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# A new version of the Chang method for the determination of the optical birefringence of nematic liquid crystals

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We report a new experimental technique for the measurement of the optical birefringence Δn of nematic liquid crystals. This new version of Chang's method is verified for (p-etoxy-benzylidene)-p-n-butylaniline (EBBA). The cell filled with EBBA is placed between crossed polarizers which make an angle of 45° with the optical axis. The wavelength dependence of the light intensity transmitted by the analyzer has been recorded at various temperatures. In the Chang method, by using the wavelengths $\lambda_i$ and $\lambda_{i+1}$ of two consecutive minima ($\lambda_i<\lambda_{i+1}$), and by considering that $\Delta n(\lambda_i) = \Delta n(\lambda_{i+1})$ the optical birefringence is calculated according to the relation $\Delta n= \lambda_i\lambda_{i+1}/d(\lambda_{i+1}-\lambda_i)$, where d is the thickness of the cell. The accuracy of Chang's method is affected on the one hand by considering only of wavelengths corresponding to minima of the transmitted light and by the other hand by completely neglecting the dispersion of optical birefringence. The method proposed here solves both weaknesses by considering all the experimental data, contained into a large spectral range, and by using the dispersion of the optical birefringence given by the three-band model. By applying a nonlinear fitting procedure on the recorded experimental data we have obtained the parameters involved in the expressions of the optical birefringence and we have computed the optical birefringence of EBBA at these temperatures. Our results are in a very good agreement with the corresponding ones obtained by using the Talbot-Rayleigh method. Unlike the Talbot-Rayleigh method, which mainly determines the ordinary and extraordinary refractive indices, that can be further used at the computation of optical birefringence, our method allows for the direct determination of the birefringence, without other intermediate steps.

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## 1. Introduction

A nematic liquid crystal (NLC) locally behaves like an uniaxial anisotropic material. The optical birefringence, defined like $\Delta n = n_e - n_o$, can be easily controlled through the variation of temperature and/or external fields. In the above, $n_e$ and $n_o$ denotes the principal extraordinary refractive index and the ordinary refractive index, respectively.

Many interference methods have been developed to determine the optical birefringence of NLCs. The interference method for wedge-shaped nematic samples was first described by Haller et al. [1], and later was applied by Van Hecke at al. [2]. Several methods are based on the interference of the ordinary and extraordinary ray in plane-parallel nematic cells [3,4]. In the interference method proposed by Chang [4] the temperature is kept constant and the wavelength is changed continuously by using a spectrophotometer. From the wavelengths of consecutive minima the birefringence can be calculated, but the dispersion of Δn must be considered [5-7] in order to achieve higher accuracy.

Much work has been done to investigate the physical origin of the refractive index dispersions of liquid crystals [8-11].

In the framework of the three-band model [10], one considers a single $\sigma\rightarrow\sigma^*$ transition (designated as the $\lambda_0$-band, located in the vacuum UV region, $\lambda_0 \sim 120$ nm) and two $\pi\rightarrow\pi^*$ transitions (designated as the $\lambda_1$- and $\lambda_2$-bands, with $\lambda_2 > \lambda_1$, placed in the nearby-ultraviolet). For this model, in the visible and infrared regions where $\lambda >> \lambda_0$, the optical birefringence $\Delta n(\lambda, t)$ is expresed as:

$$\Delta n(\lambda,t) = \Delta n_0(t) + G_1(t)\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + G_2(t)\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2}, \qquad (1)$$

where $\lambda$ is the wavelength of light, $t$ denotes the temperature of the NLC and $\Delta n_0$, $G_1$, and $G_2$ represent three temperature-dependent parameters.

