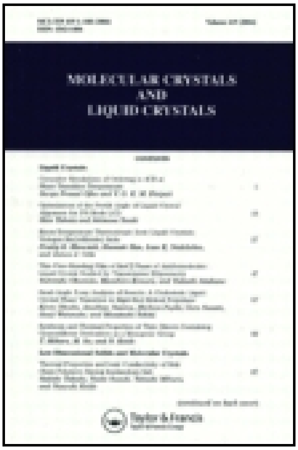

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The Anisotropic Refractive Indices of Aligned MBBA Liquid Crystal Films

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The Anisotropic Refractive Indices of Aligned MBBA Liquid Crystal Films

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The anisotropic refractive indices of unidirectionally and horizontally aligned MBBA liquid crystal films were determined by means of polarimetry and transmission measurements in the wave length region 0.42 to 0.70 μ at room temperature. The analyses show that absorption in this wave length region is negligibly small ($k_{\parallel} \cong k_{\perp} \cong 0.0005$) and that $n_{\parallel}$ decreases while $n_{\perp}$ increases with increasing wave length with the net result that the birefringence $\Delta n (= n_{\parallel} - n_{\perp})$ decreases rapidly first from 1.06 at $\lambda = 0.42\ \mu$ then slowly to 0.28 at $\lambda = 0.70 \mu$.

INTRODUCTION

The rapid advancement of nematic liquid crystals in display device applications motivated us to redetermine the anisotropic refractive indices of these materials, specifically MBBA (methoxybenzylidene butylaniline).[1] Accurate measurements have been difficult in the past for lack of well aligned crystal films. We report here our measurement of the anisotropic refractive indices of unidirectionally and horizontally aligned (with respect to glass substrate) MBBA liquid crystal films at room temperature by means of polarimetric and transmission techniques.

MATHEMATICAL FORMULATION

Determination of $\Delta n = n_\parallel - n_\perp$ by Means of Polarimetry

We define $\hat{n}_\parallel = n_\parallel - ik_\parallel$ and $\hat{n}_\perp = n_\perp - ik_\perp$ as the refractive indices parallel and perpendicular, respectively, to the liquid crystal directors. When the imaginary parts of the refractive indices are negligibly small, a unidirectionally and horizontally aligned nematic liquid crystal film placed between a pair of polarizers will transmit light at normal incidence of intensity I_0 and wave length λ according to[2]:

$$I = I_0[\cos^2\psi - \mathrm{Sin}\,2\phi\,\mathrm{Sin}\,2(\phi - \psi)\mathrm{Sin}^2\frac{\delta_t}{2}]$$
$$\delta_t = \frac{2\pi\Delta n d}{\lambda} \tag{1}$$

where ϕ is the angle that the polarizer makes with direction in the film plane and normal to the liquid crystal directors, ψ is the angle between the polarizer and analyzer, d is the film thickness, and $\Delta n = n_\parallel - n_\perp$ is the film birefringence. The transmitted intensity will have oscillations where the phase difference between consecutive absorption peaks (or valleys) is 2π, that is,

$$\delta_{t_1} - \delta_{t_2} = 2\pi d\left(\frac{\Delta n_1}{\lambda_2} - \frac{\Delta n_2}{\lambda_2}\right) = 2\pi \tag{2}$$

Provided the change in wave length between consecutive oscillations is small so that $\Delta n_1 \cong \Delta n_2 \cong \Delta n$, we have from Eq. (2),

$$\Delta n = \frac{\lambda_1\lambda_2}{d(\lambda_2 - \lambda_1)} = \frac{\bar{\lambda}^2}{d\Delta\lambda}\,. \tag{3}$$

Eq. (3) is used for the determination of Δn as function of $\bar{\lambda}$ $(=\sqrt{\lambda_1\lambda_2})$. Details of the Δn determinations have been reported by the author elsewhere.[3]

Determination of $n_\parallel$, $n_\perp$, $k_\parallel$ and $k_\perp$ from transmission measurements at normal Incidence

