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THE BIREFRINGENCE OF THIN FILMS OF SOME NEMATIC LIQUID CRYSTALS

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Birefringence and birefringence dispersion of N-(p-methoxy-benziliden)-p-n’-butylaniline (MBBA) as well as of poly-(pheny-methacrylic)-ester of cetyloxybenzoic-acid (PPMAECOBA) in tetrachloromethane (TCM) thin films have been determined. Measurements have been made, at room temperature, by two methods: interferometrically in monochromatic light and from the visible channeled spectra of thin layers. The dependence of the main refractive indices on light wavenumbers has been established using interferometrically estimated data. Having in view the good agreement between the birefringence computed with this dependence and the birefringence estimated from the visible channeled spectra, we consider that the established formulas could be used to give the visible main refractive indices of the studied NLC.

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1. Introduction

Mesogenic thermotropic and lyotropic systems are important both for fundamental research and for their applicability in optoelectronics. The field of liquid crystals attracts many workers today.

Liquid crystals are anisotropic fluids, considered as intermediate phases between the isotropic liquids and the anisotropic crystals [1-6]. The mesomorphic phase, occurring in a defined range of temperature and concentration, possesses a long range orientational order, even though it does not have a long range positional one [3-6]. In a nematic liquid crystal (NLC), the dominant statistic orientation of the long axes of the mesogenic molecules is given by the liquid crystal directory, the versor parallel with the preferential direction, determining the symmetry axis of highest order.

The refractive index of NLC-s depends both on the propagation direction of the electromagnetic waves and on their polarization state. So, it is given by a 3×3 matrix that in the main system of coordinates becomes a diagonal one. NLC-s [1-6] and cholesterics (CLC) [7] are usually uniaxial media [1-3], while some smectics [4,5] are biaxial ones.

Anisotropic uniax substances, such as NLC-s, are characterized by two values of the refractive index:

- ordinary value - n_o - measured for directions of the electric fields perpendicular on the axis of the highest symmetry order;
- extraordinary value - n_e - measured for the electric fields acting parallel with this axis.

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In the main system of coordinates, the matrix of refractive indices has only diagonal elements: $n_{11} = n_{22} = n_o$ and $n_{33} = n_e$. The main values of the refractive index are measured with linearly polarized waves. The ordinary value is measured with light having the electric field intensity parallel with the principal plane *aob* (perpendicular on the optical axis - *oc*) and the extraordinary value is measured with linearly polarized light having its electric field intensity parallel with optical axis.

Both thermotropic and lyotropic liquid crystals have the birefringence [8];

$$\Delta n = n_e - n_o \tag{1}$$

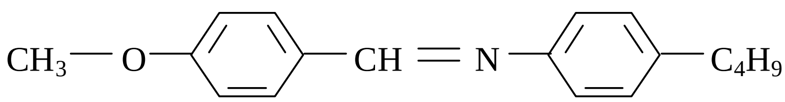
as function of the internal degree of order. Usually, the birefringence [8] is considered as a measure of the order degree in liquid crystalline sample. The order degree indicates the percent of the mesogenic molecules aligned in parallel with the nematic director. External electric or magnetic fields can increase the order parameter of the liquid crystalline sample [9-14].

Like as the refractive index, the birefringence shows dispersion in the visible range. In this paper we intend to establish the dependence of the main refractive indices and of the birefringence on the light wavenumbers in the visible range, for some NLC.

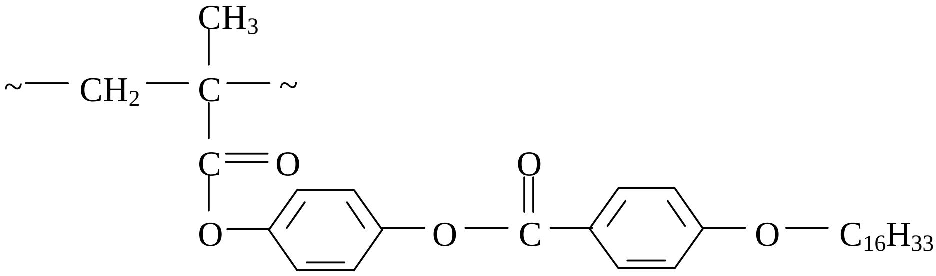
2. Experimental

In this study two types of nematic liquid crystals were used:

A) Pure N-(p-methoxy-benziliden)-p-n'-butylaniline (MBBA) purchased from Merck Company and used at 23 °C;
B) Mixture of poly-(phenyl-methacrylic) ester of cetyloxybenzoic acid (PPMAECOBA) 10^{-2} g/cm^3 in tetrachloromethane (TCM), prepared at P.Poni Institute of Macromolecular Chemistry of Iaşi, Romania, used at 23 °C as a lyotropic NLC. The molecular weight of the PPMAECOBA was determined by using the flow birefringence and optical anisotropy of the molecules, as it was described in [9]. To characterize the polymer, measurements of diffusion and sedimentation coefficients were performed and Svedberg equation was used to calculate molecular weight of the polymer (M=6.8×10^6).