In this paper we present a new experimental technique based on Chang's method. We make some improvements of the experimental setup and we develop a new technique for processing the experimental data. We take into account all the experimental data, not only those corresponding to minima of the transmitted intensity. Our method is exemplified for EBBA from Eastman Merck. The molecular structure, the UV-visible absorption spectrum, and the values $\lambda_1 = 203$ nm and $\lambda_2 = 304$ nm for the $\pi\rightarrow\pi^*$ electronic transitions of EBBA are given in Ref. [12]. The uniform planar oriented nematic layer is observed in a white light beam between crossed polarizers, where the optical axis and the polarizers enclose an angle of 45°. The wavelength dependence of the light intensity transmitted by the analyzer $I_T(\lambda, t)$ has been recorded at various temperatures (50, 55, 60, 65) °C within the nematic phase range of [36 - 80] °C of EBBA. A nonlinear fitting procedure of the recorded light intensity $I_T(\lambda, t)$ allows one to deduce the parameters involves in the calculation of

$\Delta n(\lambda, t)$. The values of the optical birefringence of EBBA obtained by our method are in a very good agreement with the corresponding ones obtained by using a new version of the Talbot-Rayleigh method [12]. Although both methods yield correspondent results, ours uses a much simple experimental setup, which allows in addition for local measurements on the sample, of about 4 μm in diameter. We use a spectrometer connected to a computer, which induces an elegant manner of recording the experimental data, in contrast to the difficult way of channeled spectra recording in the Talbot-Rayleigh method [12], which requires a diffraction grating and a CCD linear array, which must be calibrated by means a set of interference filters.

## 2. Experimental method and results

The measurements were realized by using a standard sandwich glass cell. The inner surfaces of the glasses were spin covered with a solution of poly(vinyl alcohol) and water (3:100). The thin polymeric film has been baked in an oven at 120 $^{o}$C for an hour. Subsequently, the thin film has been rubbed along a given direction in order to ensure a planar alignment of the NLC along the rubbing direction. The glass plates composing the cell have been distanced at about 54 μm by using a set of three Mylar spacers (two spacers of 23 μm each and one spacer of 8 μm) and then have been attached together by epoxidic resine.

In order to determine the thickness "d" of the empty cell, corresponding to a small marked area on one of the glass plates, at a laboratory temperature of about 23 °C, the experimental setup presented in Fig. 1 has been used.

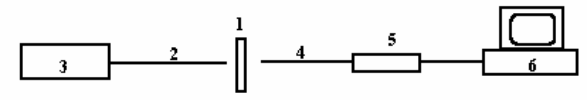


*Fig. 1. Experimental setup for empty cell thickness measurements.*

The cell (1) is empty. The LS-1-LL Tungsten Halogen light source (3) has a spectral range of 360-2000 nm. The parallel beam emerging from the optical fiber (2) is at normal incidence on the cell. The transmitted light comes to an Ocean Optics Spectrometer S 2000 (5) through the optical fiber (4). The computer (6) has a National Instruments interface. The wavelength-dependent transmitted intensity of the empty cell is presented in Fig. 2 (only within the 525-880 nm range).

The connection between d, the wavelength of the light (λ), and the k-th interference order at maximum transmittance is

$$k=2d/\lambda, \qquad (2)$$

which indicates a linear dependence between k and 1/λ. The slope B of the line $k = A + B \cdot (1/\lambda)$ obtained by linear regression of the experimental data (k,1/λ) is equal to 2d. If we assign the correct interference orders associated with the transmission maxima, then A goes to zero. The value of B is however independent of this assignment.

The first maximum is at 525.79 nm, while the second one is at 530.98 nm. If we consider the first interference order equal to 300 (associated with 525.79 nm), then the next interference order (associated with 530.98 nm) will be 299, the third interference order is of 298, and so on.

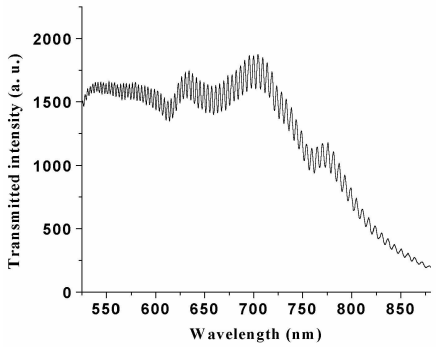


*Fig. 2. Wavelength-dependent transmitted intensity of the empty cell.*

In Fig. 3 is presented the interference order k versus 1/λ. Using a linear regression we obtain $A = 96.6587 \pm 0.0874$ and $B = 107.362 \pm 0.057 \mu m$. Consequently, the thickness of the cell, obtained in this manner, has the value $d = 53.681 \pm 0.028 \mu m$.

