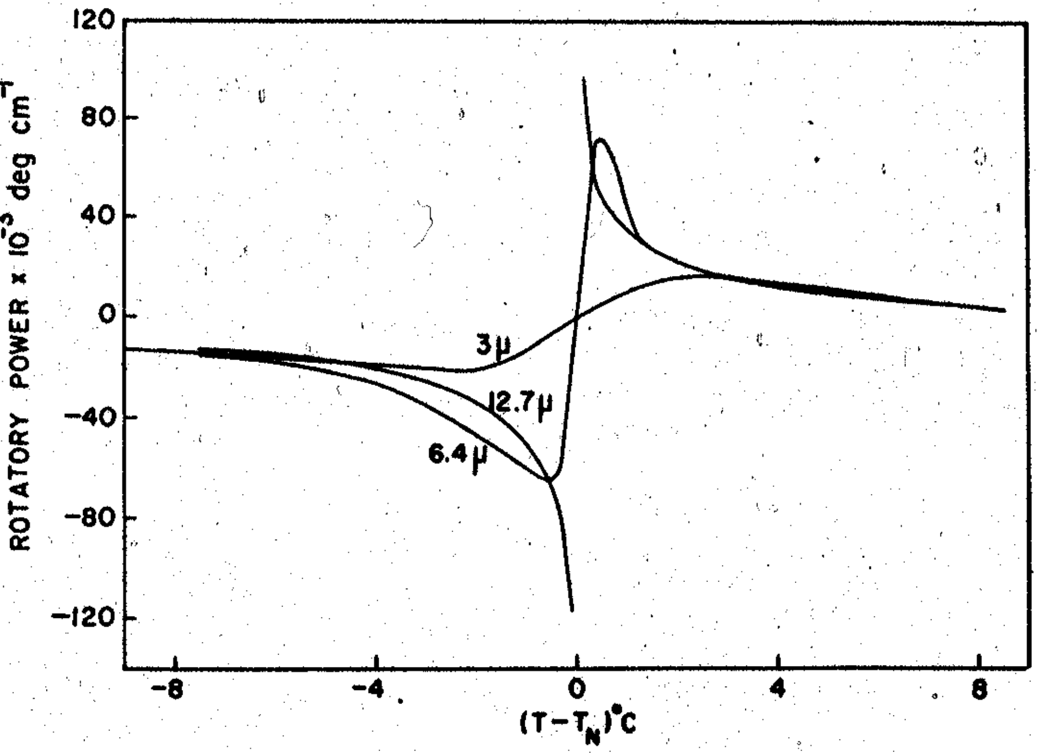


Figure 2: Experimental rotatory power as a function of temperature for a 1.6:1 by weight mixture of cholesteryl chloride and cholesteryl myristate. Sample thicknesses: ≈ 3 μm, 6.4 μm and 12.7 μm.

discussed in the light of the rigorous theory of light propagation in cholesterics of large pitch developed recently by Kini and others (see Kini, 1977). It is shown that the observed behaviour is in conformity with the predictions of this exact theory.

Chapter II deals with an absorbing compensated mixture. Saeva and Wysocki (1971) demonstrated that when linearly dichroic molecules are dissolved in a cholesteric liquid crystal the medium exhibits circular dichroism in the region of the absorption band of the solute molecules. In the present work, we have carried out detailed measurements of the circular dichroism as a function of temperature/pitch of the CM mixture in which was dissolved 1.38% by weight of linearly dichroic β-carotene. The circular dichroism was determined by accurate measurements of the intensity of right and left-circular polarised light transmitted by the sample, using a photomultiplier and a lock-in-amplifier. As is to be expected the circular dichroism changes sign on crossing T_N in a manner somewhat similar to the behaviour of the rotatory power of a non-absorbing sample. However, measurements on samples of thicknesses 4, 6.3, 8, 9.5 and 12.7 microns yielded a most unexpected result: the dichroic power (i.e., the circular dichroism per unit thickness of the sample) was found to decrease with increasing sample thickness (see Figure 3). These features cannot be interpreted on the basis of Sackmann and Voss (1972) equations obtained in the limits $P \ll \frac{\lambda}{\Delta\mu}$ and $P \gg \frac{\lambda}{\Delta\mu}$ (λ is the wavelength of light in vacuum and $\Delta\mu$ is the birefringence). It is shown that the observed features can be properly acaounted for on the basis of an extension of the rigorous theory to absorbing systems (Kini, 1977).

