CHAPTER I

INTRODUCTION

I.1 Historical Review

A characteristic optical property of anisotropic crystals is that of double refraction, or birefringence[1]. A ray of light entering such a crystal is, in general, divided into two rays, which travel through the crystal with different velocities, and usually in different directions. These two rays are polarized in planes at right angles to one another. A liquid crystal is anisotropic and exhibits the phenomenon of optical birefringence. When a beam of light strikes the surface of the liquid crystal, it will be split into two polarized components, which vibrate at right angles to each other. The two components travel at different velocities through the anisotropic medium and so are refracted at slightly different angles. They emerge from the liquid crystal as parallel beams with mutually perpendicular polarizations. One of these beams obeys the ordinary laws of refraction, and is called an ordinary ray. The other does not obey the ordinary laws of refraction, and is therefore called an extraordinary ray.

Birefringent crystals are classified as either uniaxial or biaxial. In uniaxial crystals, there is one unique direction of propagation, which is the same as that of the crystallographic axis, and is called the optic axis. The refractive indices, and the

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[1] N.H.Hartshorne and A.Stuart, Crystals and the Polarizing Microscope, 4th Edition, Edward Arnold (Publishers) Ltd., London (1970), p.101

velocities of ordinary and extraordinary rays become equal along the optic axis. In biaxial crystals, there are two special directions of propagation. In general, when a ray of monochromatic light enters a biaxial crystal, it is divided into two rays polarized in planes at right angles to one another, but neither of these rays obeys the ordinary laws of refraction; in other words, two extraordinary rays are formed. Uniaxial crystals may be divided into two classes, negative and positive crystals. In a negative crystal the extraordinary index of refraction is less than the ordinary index of refraction, whereas in a positive crystal the former is greater than the latter.

In this experiment only the nematic type of pure liquid crystals and their mixtures have been investigated. The nematic liquid crystals behave like uniaxial crystals. They exhibit positive and strong birefringence[2] - i.e., the ordinary ray has the lower refractive index. The optic axis of the nematic liquid crystal coincides with the preferred direction of the long axis of the molecule. The nematic liquid crystal is not under normal circumstances optically active[3], but if it is placed between glass surfaces and one surface is rotated slightly, the deformation of the structure by adhesion to the glass surface may result in an optically active system. Their refractive indices are very sensitive to temperature. The ordinary index increases when the liquid crystal is heated, whereas the extraordinary index decreases; thus the birefringence falls rapidly with rise of temperature. At a nematic-isotropic

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[2] S.Chandrasekhar and D.Krishnamurti, Phys. Letters, 23 (1966), 459

[3] G.H.Brown, American Scientist, 60 (1972), 68

transition point there is a discontinuous change in the refractive indices and the birefringence drops abruptly to zero. It is also known that the temperature coefficient of the extraordinary index of refraction is large and negative whereas that of the ordinary index of refraction is usually small and positive.

The extraordinary and ordinary indices of refraction for p-azoxyanisole (PAA) were first measured by observing Newton's rings. Owing to birefringence and random distribution of swarms of molecules, it has been postulated that gradients of refractive index occur in liquid crystals, and that those can give rise to a scattering coefficient[4] proportional to the square of the difference between the ordinary and extraordinary indices. For the anisotropic liquid crystals,[5] this difference between the indices decreases as a function of the temperature up to the nematic-isotropic transition, at which a discontinuity of the indices occurs.