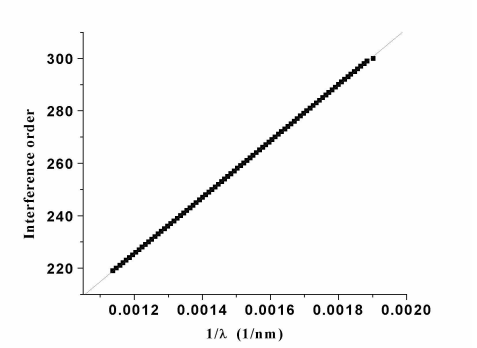


*Fig. 3. Interference order versus 1/λ for the empty cell.*

The experimental setup presented in Fig. 4 has been used in our new method. In order to verify the validity of this technique, we used the nematic liquid crystal EBBA. The cell filled with EBBA is placed within a special electric oven (2), which is connected to a temperature controller (12), allowing the sample to be cooled and heated at a 1 °C/min linear temperature rate. The temperature was measured with a Constantan-Copper thermocouple connected to a KEITHLEY 2000 multimeter of 0.01 °C precision (11). The computer (13) has two interfaces: DAS 1601 and IEEE 488. The oven is placed on the table (3) of an IOR-MC5A microscope (1). The sample was illuminated with white light from a quartz-Halogen lamp. The experimental setup also contains a polarizer (4) and an analyzer (5). The output image is displayed on the screen (7) by using the device (6). By a proper placement of the cell, the measurement of the optical birefringence has been performed within the marked area. The optical fiber (8) has a small diameter, of 400 μm, which allows for a local measurement on the sample, of about 4 μm in diameter. The spectrometer (9) is connected to the computer (10) via a National Instruments interface.

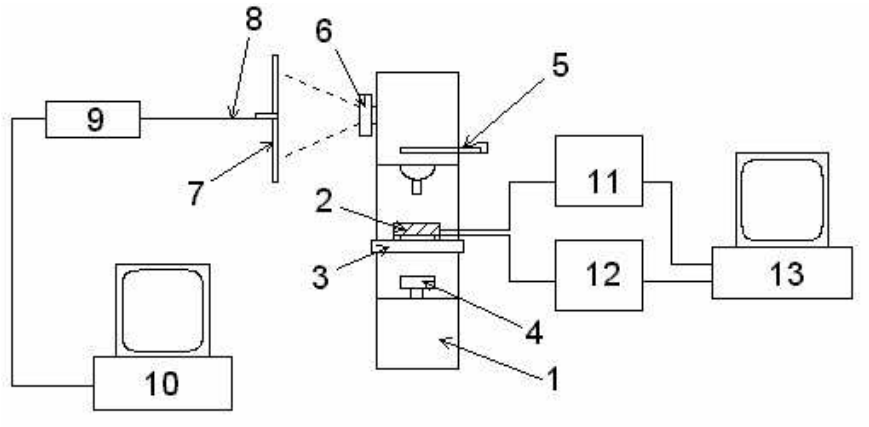


*Fig. 4. Experimental setup for the measurement of the optical birefringence of NLC.*

The sample is maintained with the optical axis at 45° to the crossed polarizers. The transmitted light $I_T(\lambda,t)$ is recorded using the spectrometer at various temperatures (50, 55, 60, 65) °C within the nematic phase range. We record the intensity $I_I(\lambda)$ in the absence of cell for parallel polarizers. The dark signal $D(\lambda)$ is obtained by switching off the quartz-Halogen lamp. We give in Fig. 5 the wavelength-dependent transmitted intensity at 50 °C.