MBBA



PPMAECOBA

A special cell that contains the NLC thin layer (Fig.1) was used. This cell consists from two glass plates, provided with a special layer of lecithin on their internal sides (named molecular orientation layer) and separated by four spacers with a calibrated weight (determining the thickness of the NLC anisotrope layer). In the upper glass plate a filling aperture is made, through which NLC can be introduced in the cell. The walls of the cell were cleaned in distilled water using an ultrasonic method and were covered by a thin molecular orientation layer of lecithin, obtained by slowly moving the internal walls of the cell through a solution of 5% lecithin in water.

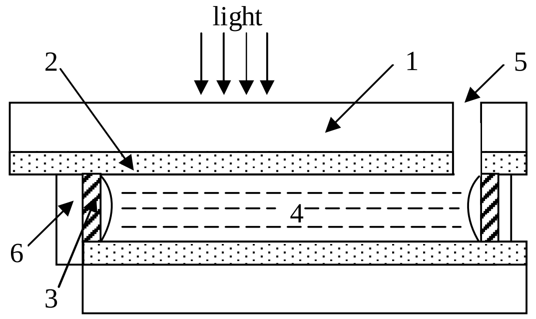


Fig. 1. The schematic representation of the cell containing NCL.

The experiments were made with layers of a fixed thickness, $L = 14\mu m$, determined by the spacers. The cell is sealed on the outside, around the contour, with epoxy resin. The dominant orientation of the long molecular axes was mechanically ensured [2,12].

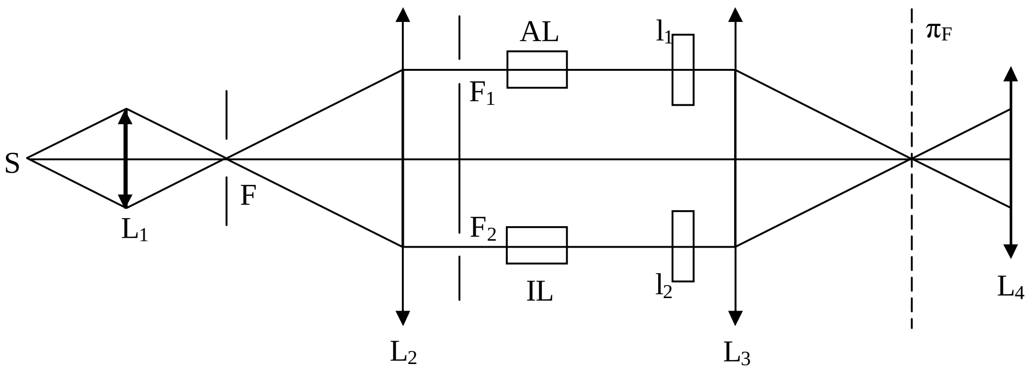


Fig. 2. Standard schematic representation of the Rayleigh interferometer S-monochromatic source; F-slit, F_1 and F_2- slits of diffraction grating; AL-anisotrope layer; IL –isotrope layer; l_1 and l_2- comensatory system; L_1, L_2, L_3, L_4 - lens.

The values of the ordinary and extraordinary refractive indices were interferometrically estimated using a Rayleigh interferometer (Fig. 2). Two identical polarizers are introduced in the two beams of the interferometer. The NLC layer (contained in the special cell) has been introduced in the measure beam (light propagates perpendicularly on the optical axis) and an identical cell filled with benzene (n=1.50) in the case of MBBA, or with α-brome-naphthalene (n=1.65) in the case of PPMAECOBA has been introduced in the comparison beam. So, the pathway differences in the two beams were small enough that the zero-fringe is moved in the visual field of the interferometer. Refractive index $n_i, i = o, e$ has been estimated with the formula:

$$n_i = n + \frac{k\lambda}{L}; i = o, e \tag{2}$$

In (2) k is the order of the monochromatic fringe that coincides with the zero fringe from the fixed system of fringes [15]. The main values of the refractive index were determined with the polarizer from the measure beam having its transmission direction parallel and perpendicular on the optical axis.