The values of the refractive indices of p-azoxyphenetole(PAP) in the mesomorphic state have been measured by means of Newton's rings at various temperatures and wavelengths[6]. Variations in refractive index with temperature and wavelength were obtained and these were found to be in agreement with the data obtained from studies of magnetic birefringence. Data on PAA are more complete, and the figures obtained for all values of refractive indices at several wavelengths and temperatures were found to satisfy Born's relation:

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[4] L.S.Ornstein, Ann. Physik , [4]74 (1924), 445

[5] A.Van Wijk, Ann. Physik, [5]3 (1929), 879

[6] P.Chatelain, C.R.Acad.Sci.Paris 200 (1935), 412

$$\frac{1}{3\rho}\left[\frac{n_e^2-1}{n_e^2+2} + 2\,\frac{n_o^2-1}{n_o^2+2}\right] = \frac{1}{\rho_i}\,\frac{n_i^2-1}{n_i^2+2} = \text{constant.}$$

which can be deduced theoretically from the polarizability and orientation of the molecules[7]. Born's relation has been checked by Chatelain and Pellet[8]. They have improved the method for measuring the refractive indices of PAA and PAP by using the methods of a small-angle prism. They also discussed the different modes of calculation of the field of molecular polarization and modified the classical calculation based on the Lorentz-Lorenz relation.

Falgueirettes[9] studied the refractive indices for the nematic structure of p-butoxybenzoic acid by the method of Newton's rings. Recently (1970), Jeppensen and Hughes[10] also measured the refractive indices of 4-4'-dihexoxyazoxybenzene by using this method.

Chatelain[11] has obtained values for the refractive index of PAA at different temperatures using light of a wavelength of 546 mμ. In these studies Chatelain had his samples in thin layers between rubbed, parallel glass plates. The extraordinary refractive index was found to be much more strongly dispersed than the ordinary refractive index and there was a difference in the absorption of the two rays in the visible region. With a layer 0.02 mm. thick at 120°C, the ordinary ray was transmitted down to 422 mμ. It can be seen that PAA in this state shows strong positive dichroism for

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[7] P.Chatelain, C.R.Acad.Sci.Paris, 203 (1969), 1169

[8] P.Chatelain and O.Pellet, Bull.soc.franc.minéral. 73 (1950), 154

[9] J.Falgueirettes, C.R.Acad.Sci.Paris,234 (1952), 2619

[10] M.Jeppensen and W.Hughes, Am.J.Phys., 38 (1970), 199

[11] P.Chatelain, Bull.soc.franc.minéral., 60 (1937), 280

blue light. Chatelain showed that sections up to 1 mm. thick can be prepared in a uniaxial state and that the wall action and magnetic field give exactly the same orientation effect on the molecules at a given temperature.

The double refraction (n_e-n_o) of PAA was determined by Kast[12]. He measured the interference fringes of an anisotropic layer enclosed between a plane slide and a lens, with the molecular axes oriented parallel to the plane slide and aligned azimuth, at a temperature of 127°C. He found that the square of the double refraction decreases as the temperature increases. He also showed that a plot of the refractive index of the isotropic liquid of PAA versus the wavelength at 140°C was nearly a straight line. Similar measurements were previously made by Van Wijk[13] in the whole anisotropic region of PAA which extends from 116 to 134°C, using a plane parallel layer and counting the interference fringes in the spectrum.

In 1964, Chatelain and Brunet-Germain[14], measured the refractive indices of PAA and PAP and their mixtures at different wavelengths using the prism method described by Chatelain and Pellet[8]. They observed that the refractive indices of various mixtures could be evaluated from the refractive indices of the constituents if the reduced temperatures were used. They also found that the temperature of isotropic melting of mixtures, t_{fm}, lies between the temperatures of isotropic melting of PAA, t_{fa}, and of PAP, t_{fp}.

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[12] W.Kast, <u>Ann. Physik</u>, 33 (1938), 185

[13] A.Van Wijk, <u>Ann. Physik</u>, 5 (1929), 879

[14] P.Chatelain and Brunet-Germain, <u>C.R.Acad.Sci.Paris</u>, 259 (1964), 127

They also calculated the refractive indices of mixtures of various compositions from those of the pure compounds at the same values of the relative temperature. Then they calculated the refractive indices of the mixture from the expressions:

$$n'_{em} = n_{ea}(1-\tau) + n_{ep}\tau$$

$$n'_{om} = n_{oa}(1-\tau) + n_{op}\tau$$

where τ is the mole fraction of PAA in the mixture of this compound with PAP. From these expressions, the extraordinary refractive index of the ordinary refractive index at temperature 140°C, $\tau = 0.4 (40\%)$ and wavelength 589 mμ, are 1.802 and 1.550 ; but from experiment, they measured 1.799 and 1.552.