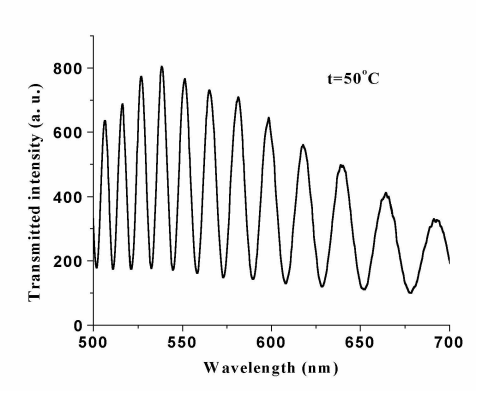


*Fig. 5. Wavelength-dependent transmitted intensity at 50 °C.*

In the ideal case the transmitted intensity $I_T(\lambda,t)$ is given by Fresnel's law:

$$I_T(\lambda,t) = I_I(\lambda)\cdot \sin^2\left(\frac{\pi\cdot\Delta n(\lambda,t)\cdot d}{\lambda}\right) \qquad (3)$$

In our experiment we must pay attention to several factors, like the dark signal $D(\lambda)$, the spectral distribution of the lamp, and also the spectral sensitiveness of the spectrometer. The most important of them is the dark signal, which is obtained by switching off the light source. Therefore, we should accordingly modify the relation (3) as follows:

$$\sin^2\left(\frac{\pi\cdot\Delta n(\lambda,t)\cdot d}{\lambda}\right) \propto \frac{I_T(\lambda,t)-D(\lambda)}{I_I(\lambda)-D(\lambda)} \equiv T(\lambda,t) \qquad (4)$$

In Fig. 6 the solid line indicates the transmittance $T(\lambda,t)$ at a temperature of 50 °C. We remark that the values of minima and maxima of the transmittance are not equal to zero and one, respectively, which is a consequence of neglecting some factors that influence the measurement. The transmittance has been rescaled by considering two polynomials, denoted by $y_{min}$ and $y_{max}$, which interpolate the minima of transmittance and the maxima of transmittance, respectively. Using a four-parameter Levenberg-Marquardt nonlinear fitting procedure in Microcal Origin 6.0 and the expression of the optical birefringence given by the three-band model, we determine the parameters $\Delta n_0(t)$, $G_1(t)$, and $G_2(t)$ involved with the computation of $\Delta n(\lambda,t)$, and also the thickness "d(t)" of the cell, which is also a temperature-dependent parameter. The probe function that has been used has the following form:

$$y_{min} + (y_{max} - y_{min})\cdot \sin^2\left(\pi\cdot\left(\Delta n_0 + G_1\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + G_2\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2}\right)\cdot d/\lambda\right) \qquad (5)$$

The dashed line in Fig. 6 signifies the result of the fitting procedure of $T(\lambda,t)$ at the same temperature t = 50 °C.

Using the same procedure as in the case t = 50 °C, we can determine the fitting parameters for other temperatures as well, see Table 1.

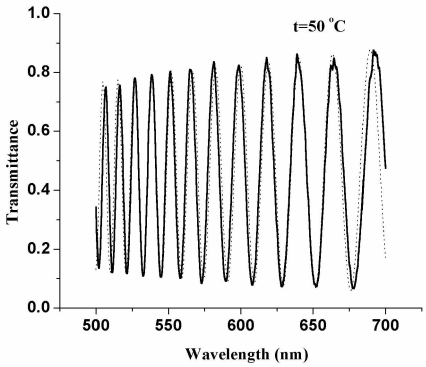


*Fig. 6. Determination of the parameters $\Delta n_0$, $G_1$, $G_2$, and d using the fitting procedure. The temperature is of 50 °C.*