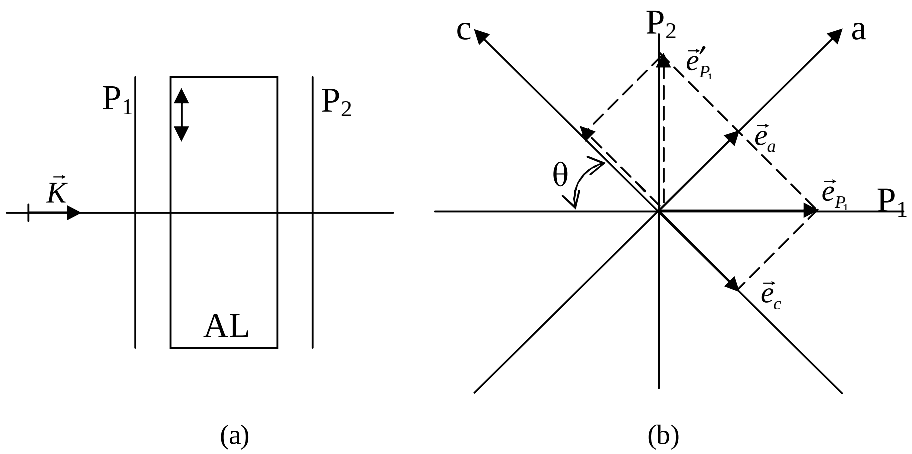


Fig. 3. (a) The device attached in the measure beam of the spectrophotometer for obtaining channeled spectra; (b) The relative orientation of the transmission directions of the polarizers and the main axis of NLC.

The device used in obtaining channeled spectra is illustrated in Fig. 3a. The anisotrope layer of NLC is placed between two crossed polarizers, that provide light polarization (P_1) and the analysis of the emergent light from the anisotrope layer (P_2). The relative orientation of the transmission directions of the polarizers and of the principal axes of NLC layer is suggested in Fig. 3b.

If the principal axes bisect the angles between the transmission directions of the polarizers ($\theta = 45^0$), the conditions in which the channels are obtained at zero light intensity and the maxima from the channeled spectra are of the highest intensity, are ensured. The channeled spectra were registered at a Specord UV VIS spectrophotometer with a Data Acquisition System, having in the measure beam the above described device and two polarizers in parallel in the comparing beam.

To determine the birefringence, dispersion $\delta(\Delta n)$, and the channel order *k*, one can use three equations, which represent the conditions of the appearance of two consecutive channels and of the maximum between them [11]:

$$\begin{aligned} &2\pi\bar{\nu}_{2k}(\Delta n - \delta(\Delta n))L = 2k\pi \\ &2\pi\bar{\nu}_{2k+1}\Delta n L = (2k+1)\pi \\ &2\pi\bar{\nu}_{2(k+1)}(\Delta n - \delta(\Delta n))L = 2(k+1)\pi \end{aligned} \tag{3}$$

Solutions of the system (3) are:

$$\begin{aligned} &k = \frac{\bar{\nu}_{2k+1}(\bar{\nu}_{2(k+1)} - \bar{\nu}_{2k})}{2[\bar{\nu}_{2(k+1)}(\bar{\nu}_{2k+1} - \bar{\nu}_{2k}) - \bar{\nu}_{2k}(\bar{\nu}_{2(k+1)} - \bar{\nu}_{2k+1})]} - \frac{1}{2} \\ &\Delta n = \frac{\bar{\nu}_{2(k+1)} - \bar{\nu}_{2k}}{2L[\bar{\nu}_{2(k+1)}(\bar{\nu}_{2k+1} - \bar{\nu}_{2k}) - \bar{\nu}_{2k}(\bar{\nu}_{2(k+1)} - \bar{\nu}_{2k+1})]} \\ &\delta(\Delta n) = \frac{1}{2\bar{\nu}_{2k}L}[1 - \frac{(\bar{\nu}_{2(k+1)} - \bar{\nu}_{2k})(\bar{\nu}_{2k+1} - \bar{\nu}_{2k})}{2\bar{\nu}_{2(k+1)}(\bar{\nu}_{2k+1} - \bar{\nu}_{2k}) - \bar{\nu}_{2k}(\bar{\nu}_{2(k+1)} - \bar{\nu}_{2k+1})}] \end{aligned} \tag{4}$$

Birefringence can be estimated only by the measurements in the channeled spectra, if one knows the anisotropic layer thickness.

3. Results

The results of the measurements for MBBA are contained in Tables 1 and 2 and for PPMAECOBA in TCM in Tables 3 and 4.

Table 1. Main refractive indices of MBBA, interferometrically estimated ($L = 14\mu m$).

Nr.	$\bar{\nu}(cm^{-1})$	n_o	n_e	Δn
1	19440	1.649	1.780	0.131
2	16960	1.571	1.691	0.120
3	15800	1.560	1.675	0.115

Table 2. Wavenumbers, channeled orders and birefringence for MBBA ($L = 14\mu m$).