The above measurement was repeated by Brunet-Germain[15] in 1970. She found that at wavelength 589 mμ, 138°C and $\tau = 0.4$, the extraordinary and the ordinary index are 1.801 and 1.551, respectively. Brunet-Germain's calculated results agree well with the experimental results. She also showed that, for PAA and PAP, "relative temperatures" and "reduced temperatures" are equivalent. She also used the theory of Maier and Saupe[16,17], which indicated that for all nematic liquid crystals the properties are comparable at the same values of the "reduced temperature". Brunet-Germain concluded from her results that the indices of mixtures of various compositions can be calculated from those of the pure compounds considered at the same values of the "relative temperature".

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[15] M.Brunet-Germain, Mol.Cryst.Liquid Cryst.,11 (1970), 289

[16] W.Maier and A.Saupe, Z.Naturforsch., 14a (1959), 882

[17] W.Maier and A.Saupe, Z.Naturforsch., 15a (1960), 287

The calculated indices and the experimental indices are in good agreement because the molecules of PAA and PAP have similar structures, but this is certainly not true for all nematic liquid crystals.

In the same year (1970), Brunet-Germain[18] measured the refractive indices of N-(p-Methoxybenzylidene)-p-butylaniline (MBBA) using the method described by Pellet and Chatelain. She showed that, in the case of this substance, with increasing time after preparation, the extraordinary index decreased whereas the ordinary index increased.

In 1971, Pelzl and Sackmann[19] measured the refractive indices of 32 liquid crystalline substances and studied their dependence on temperature and wavelength. The measurements of the refractive indices were carried out by using Abbe's double-prism method in which the crystalline liquid is a thin film between the hypotenuse areas of two rectangular prisms. Such film could be obtained from the nematic states and the smectic modifications A and B. They have shown that the double refraction is strong and, at the phase transition between two liquid crystalline modifications, the double refraction changes discontinuously. The double refraction and the extraordinary index in the nematic state decrease with rising temperature, whereas the ordinary index increases with increasing temperature. With increasing number of carbon atoms in the side chains, the refractive indices n_e, n_o and n_i decrease. They have also shown that in the nematic state the dispersion of the extraordinary index increases with decreasing temperature and the dispersion of the ordinary index decreases.

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[18] M.Brunet-Germain, <u>C.R.Acad.Sci.Paris</u>, Ser.B 271 (1970),1075

[19] G.Pelzl and H.Sackmann, <u>in Symposia of the Faraday Society</u>, No.5, 1971 : <u>Liquid Crystals</u>,(The Faraday Division, Chemical Society, London, 1972), p.68

Leelaprute[20] has investigated the refractivity of six nematic liquid crystals and their mixtures at the wavelength of sodium light by using the method of minimum deviation. The contours of n_e in the temperature-composition plane have been illustrated for three binary mixtures. An interesting result obtained from these patterns is that, in the case of mixtures of very similar compounds such as p-(p-ethoxyphenylazo)phenyl hexanoate (EPP-Hex) and p-(p-ethoxyphenylazo) phenyl heptanoate (EPP-Hep), the value of n_e shows a broad minimum with respect to composition at all temperatures within the nematic region. It has been suggested that this effect may arise from the cis-trans isomerization of the constituent azo-compounds.