A schematic sectional view of the liquid crystal cell is shown in Figure 1. Employing normal incidence, we write the following expression for the transmittance,[4]

$$T = \frac{t_1 t_2 \exp[-2\pi i(n+ik)d/\lambda]}{1 + r_1 r_2 \exp[-4\pi i(n+ik)d/\lambda]}\exp(2\pi i n_0 d/\lambda)$$
$$r_1 r_2 = \frac{-[n^2 - n_0(n-ik)]^2}{[n^2 + n_0(n-ik)]^2} \tag{4}$$

$$t_1 t_2 = \frac{4n_0 n^2 (n-ik)}{[n^2+n_0(n-ik)]^2}$$

where the subscripts $\parallel$ and $\perp$, corresponding respectively to the parallel and perpendicular orientations, have been dropped for simplicity. All the parameters in Eq. (4) have been defined, except n_0, which is the refractive index of the glass substrate. It will be noted that n_0,† $n_\parallel$, $n_\perp$, $k_\parallel$ and $k_\perp$ are wave length dependent. After rearrangement, Eq. (4) can be rewritten as,

$$T = \frac{4\, n_0\, n^2\, (n - i\, k) \exp{(Gk)} \exp{(i\, Gn)}}{(A + i\, B) - (C + i\, D) \exp{(-2\, i\, Gn)} \exp{(2\, Gk)}} \exp{(i\, Gn_0)}$$

$$A = n^2\, (n + n_0)^2 - n_0^{\,2}\, k^2 \tag{5}$$

$$B = -2\, n\, n_0\, k\, (n + n_0)\ , \quad G = 2\, \pi\, d\, /\, \lambda$$

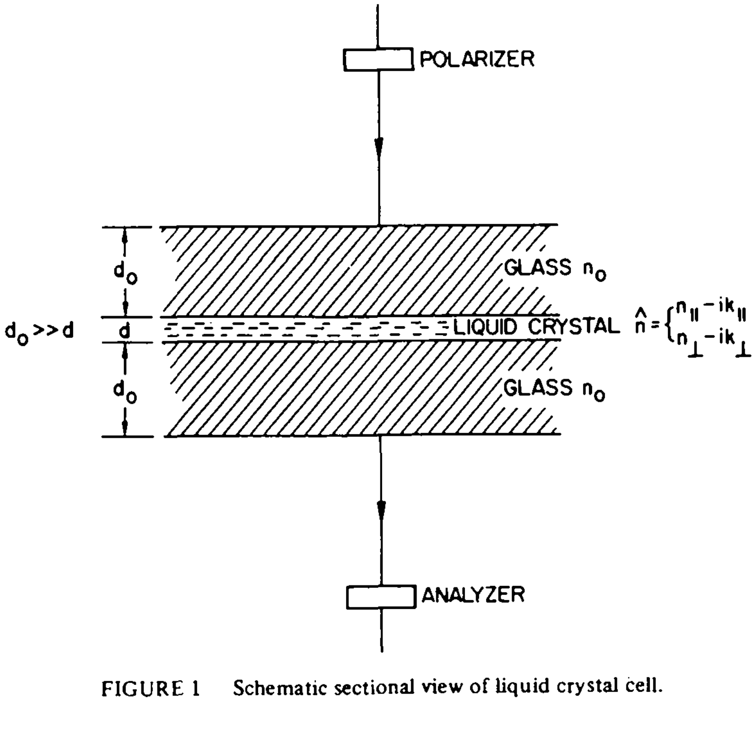

FIGURE 1 Schematic sectional view of liquid crystal cell.

† n_0 for the glass substrate used has the following values: 1.535, 1.519, 1.510 and 1.508 at $\lambda = 0.42$, 0.50, 0.60 and 0.70μ, respectively.

$$C = [n^2 (n - n_0)^2 - n_0{}^2 k^2] \exp(2Gk)$$
$$D = [2 n n_0 k (n - n_0)] \exp(2Gk)$$

The expression for the energy of the transmitted beam is,

$$TT^* = \frac{16 n_0{}^2 n^2 (n^2 + k^2) \exp(2Gk)}{A^2 + B^2 + C^2 + D^2 + 2(AC+BD)\cos(-2Gn) + 2(BC - AD)\sin(2Gn)} \tag{6}$$

Eq. (6) is actually a pair of expressions for the two separate cases where the polarizer and analyzer are, respectively, parallel and perpendicular to the liquid crystal directors. Since the polarizer and analyzer are parallel to each other, the cos ($-2Gn$) function is unity and the sin ($2Gn$) function is zero, as the phase difference is zero. We further assume $k_{\parallel} \cong k_{\perp} \cong k$ and obtain the following working equations:

$$TT^*_{\parallel} = \frac{16 n_0{}^2 n_{\parallel}{}^2 (n_{\parallel}{}^2 + k^2) \exp(2Gk)}{A^2 + B^2 + C^2 + D^2 + 2(AC + BD)}$$
$$TT^*_{\perp} = \frac{16 n_0{}^2 n_{\perp}{}^2 (n_{\perp}{}^2 + k^2) \exp(2Gk)}{A^2 + B^2 + C^2 + D^2 + 2(AC + BD)} \tag{7}$$