Chapters III and IV are concerned with the optical properties in the regime of wavelengths comparable to the pitch. The exact theory of light propagation along the helical axis of a cholesteric was developed by Mauguin (1911), Oseen (1933) and de Vries (1951) and has been discussed in various forms by other authors (Kats 1971, Nityananda 1973, Joly 1972, Aihara and Inaba 1971, Marathay 1971). An alternate approach to the problem was put forward by Chandrasekhar and Srinivasa Rao (1968). This theory is closely analogous to Darwin's dynamical theory of X-ray diffraction from crystals (1914). In chapter III we derive this theory in a complete form avoiding certain minor inconsistencies that were present

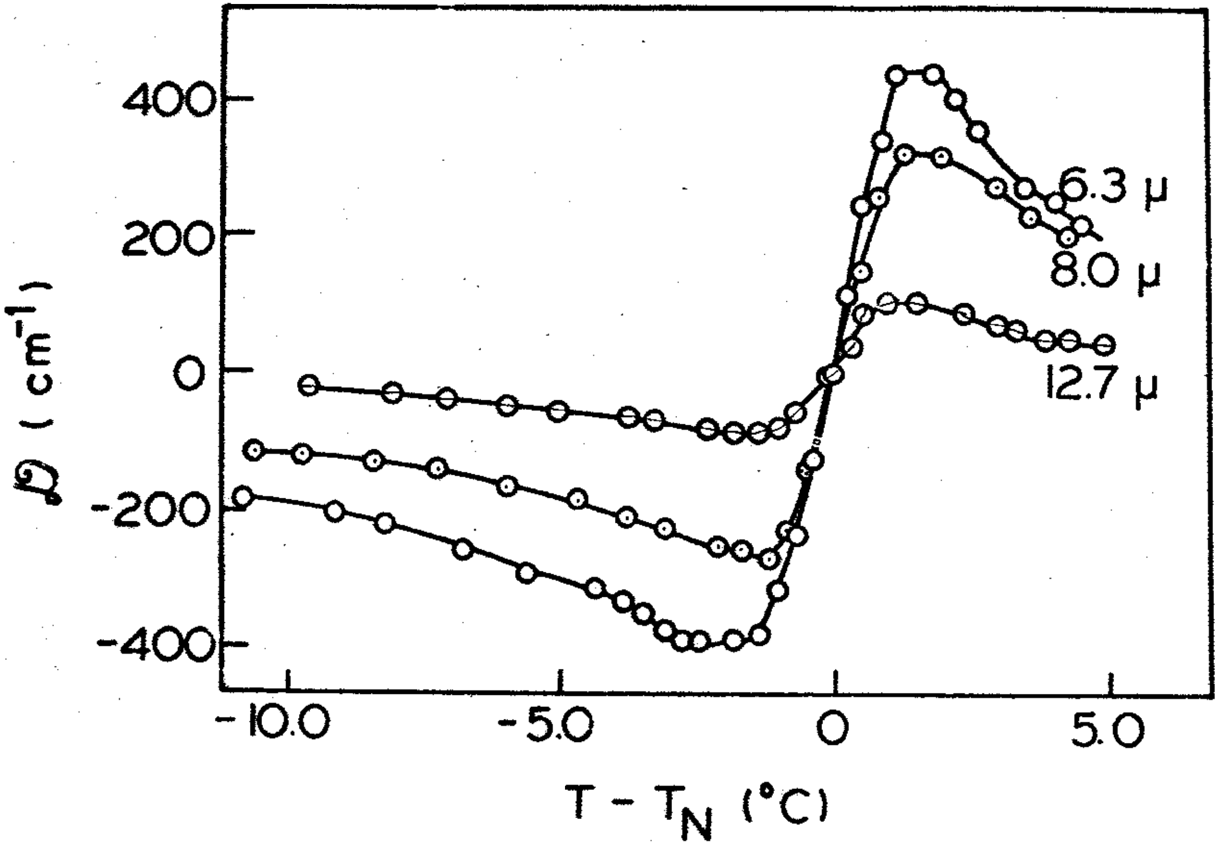


Figure 3: Experimental values of dichroic power versus temperature for different thicknesses of the sample in a 1.64:1 by weight mixture of cholesteryl chloride and cholesteryl myristate containing 1.48% by weight of β-carotene.