In 1972, Dolphin, Muljiani, Cheng and Meyer[21] measured the refractive indices of the racemic forms of p-ethoxybenzal-p-(β-methylbutyl)aniline(EBMBA) and p-butoxybenzal-p-(β-methylbutyl) aniline(BBMBA) at wavelength 6328 Å , by using a Pulfrich refractometer. They calculated the average index from the expression :

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

and compared it with the isotropic liquid index. They plotted the refractive indices versus temperature as shown in Fig. 1 and Fig. 2

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[20] S.Leelaprute , <u>Refractivity of Nematic Liquid Crystals</u>, M.Sc. Thesis, Department of Chemistry, Mahidol University, Bangkok, 1972

[21] D.Dolphin, Z.Muljiani, J.Cheng and R.B.Meyer, <u>J.Chem.Phys.</u> 58 (1973), 2

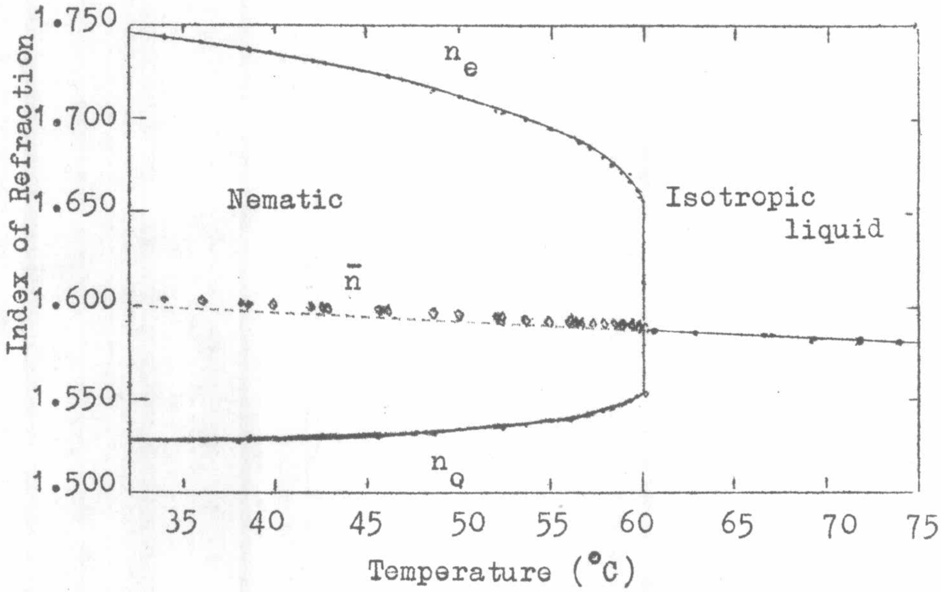

Fig.1 Indices of refraction of EBMBA (After Ref.21)