where A, B, C and D are given by Eq. (5) for each of the parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) orientations. In actuality, the absolute transmitted intensities $TT^*_{\parallel}$ and $TT^*_{\perp}$ vary considerably from film to film, as the transmittances are of the order of unity. However, for a given film, the ratio $TT^*_{\parallel}/TT^*_{\perp}$ is much more accurate and reproduces reasonably well from film to film. The $\Delta n(=n_{\parallel} - n_{\perp})$ measurements are also very accurate. We first assume a given value of k and $n_{\parallel}$ and $n_{\perp}$ values are solved by means of a computer and the computations are reiterated until self-consistency. Independent laboratory measurements of $\bar{n}(=1/3 n_{\parallel} + 2/3 n_{\perp})$ at fixed wave lengths provide additional checks of the consistency of our solutions.

EXPERIMENTAL RESULTS

The experimental cell was made of glass slides spaced with Mylar sheets of the appropriate thickness. Previous to mounting, the glass substrates were rubbed unidirectionally with $1/4\mu$ diamond paste, cleaned, and treated with a proprietary surfactant to promote unidirectional alignment. The cell, after thickness measurements, was filled with distilled MBBA (nematic to isotropic transition temperature 318.4 to 319.2°K) and checked for alignment homogeneity between a pair of crossed polarizers. Only those cells giving uniform brightening

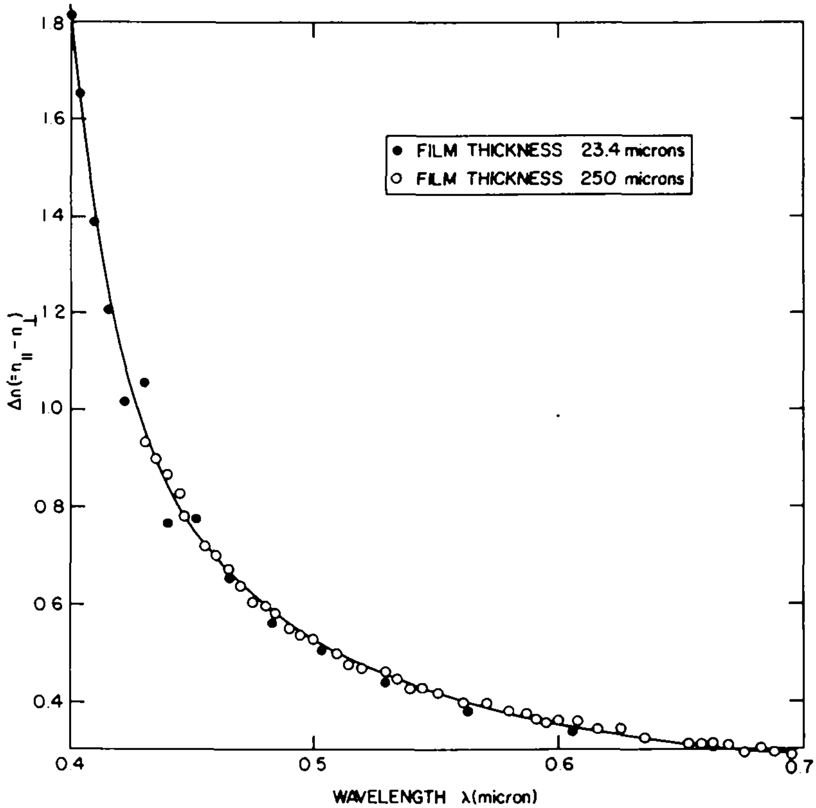

FIGURE 2 Δn vs. λ for MBBA films 23.4 and 250μ thick.

and darkening over the whole film for every 90° rotation of the film (with respect to the crossed pair of polarizers) were used for the birefringence and transmittance measurements. All the measurements were made at room temperature (293±1°K).

A cary-14 spectrophotometer equipped with a pair of Glan-Thompson prisms as the polarizer and analyzer was used in this study. For determinations of Δn described in Sec. 2(A), the liquid crystal film is oriented to give $\phi = 45°$ and $\psi = 90°$. For transmittance measurements described in Sec. 2(B), $TT^*_{\parallel}/TT^*_{\perp}$ dependence on wave length for several films was measured as the ratio of transmitted intensities for the parallel and perpendicular orientations. Another important measurement is the film thickness; this is done accurately over the entire wave length region of interest by means of polarimetry employing the empty cell before filling with the liquid crystal.[3] For example, the measurements of one