in the original formulation. We also give detailed numerical calculations of the reflection coefficient, rotatory power, etc. for the semi-infinite medium as well as for finite film and compare them with the values computed from the exact electromagnetic theory.* It is shown that in the neighbourhood of the reflecting region the simple dynamical approach is quite adequate for all practical calculations.

In Chapter IV we discuss an entirely new phenomenon, namely, the optical analogue of the Borrmann effect in cholesterics. The Borrmann effect is the anomalous increase in the X-ray intensity (over and above that due to normal absorption) when an absorbing crystal is set for Bragg reflection (Borrmann 1941). This is a consequence, of the dynamical theory of X-ray diffraction (Ewald 1965). We report here the discovery of a similar effect in absorbing cholesterics in the vicinity of the reflection band? The chapter begins with a discussion of the dynamical theory (which was treated in the previous chapter) taking into account the effect of absorption. It is shown that under suitable circumstances there is an enhancement of the transmitted intensity for left (or right) circularly polarised light, if the structure is left (or. right)

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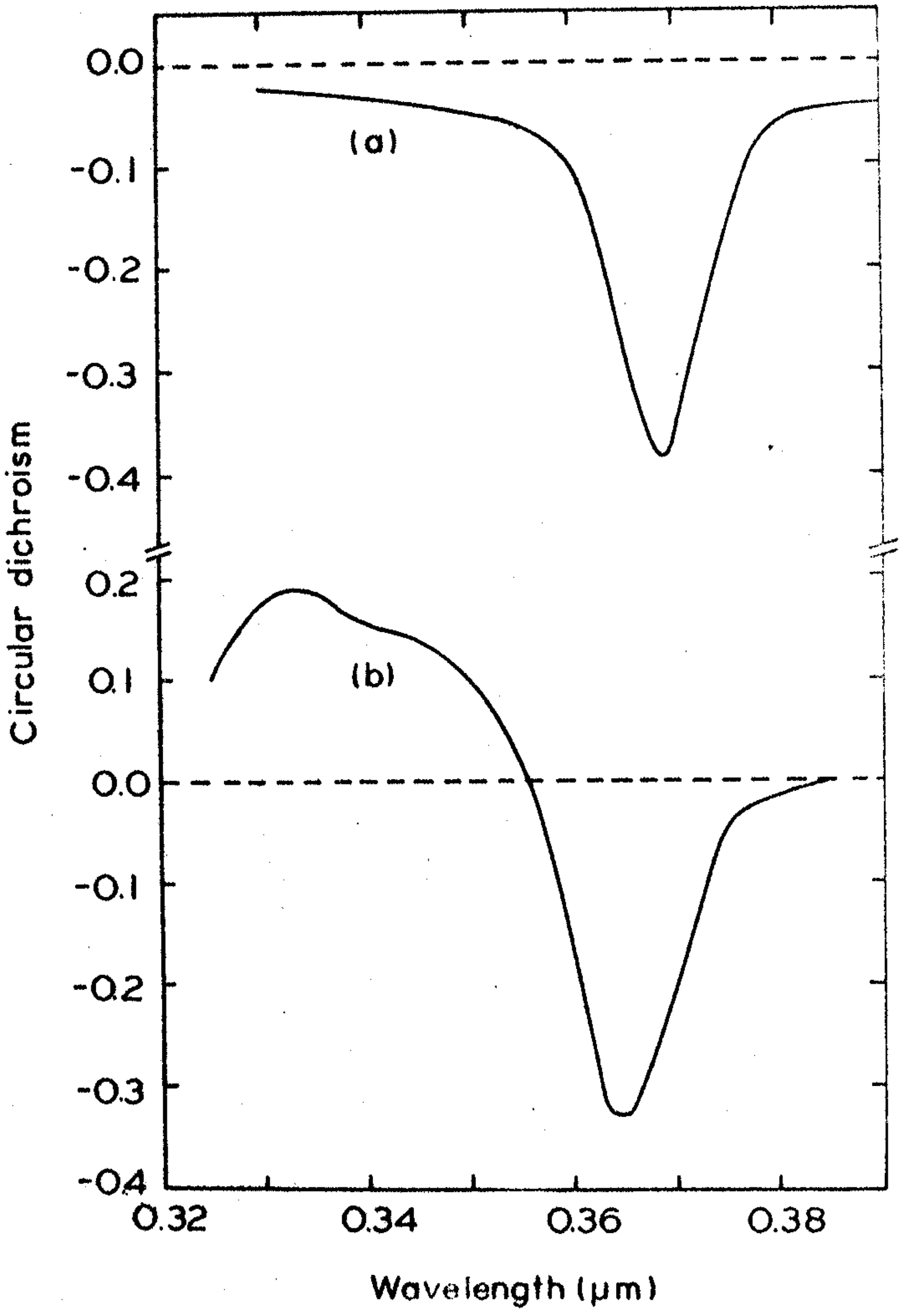
* The exact electromagnetic theory of the effect was first worked out by Nityananda and Kini, 1973.

