

**STUDIES ON BIREFRINGENCE, OPTICAL TEXTURES
AND
MOLECULAR ORDERING OF LIQUID CRYSTALS**

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THESIS SUBMITTED TO THE UNIVERSITY OF MYSORE
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June 12, 1981



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PREFACE

During the past two decades considerable interest has grown with regard to the study of the liquid crystalline phase¹⁻⁵. This phase is also referred to as the mesomorphic or the mesophase. The mesophases are broadly classified as nematic, cholesteric, smectic and discotic phases. Because of the anisotropic nature of the polarizabilities of the individual molecules and because of the characteristic nature of the molecular arrangement in the different phases, there arises in almost all the above phases a birefringence which is strongly dependent on temperature. For example, the nematic phase in which there exists statistical orientational order about a single direction (optic axis), behaves as a birefringent medium which is uniaxial positive. The smectic (A and B) mesophases are also uniaxial positive. Here, the molecules are arranged in layers with the long axes of the molecules perpendicular to the layers. In smectic A, there is no lateral positional order in each layer. In smectic B, there is lateral order. The cholesteric phase, on the other hand, exhibits negative birefringence. The cholesteric phase consists of individual layers in which the molecules are aligned with their long axes along a specific direction (director)

but this specific direction of the director rotates smoothly on passing from layer to layer, so as to form a helical structure. The different mesophases exhibit diverse optical behaviour and characteristic textures. The present thesis incorporates the results of the author's theoretical and experimental investigations on different mesophases exhibited by different compounds. The preface here gives a general introduction as well as a summary of the salient features and results dealt with in the different chapters of the thesis.

The optical anisotropy of the molecules plays a fundamental role with regard to the birefringence and in Chapter 1 is given a brief introduction to the topic, with particular reference to the orientational order parameter in nematic liquid crystals. In this chapter is dealt with the relationship between the refractive indices, local field, principal polarizabilities, effective polarizabilities and the orientational order. Experimental investigations on the refractive indices, densities and their temperature variations were carried out by the author in the case of three compounds namely

- 1) 4,4'-bis(hexyloxy)azoxy benzene
- ii) 4,4'-bis(heptyloxy)azoxy benzene

iii) N-(4-hexyloxy benzylidene)-p-toluidine(HBT).

The first two compounds were chosen for investigations because they possess molecular structure similar to p-azoxyanisole(PAA) and the last compound has a structure similar to p-methoxy benzylidene p-butylaniline(MBBA). As is well known, PAA and MBBA have been extensively investigated by earlier workers. The refractive indices of the above compounds were determined using a Goniometer Spectrometer and by making use of a hollow prism (as a container for the specimen). The details of the experimental technique adopted by the author are described in Chapter 2 and the data are presented for the above three compounds. The index data have been obtained for different wavelengths at different temperatures. The above data were used to calculate the anisotropy of the Lorentz field factors ($L_o - L_e$) and the orientational order parameter (S) and the results are discussed in Chapter 3. The orientational order parameter decreases with increase of temperature and it is found that there is approximately a linear variation of ($L_o - L_e$) with S indicating that the anisotropy of the molecular distribution and orientational order parameter decrease in-step with each other. Besides, it is found that the order parameters in the case of HBT are generally

higher than in the case of MBBA, at the same reduced temperature $T_{NI}-T$. Further, the value of L_o-L_e in the case of HBT is greater than in MBBA. The molecule of HBT is longer than that of MBBA. Hence, it is reasonable that the anisotropy of molecular distribution and orientational order in HBT is greater than in MBBA.

The orientational order parameters and the anisotropy of the Lorentz field factors in the case of a homologous series of compounds are calculated and discussed in Chapter 4. The compounds, n-alkyl-p-(4-ethoxy benzylidene amino)- α -(methyl cinnamates, have the molecular formula $C_2H_5O(C_6H_4)CH=N(C_6H_4)CH=C(CH_3)(COOR)$ where R is alkyl group $CH_3(CH_2)_n$ ($n = 1, 2, \dots, 8$). These compounds form an interesting homologous series, in that they exhibit both nematic and smectic A mesophases. For the homologues $n = 1$ to $n = 8$, experimental data on the refractive indices were reported by Pezl and Sackmann⁶. Although density data are not available for the above compounds, it is shown that it is possible to calculate the optical anisotropy and the orientational order in the case of these compounds. The order parameters are found to exhibit the well known zig-zag alternation with increase in the number of carbon atoms of the alkyl chain. The anisotropy (L_o-L_e), of the Lorentz field factors is found

to decrease with increasing number of carbon atoms indicating that as a consequence of the numerous conformations possible for the alkyl group, there is a reduction in the anisotropy of the polarization field. The calculated values of the optical anisotropy of the different molecules are approximately equal, indicating that the optical anisotropy arises mainly from the central rigid portion of the molecule and that the contribution of the alkyl chain to the optical anisotropy is not significant.