TABLE I

Summary of computer results in comparison with experimental observations

λ, μ	Calculated						Observed [a]	
	$n_{\parallel}$	$n_{\perp}$	$\bar{n}$	$TT^*_{\parallel}/TT^*_{\perp}$			$TT^*_{\parallel}/TT^*_{\perp}$	Δn
				$k = 10^{-4}$	$k = 5 \times 10^{-4}$	$k = 10^{-3}$		
0.42	2.355	1.290	1.645	0.858	0.861	0.805	0.867	1.065
0.44	2.111	1.320	1.584	0.921	0.922	0.890	0.950	0.791
0.46	1.981	1.340	1.554	0.950	0.950	0.931	0.968	0.641
0.48	1.899	1.360	1.540	0.964	0.965	0.951	0.973	0.539
0.50	1.849	1.370	1.530	0.972	0.972	0.962	0.975	0.479
0.55	1.779	1.400	1.526	0.980	0.980	0.974	0.983	0.379
0.60	1.744	1.420	1.528	0.983	0.983	0.978	0.981	0.324
0.65	1.724	1.430	1.528	0.985	0.985	0.981	0.985	0.294
0.70	1.713	1.430	1.524	0.986	0.987	0.983	0.986	0.283

[a] Averaged over four experiments.

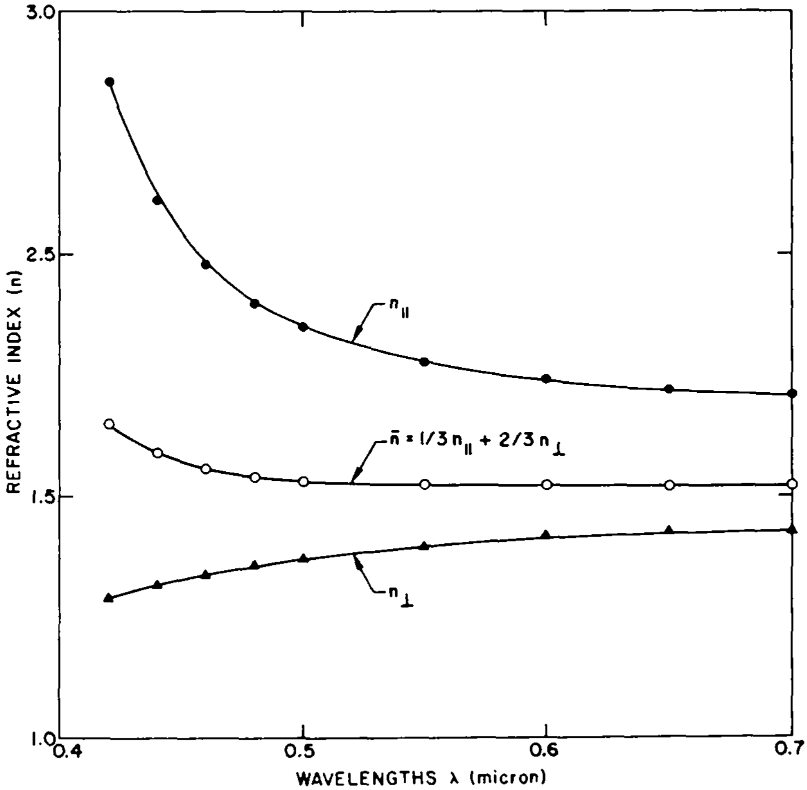

FIGURE 3 $n_{\parallel}$, $n_{\perp}$ and n vs. λ for MBBA films ($k_{\parallel} \cong k_{\perp} \cong 0.0005$).

cell in the wave length region 0.40 to 0.70μ yielded 47 thickness values averaged to give a true film thickness of 23.4 ± 1.6μ.

Figure 2 reproduces the Δn variations with λ for two cells 23.4 and 250μ thick, respectively. The computer solutions of $n_{\parallel}$ and $n_{\perp}$ ($k = 0.0005$) from the average of four separate $TT_{\parallel}^{*}/TT_{\perp}^{*}$ determinations as well as $n(=1/3n_{\parallel} + 2/3n_{\perp})$ are plotted vs. λ in Figure 3. The $n_{\parallel}$, $n_{\perp}$, k and $TT_{\parallel}^{*}/TT_{\perp}^{*}$ values at various wave lengths are listed in Table 1.

DISCUSSION

Our $n_{\parallel}$ values for MBBA are close to, but our $n_{\perp}$ values are very different from those reported by MBG of Ref. (1). Our analyses show further that $n_{\parallel}$ decreases while $n_{\perp}$ increases with increasing wave length, a very unusual but interesting result. Our data are reasonably good and the analyses rigorous. The finding may be of theoretical significance. We simply present our data and analyses here and leave the theoretical interpretation for future consideration.

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