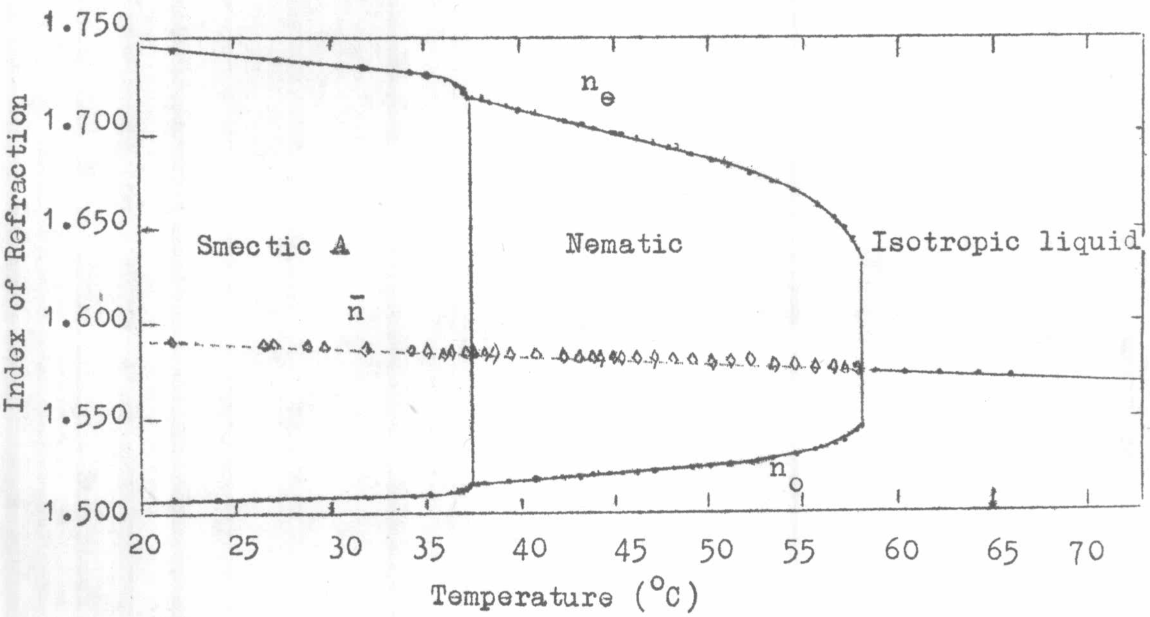

Fig.2 Indices of refraction of BBMBA (After Ref.21)

They concluded that the average indices of the nematic phase and of the smectic phase, and the isotropic liquid index join together in a straight line. They obtained an estimate for the volume expansion coefficient of these compounds, from the Lorentz-Lorenz relation:

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

where $\bar{n}$ is the average index.

$\bar{\alpha}$ is the mean molecular polarizability.

N is the number of molecules per volume.

Assuming that $\bar{\alpha}$ is independent of temperature, then the temperature dependence in the average index must be due to the temperature dependence of the density, N. Thus the volume expansion coefficient is

$$\beta = \frac{1}{V}\frac{dV}{dT} = -\frac{1}{N}\frac{dN}{dT}$$

$$= -(d/dT)\ \ln\left[(\bar{n}^2-1)/(\bar{n}^2+2)\right]$$

They also plotted $\ln\left[(\bar{n}^2-1)/(\bar{n}^2+2)\right]$ versus temperature. They found that for both compounds, the graph is linear except near the transitions. From the slope of the graph, they obtained the following volume expansion coefficients:

racemic EBMBA:	0.80×10^{-3} /°C	nematic liquid.
	0.62×10^{-3} /°C	isotropic liquid.
racemic BBMBA:	0.43×10^{-3} /°C	smectic phase.
	0.73×10^{-3} /°C	nematic liquid.
	0.74×10^{-3} /°C	isotropic liquid.

Recently, Müller and Stegemeyer[22] have studied the birefringence of compensated cholesteric liquid crystals by using a commercial Abbé refractometer. At the compensation temperature, a homeotropic nematic texture was achieved, as indicated by an exchange of extraordinary and ordinary ray and the strong increase of birefringence.

I.2 Purpose of the Present Experiments.

The principal purpose of this initial study is an attempt to elucidate the relationships between the extraordinary index, the ordinary index and the relative temperature (t_f-t). The method of minimum deviation, using a small-angle prism of liquid crystals, is used to measure the two spectral lines of the extraordinary and ordinary rays. The minimum deviation angles of six liquid crystals and their mixtures are obtained at different temperatures in the nematic range. The phase equilibria of the binary mixtures studied have already been investigated by Pdungsap[23] and Buanam-om[24].

The contours of the extraordinary refractive indices in the temperature-composition plane, and the temperature dependence of the refractive indices at different compositions, are demonstrated. The double refraction of six compounds and their mixtures is plotted against the difference between the measured temperature and the transition temperature. The relationships between the extraordinary index, the ordinary index, the average index, the isotropic liquid index and the temperature observed of six pure compounds and their mixtures are demonstrated.

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[22] W.H.Müller and H.Stegemeyer, Ber.Bunsenges.Physik.Chem. 77 (1973), 20

[23] L.Pdungsap, Phase Equilibria of Mixed Liquid Crystals, M.Sc. Thesis, Department of Chemistry, Mahidol University, Bangkok, Thailand., 1972

[24] C.Buanam-om, Thermal Properties and Phase Behaviors of Liquid Crystals, M.Sc. Thesis, Department of Chemistry, Mahidol University, Bangkok, Thailand., 1973