Birefringence studies were carried out by the author, also in the case of cholesteryl oleyl carbonate. This compound is interesting in that it exhibits the cholesteric and the smectic A mesophases and it is weakly birefringent. The results of the measurements of density, refractive indices and viscosity of COC in the smectic, cholesteric and isotropic phases are reported and discussed in Chapter 5. The principal polarizabilities α_{\parallel} and α_{\perp} (respectively, for vibrations parallel and perpendicular to the long axes of the molecules) are calculated and it is found that the values of α_{\perp} in the cholesteric and smectic phases are equal. There is a systematic decrease in the optical anisotropy at the higher temperatures. This feature is explained as arising due to the end chains of the molecules being not fully extended and as due to the

numerous conformations possible at the higher temperatures. From the viscosity data in the cholesteric and isotropic phases, the corresponding flow activation energies are calculated.

In Chapter 6 are presented the author's investigations on the dielectric constant of 4,4'-bis(heptyloxy)azoxy benzene, anisylidene-p-amino phenyl acetate and anisylidene-p-amino phenyl butyrate, in benzene solutions. From these measurements and the available refractive index data on these compounds, the dipole moments of these nematogenic molecules are calculated. The dipole moments are also evaluated theoretically as the vector sum of the different bond moments and it is found that there is reasonable agreement between the experimental and theoretically calculated values. It may be mentioned that the dipole moment of 4,4'-bis(heptyloxy)azoxy benzene is in close agreement with the dipole moment value for p-azoxyanisole, which has a similar molecular structure.

Numerous striking optical textures are known to be exhibited by the smectic mesophase. Dodecyl benzene sulfonic acid and the mixtures of its sodium salt with (i) water, (ii) methane sulfonic acid are found to exhibit the smectic A phase, and Chapter 7 is devoted to the author's

investigations on these, with special reference to X-ray diffraction, optical textures, and molecular orientation. X-ray studies reveal sharp rings at low angles of scattering and the diffuse ring at the higher angles, confirming that the phase here is the smectic A phase. The smectic A phase of the above compound and mixtures is found to exhibit the characteristic optical textures like batonnets, droplets and focal conics. Using a sensitive interference technique, the author has studied the molecular orientation in batonnets and droplets. In the case of a 'droplet' the molecules are arranged in smectic layers, the different smectic layers being concentric as the layers of an onion. It is confirmed also that the molecular ordering in the batonnets corresponds to that in G batonnets. Here, the molecules are arranged in smectic layers which are normal to the central long axis of the batonnet. Low angle optical scattering patterns were also recorded by the author in the case of the droplets using He-Ne laser radiations of $6328\overset{\circ}{\text{A}}$. The geometry of the patterns confirms the molecular orientation, described above in the case of 'droplets'. The interference studies had also enabled the author to determine the birefringence and optical anisotropy in the case of dodecyl benzene sulfonic acid. Chapter 7 also includes the presentation and interpretation of the vibrational infrared absorption

spectra of dodecyl benzene sulfonic acid, sodium dodecyl benzene sulfonate and methane sulfonic acid. Certain general features which have emerged from our studies in the different mesophases are dealt with in the concluding chapter.

Most of the above investigations have been published or accepted for publication as papers and a list of them is given below.

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2. Refractive indices and orientational order of nematic N-(4-hexyloxy benzylidene)-p-toluidine, by R.Somashekar and D.Krishnamurti, in *Proceedings of the Nuclear Physics and Solid State Physics Symposium, Pune, December 26-30, 1977, Volume 20C (Solid State Physics)*.
3. Mesomorphic behaviour of dodecyl benzene sulfonic acid and its sodium salt, by D.Krishnamurti and R.Somashekar, in *Molecular Crystals and Liquid Crystals*, 65, 3 (1981).
4. Orientational order in n-alkyl-p-(4-ethoxy benzylidene amino)- α -methyl cinnamates, by D.Krishnamurti and R.Somashekar, in *Molecular Crystals and Liquid Crystals* (In press).

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