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Roger Chang^a

^a Rockwell International Science Center, Thousand Oaks, California

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THE ANISOTROPIC REFRACTIVE INDICES OF MBBA

ROGER CHANG

Rockwell International Science Center,
 Thousand Oaks, California

(Submitted for publication May 20, 1976)

The anisotropic refractive indices of MBBA at room temperature from optical interference measurements were re-evaluated using the exact formula for wavelength dispersion. This re-evaluation brings into agreement all the published results on the subject by various investigators employing different measuring techniques.

We have reported our initial results on the anisotropic refractive indices of MBBA at room temperature from optical interference measurements.^(1,2) In these investigations the transmitted intensity versus wavelength of light (polarizer and analyzer parallel and at an angle of $\pi/4$ with respect to the liquid crystal director) shows oscillations where the phase difference between each two consecutive oscillations is 2π . The exact formula for the phase shift between each two consecutive oscillations is,

$$2\pi d \left(\frac{\Delta n_{\lambda_1}}{\lambda_1} - \frac{\Delta n_{\lambda_2}}{\lambda_2} \right) = 2\pi \quad (1)$$

where d is the film thickness; λ_1, λ_2 are the wavelengths of the two consecutive peak (or valley) positions; Δn_{λ_i} are the corresponding birefringences ($\Delta n = n_{\parallel} - n_{\perp}$, n_{\parallel} and n_{\perp} being the refractive index parallel and perpendicular to the liquid crystal director) at wavelengths λ_1 and λ_2 . In our earlier communications^(1,2) we made the approximation $\Delta n_{\lambda_1} \cong \Delta n_{\lambda_2} = \Delta n_{\lambda}$, and equation (1) becomes

$$2\pi d \Delta n_{\lambda} \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) = 2\pi, \quad \lambda = \sqrt{\lambda_1 \lambda_2} \quad (2)$$

The approximation given by equation (2) overestimates the birefringence (Δn) values by about 20 to 30 percent in the red

region. At shorter wavelengths, however, the errors introduced can be substantial.⁽³⁾ The exact equation (1) was used in our later investigations of the orientational order parameters of nematic liquid crystals.^(4,5) Very recently, Kuczynski and Stryla⁽⁶⁾ reported an interference method for the determination of refractive indices and birefringence of nematic liquid crystals. These investigators are probably not aware of our earlier work discussed in references (1) and (2). They used the same approximate equation (2) for birefringence calculations. The results are erroneous. We feel that a re-evaluation of our earlier data in terms of the exact equation (1) is in order. Equation (1) can be rearranged to give,

$$\Delta n_{\lambda_i} = \left(\frac{1}{d} + \frac{\Delta n_{\lambda_{i+1}}}{\lambda_{i+1}} \right) \lambda_i \quad (3)$$

where λ_i and λ_{i+1} are the consecutive wavelength positions of the peaks (or valleys) of the spectrophotometer trace. Equation (3) says that the birefringence at successive lower or higher wavelengths can be obtained exactly from a known value of the birefringence at any given wavelength. The best estimated values of the refractive indices and birefringence of MBBA at room temperature (22°C) from ours as well as other published information^(7,8) are $n_{||} = 1.76$, $n_{\perp} = 1.54$, $\Delta n = 0.22$, at $\lambda = 6300$ to 6500 Å. Provided with this information, we recalculated the refractive indices and birefringences of MBBA at room temperature from the data presented in reference (2) using the exact equation (1). The results shown in Tables I and II are in substantial agreement with those reported previously by Brunet-Germain⁽⁷⁾ and Haller et al⁽⁸⁾. We conclude the following: (a) The exact equation (1) must be used for birefringence calculations. (b) Optical interference technique reported here^(1,2,6) is a very useful one in evaluating quantitatively the anisotropic refractive indices and dispersion of these indices of liquid crystals. (c) Existing published results on the refractive indices of MBBA by various techniques are in good agreement.

TABLE 1. Dispersion of Birefringence of MBBA (22°C)
from Optical Interference Measurements

$\lambda, \text{\AA}$	Δn	$\lambda, \text{\AA}$	Δn	$\lambda, \text{\AA}$	Δn
6398	0.220	5806	0.232	4900	0.280
6348	0.221	5703	0.235	4850	0.285
6298	0.221 ⁵	5608	0.238	4802	0.290
6251	0.222	5515	0.240	4750	0.294
6205	0.223	5413	0.244	4700	0.299
6160	0.224	5399	0.248	4652	0.303
6115	0.225	5346	0.252	4601	0.307
6073	0.226	5296	0.256	4550	0.311
6031	0.227	5200	0.258	4500	0.315
5992	0.228	5143	0.261	4450	0.318 ⁵
5954	0.228 ⁵	5100	0.267	4400	0.322
5915	0.229	5001	0.270	4350	0.325
5877	0.230	4946	0.275	4300	0.328

TABLE 2. Re-evaluation of $n_{||}$ and n_{\perp} of MBBA (22°C)
from Transmission Measurements

λ, micron	Calculated				Observed	
	$n_{ }$	n_{\perp}	\bar{n}	$TT_{ }^*/TT_{\perp}^*$ ($k=5 \times 10^{-4}$)	$TT_{ }^*/TT_{\perp}^*$	Δn
0.44	1.901	1.578	1.685	0.947	0.950	0.322
0.46	1.881	1.573	1.675	0.951	0.968	0.308
0.48	1.858	1.568	1.664	0.956	0.972	0.290
0.50	1.834	1.563	1.653	0.961	0.975	0.271
0.55	1.796	1.554	1.634	0.968	0.983	0.242
0.60	1.775	1.548	1.623	0.972	0.981	0.227
0.65	1.762	1.543	1.616	0.974	0.985	0.219
0.70	1.753	1.540	1.611	0.976	0.986	0.213

- (a) $\bar{n} = \frac{1}{3} n_{||} + \frac{2}{3} n_{\perp}$
- (b) $TT_{||}^*/TT_{\perp}^*$ is ratio of transmitted intensity for parallel polarization to that for perpendicular polarization.
- (c) k is the assumed absorption coefficient for both parallel and perpendicular polarizations.

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