*Table 1. Fitted parameters $\Delta n_0$, $G_1$, $G_2$, d, and $\chi^2$ (chi-square) at various temperatures.*

| Temperature (°C) | $\Delta n_0$ | $G_1$ ($10^{-6}$ nm$^{-2}$) | $G_2$ ($10^{-6}$ nm$^{-2}$) | d (nm) | $\chi^2$ ($10^{-3}$) |
|---|---|---|---|---|---|
| 50 | 0.10999 | 0.9691 | 0.9501 | 53799 | 1.57 |
| 55 | 0.10990 | 0.9520 | 0.9375 | 53934 | 2.92 |
| 60 | 0.10951 | 0.9428 | 0.9212 | 54317 | 2.53 |
| 65 | 0.10879 | 0.9363 | 0.9134 | 54490 | 1.05 |

We remark that the thickness "d(t)" of the cell increases as the temperature t of the cell increases and these values are in a good agreement with the value obtained in the case of the empty cell.

Using the data listed in Table 1 and the relation (1), we obtain the wavelength-dependent birefringence at these temperatures, see Fig. 7.

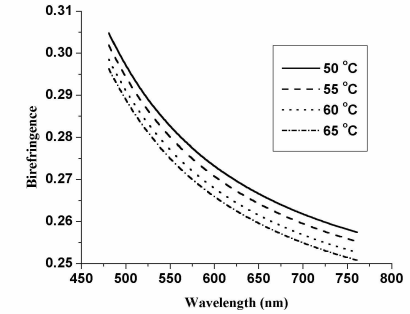


*Fig. 7. Birefringence versus wavelength at various temperatures.*

## 3. Discussion

The values of the fitting parameters $\Delta n_0(t)$, $G_1(t)$, and $G_2(t)$ for the EBBA have been obtained by using a new version of the Talbot-Rayleigh method [12]. As an example, for the temperature t = 50 °C, the values of these parameters reported in Ref. [12] are 0.110767, $1.00023 \cdot 10^{-6}$ nm$^{-2}$, and $0.95208 \cdot 10^{-6}$ nm$^{-2}$ respectively. We remark a good agreement between these values and the corresponding ones obtained by using our new method.

In Fig. 8 we expose the birefringence dispersion obtained by using both methods at a temperature of 50 °C. The solid line indicates the optical birefringence obtained by our new method, and the dashed line shows the result previously reported in [12]. The relative difference between the values of the optical birefringence obtained by these two methods is less than 0.9%.

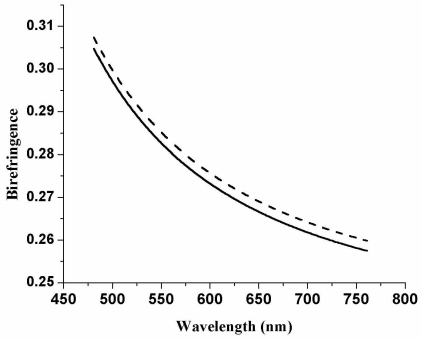


*Fig. 8. Birefringence versus wavelength at 50 °C using both methods.*

## 4. Conclusions

We presented a new experimental technique, which is a new version of the Chang method, for the measurement of the optical birefringence for nematic liquid crystals. The method has been exemplified for EBBA. The cell filled with the nematic liquid crystal has been placed between crossed polarizers, such that the optical axis makes an angle of 45° with the polarizers. The wavelength dependence of the light intensity transmitted by the analyzer $I_T(\lambda,t)$ has been recorded at various temperatures. In order to increase the accuracy of the Chang method, we have developed a new technique of processing experimental data where, unlike Chang's method, we essentially considered all the experimental data and the dispersion of optical birefringence $\Delta n(\lambda,t)$ in the framework of the three-band model. By applying a nonlinear fitting procedure on the $I_T(\lambda,t)$, we have obtained the parameters $\Delta n_0$, $G_1$, and $G_2$ involved in the calculation of $\Delta n(\lambda,t)$. The comparison between the values of the optical birefringence $\Delta n(\lambda,t)$ obtained by our new method and those previously reported [12] emphasizes a good agreement between these methods. The main advantage of our direct method, compared with the indirect one from [12], is that it is especially deviced for a fast, simple, and elegant calculation of optical birefringence.

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