handed. This is indeed the analogue of the Borrmann effect. Physically the origin of this effect can be explained on the basis of dynamical theory as follows. In a left handed cholesteric standing waves are set up inside the medium due to the interference between the primary and the reflected left circularly polarised waves, The phase of the Bragg reflected wave with respect to the primary wave varies from π to 0 as λ increases from the shorter wavelength edge of the reflection band to the longer wavelength edge. Hence the electric vector in the medium makes an angle $\pi/2$ with respect to the director on the shorter wavelength side, and is along the director on the longer wavelength side. If the medium were to consist of linearly dichroic molecules aligned parallel to the local director then the left circular wave suffers minimum absorption at the shorter wavelength edge and maximum absorption at the longer wavelength edge of the reflection band. This results in anomalous increase in the transmitted intensity of the left circular wave on the shorter wavelength side which is over and above the normal attenuation due to mean absorption. The existence of this effect has been experimentally demonstrated in cholesteryl nonanoate containing small quantities of p-azoxyanisole or n-p-methoxybenzylidene-p-phenyl azoaniline (which are linearly dichroic molecules). When the reflection band is adjusted to overlap with the strongly dichroic band of the solute molecules the transmission and circular dichroism (Figure 4) exhibit the features predicted by the theory. Also are presented a detailed experimental study of this effect in thin films of cholesteryl nonanoate containing varying amounts of p-azoxyanisole. It is shown that there is qualitative agreement between the experimental results and those calculated on the basis of the dynamical theory.

The last chapter describes optical studies on the twisted smectic C (TSC) phase and the twisted nematic (TN or cholesteric) phase exhibited by p-n-heptyloxyazoxybenzene (HOAB) mixed with small quantities of cholesteryl benzoate. The TSC phase, like the TN or cholesteric phase, also has a very high rotatory power for light propagation along the twist axis. Detailed measurements have been carried out of the rotatory power ρ, pitch P and layer birefringence $(\Delta\mu)$ as functions of temperature. All these quantities (ρ, P and $\Delta\mu$) change discontinuousl at the TSC-TN phase transition, the values being higher

Figure 4: Experimental curves of circular dichroism as a function of wavelength~(a) pure cholesteryl nonanoate (non-absorbing), (b) mixture of cholesteryl nonanoate and PAA (0.98%)(absorbing).


0.0
-0.1
-0.2
-0.3
-0.4
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
(a)
(b)
Circular dichroism
0.32
0.34
0.36
0.38
Wavelength (μm)

in the lower temperature phase. These studies have also led to the first evidence for a new skew-cybotactic (or tilted) form of a cholesteric. The observed value of ρ of the TN phase is found to be incompatible with that calculated from the exact theory using the measured values of $\Delta\mu$ and P when the structure is assumed to be of the usual cholesteric type in which the director is normal to the helix; the theoretical value of ρ is much higher, indicating that the molecules in this phase are not normal but inclined to the helical axis. This has been confirmed directly by X-ray studies on this system. The diffraction pattern reveals an inner ring (Figure 5) characteristic of a skew-cybotactic type of cholesteric structure in which the preferred molecular direction is tilted at about 39° with respect to the helical axis.