Nr.	$\bar{\nu}(cm^{-1})$	k	[k]	Δn
1	13390	2,166	2	0.106689
2	15630			0.114249
3	17640	3.069	3	0.121477
4	19840			0.126008
5	21900	4.225	4	0.130463
6	23165			0.138756
7	24300	5.226	5	0.146972
8	25590			0.153520
9	26785	6.314	6	0.160004

Table 3. Main refractive indices of for PPMAECOBA (M=6.810^6) in TCM (C=10^{-2} g/cm^3), ($L = 14\mu m$), interferometrically estimated.

Nr.	$\bar{\nu}(cm^{-1})$	n_o	n_e	Δn
1	19437	1.5729	1.7773	0.2044
2	16960	1.5437	1.7184	0.1747
3	15802	1.5396	1.6986	0.1590

Table 4. Wavenumbers, channeled orders and birefringence for PPMAECOBA (M=6.810^6) in TCM (C=10^{-2} g/cm^3); ($L = 14\mu m$).

Nr.	$\bar{\nu}(cm^{-1})$	k	[k]	Δn
1	16650	4.17	4	0.1716
2	17550			0.1832
3	18350	5.33	5	0.1946
4	19310			0.2034
5	20200	5.88	6	0.2122
6	21480			0.2161
7	22710	6.78	7	0.2202
8	24000			0.2232
9	25250	7.89	8	0.2263
10	26530			0.2289

From Tables 1-4 it results a decrease of the main refractive indices and of the birefringence with the increase of the wavelength.

4. Discussions

MBBA is a positive NLC ($\Delta n > 0$). Conventionally, the main axis oc is considered as being optical axis of NLC parallel with the liquid crystal directory [12,13]. In these conditions the ordinary values of the refractive index are determined for light propagation direction parallel with *oc* axis, having its electric field intensity in the principal plane *aob*.

The lyotropic liquid crystal achieved from PPMAECOBA 10^{-2} g/cm^3 in tetrachloromethane (TCM) has the highest order symmetry axis parallel with the direction of the long side chains of the bulk polymer [9]. The induced anisotropy by the molecular orientation layer of the cell is increased by the intrinsic anisotropy induced by the supermolecular aggregates formed in PPMAECOBA/TCM mixture, in which the side chains are oriented by dipolar interactions [11].

The interferometrically estimated main refractive indices were used to obtain the coefficients N, A and B in equations (5) and (6) in which indices *o* and *e* refer to ordinary and extraordinary values and $\bar{\nu}(cm^{-1})$ is the wavenumber of the monochromatic radiation.

$$n_o^2 = N_o^2 + A_o\bar{\nu}^2 + B_0\bar{\nu}^4 \tag{5}$$

$$n_e^2 = N_e^2 + A_e\bar{\nu}^2 + B_e\bar{\nu}^4 \tag{6}$$

The values of the computed constants N, A and B, for the main refractive indices of MBBA and PPMAECOBA are listed in Table 5. One can see that N, A and B depend on the NLC nature.

Table 5. Solutions of Equtions (5) and (6) for the mean refractive indices estimation.

NLC	n	N	A	B
MBBA	n_e	1.8912	-0.6999×10^{-8}	0.1567×10^{-16}
MBBA	n_o	1.8055	-0.6970×10^{-8}	0.1466×10^{-16}
PPMAECOBA	n_e	1.6508	-0.3476×10^{-9}	0.3957×10^{-17}
PPMAECOBA	n_o	1.6329	-0.2503×10^{-8}	0.5279×10^{-17}

Using formulas (5) and (6), the main refractive indices for the visible range can be estimated with a good precision, because, the birefringence computed with the resulted values for the main refractive indices, is in a good accordance with the birefringence estimated from the channeled spectra.

The birefringence estimated on the basis of relations (5) and (6) has been fitted as function of light wavenumber:

$$\Delta n = \Delta n_0 + B_1\bar{\nu} + B_2\bar{\nu}^2 \tag{7}$$

The fitting parameters in formula (7) are listed in Table 6. R describes the quality of the fit.

Table 6 Fitting constants in relation (7).

NLC	Δn_0	B_1	B_2	R
MBBA	0.0557	3.3796×10^{-6}	2.4473×10^{-11}	0.999
PPMAECOBA	-0.2751	3.9773×10^{-5}	-7.7530×10^{-10}	0.997

5. Conclusions

At room temperature, the mesogenic molecules of MBBA and the side chains of PPMAECOBA in TCM are so well oriented that NLC-s birefringence have measurable values.

Our experiments provide the good concordance between the interferometric data and those obtained from the visible channeled spectrum.

A decrease of the main refractive indices as well as of birefringence with the wavelength increasing has been evidenced, both for MBBA and PPMAECOBA in TCM.

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