Most of the results described above have been reported in the following publications of which the present writer is a co-author:

1. Theory of the optical properties of non-absorbing compensated cholesteric liquid crystals (with S. Chandrasekhar, G.S.Ranganath, U.D. Kini), Molecular Crystals and Liquid Crystals, 24, 201 (1973).

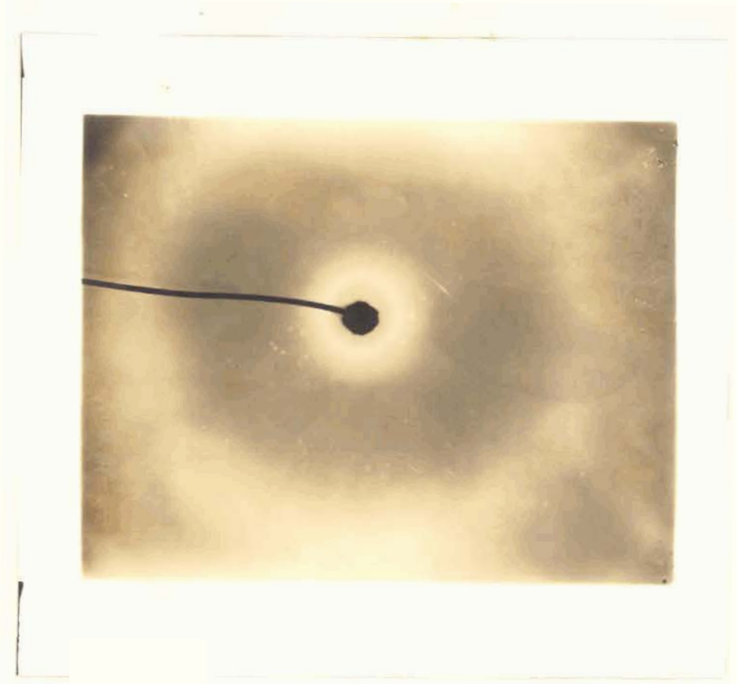


Figure 5: X-ray diffraction pattern for unaligned sample. The sample is 0.9 HOAB + 0.1 cholesteryl benzoate mixture in the twisted nematic phase.

2. Optical properties of mixtures of right- and left-handed cholesteric liquid crystals (with G. S. Ranganath, S. Chandrasekhar, U.D. Kini and S. Ramaseshan), Chemical Physics Letters, 19, 556 (1973).

3. Circular dichroism in absorbing mixtures of right- and left-handed cholesterics (with G.S. Ranganath, S.R. Rajagopalan and U.D. Kini), Proc. International Liquid Crystals Conference, Bangalore, December 3-8, 1973 - Pramana Supplement 1, p. 353

4. Dynamical theory of reflection from cholesteric liquid crystals (with S. Chandrasekhar, G. S. Ranganath), Proc. International Liquid Crystals Conference, Bangalore, December 3-8, 1973 - Pramana Supplement 1, p. 341.

5. Anomalous transmission (Borrmann effect) in absorbing cholesteric liquid crystals (with R. Nityananda, U.D. Kini and S. Chandrasekhar) - Proc. International Liquid Crystals Conference, Bangalore, December 3-8, 1973 - Pramana Supplement 1, p. 325.

6. An experimental study of the anomalous transmission (Borrmann effect) in absorbing cholesteric liquid crystals, Molecular Crystals and Liquid Crystals, 35, 267 (1976).

7. Optical and X-ray studies on the twisted smectic C and twisted nematic phases: Evidence for a Skew-Cybotactic type of cholesteric structure (with S. Chandrasekhar) - Molecular Crystals and Liquid Crystals (in press).

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For a detailed treatment of the, structure and properties of the various mesophases, see for instance, 'Liquid Crystals' by S. Chandrasekhar, Reports on Progress in Physics, **39**, 613 (1976); 'Liquid Crystals' by S. Chandrasekhar, Cambridge Monograph on Physics, Edited by M.M.Woolfson and J.M.Ziman, Cambridge University Press.