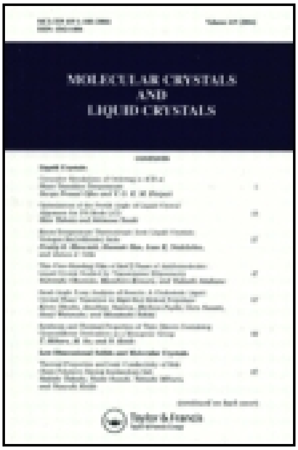

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Measurement of Azimuthal Anchoring Energy of Nematic Liquid Crystal on Photoaligning Polymer Surface

D. Andrienko [a] , A. Dyadyusha [a] , A. Iljin [a] , Yu. Kurioz [a] & Yu. Reznikov [a]

[a] Institute of Physics of National Academy of Science, Prospect Nauki 46, Kyiv, 252022, Ukraine

Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., Vol. 321, pp. 271–281
Reprints available directly from the publisher
Photocopying permitted by license only

Measurement of Azimuthal Anchoring Energy of Nematic Liquid Crystal on Photoaligning Polymer Surface

D.ANDRIENKO, A.DYADYUSHA, A.ILJIN, YU.KURIOZ and YU.REZNIKOV, Institute of Physics of National Academy of Science, Prospect Nauki 46, Kyiv 252022 Ukraine

A method to determine the surface azimuthal anchoring energy of a nematic liquid crystal is proposed. The technique implies the measurement of the director deviation on the cell substrate as a function of strength and direction of the applied magnetic field. As an example, the dependence of the azimuthal anchoring coefficient on the exposure time is measured at the interface between the nematic K15 and polyvinylcinnamate film exposed by UV light. The analogous measurements performed in a wedge cell show that the method with magnetic field is more precise.

Keywords: liquid crystal, azimuthal anchoring, magnetic field method

INTRODUCTION

Molecular interaction at the interface between a nematic liquid crystal and orienting substrate establish a definite orientation of the director $\boldsymbol{n}$ in the cell. In the absence of external fields and in the half-infinite cell the director $\boldsymbol{n}$ coincides with an easy orientation axis $\boldsymbol{e}$. Two basic parameters characterize the anchoring phenomenon: direction of the easy axis and anchoring coefficient W which measures the work needed to deviate $\boldsymbol{n}$ from the easy axis.

Surface alignment has been widely used to obtain a uniform director configuration in liquid crystal cells. Despite its practical importance, the mechanism of the director alignment is not well understood and interaction has usually been characterized by a cosine-square dependence on the deviation angle with respect to the easy axis[1].

There have been several attempts to measure azimuthal anchoring coefficient W. Sato *et al*[2] proposed to use the Cano wedge cell, Jiang *et al*[3] used twisted nematic cell, Vorflusev *et al*[4] used thin wedged cell and took into account braking of the Mauguin condition, Akahane *et al*[5] proposed to measure actual twist angle in a thin symmetric cell. However, these methods require chiral-molecule-doped nematic liquid crystals, application of extra-high magnetic fields and precise optical measurements.

At the same time new perspective methods to produce high-quality liquid crystals orientation without polymer rubbing under the irradiation of polymers by polarized UV-light have been developed[6-8]. One of the accomplishments of these methods is a possibility of the reliable and smooth control of the anchoring energy on the photosensitive surface. Thus, the systematic measurements of anchoring parameters is of great importance for understanding the mechanisms of photoinduced alignment.

In this paper we introduce a new method of studying the azimuthal anchoring coefficient in nematic liquid crystal cell and present the systematic measurements of anchoring energy of liquid crystal on a photoaligning surface and their dependence on UV-light exposure. We also used an independent method of anchoring measurement in a wedge cell to compare the results and accuracy of methods.

1. THEORY

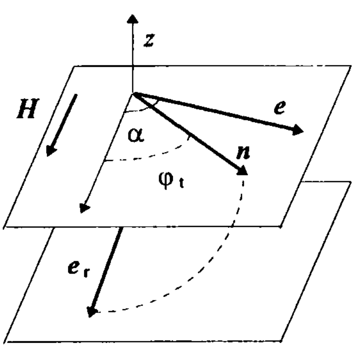

FIGURE 1. Cell geometry

In order to measure an azimuthal anchoring energy, the following cell geometry is proposed. It is constructed from the reference substrate with strong anchoring and tested substrate with unknown anchoring. Initial directions of the easy axes on the tested and reference plates make angle α, resulting in the twisted structure of the director $\boldsymbol{n}$ in the cell (Fig.1).

Since the reference plate possesses strong anchoring, the director on this plate is parallel to the easy axis direction. On the tested plate the director angle φ_t in general case differs from the direction of the tested easy axis.

A magnetic field $\boldsymbol{H}$ is applied to the cell along the reference easy axis decreasing the angle φ_t. Such application of field guarantee the director on the reference substrate be parallel to the reference easy axis. Moreover, the increase of the applied field decreases the twist angle. For small anchoring energies this leads to the propagation of light in the Mauguin regime, i.e. the position of analyzer gives actual twist angle φ_t for all values of the applied field.

The dependence φ_t *vs.* H can be determined both theoretically and experimentally. With known $\boldsymbol{H}$, χ_a and elastic constants, the comparison of experimental and calculated dependence $\varphi_t(H)$ restores the surface anchoring energy as a function of azimuthal angle.

Consider a nematic cell with plates located at $z = L$, 0; the director $\boldsymbol{n}$ is confined to the (x,y) plane of Cartesian coordinates. The magnetic field is applied in the (x,y) plane along the easy axis $\boldsymbol{e}_r$. The free energy per unit area of the cell is[9]

$$F = \tfrac{1}{2}\int_0^L \left[K_2\left(\frac{\partial\varphi}{\partial z}\right)^2 - \chi_a H^2 \cos^2\varphi \right] dz - \tfrac{1}{2} W \cos^2(\alpha - \varphi_t), \tag{1}$$

where $\varphi(z)$ describes director distortions, K_2 is the twist elastic constant, anchoring energy is taken in the Rapini form[1].

Minimization of Exp.(1) leads to the equations for the director and boundary conditions

$$\begin{cases} L^2 \dfrac{\partial^2\varphi}{\partial z^2} - \xi_H{}^2 \sin 2\varphi = 0 \\ L\left.\dfrac{\partial\varphi}{\partial z}\right|_L - \tfrac{1}{2}\xi \sin 2(\alpha - \varphi_t) = 0, \quad \varphi(z=0) = 0 \end{cases} \tag{2}$$

where $\xi_H = HL\sqrt{\chi_a/K_2}$, $\xi = WL/K_2$.

Integration of the system (2) yields the director distribution $\varphi(z)$ in the cell

$$\sin\varphi = \frac{a}{s}\,\mathrm{sd}\left(s\tfrac{z}{L}, r\right), \tag{3}$$

where $a^2 = \left[\tfrac{1}{2}\xi \sin 2(\alpha - \varphi_t)\right]^2 - \left[\xi_H \sin\varphi_t\right]^2$, $s^2 = a^2 + \xi_H^2$, $r = \xi_H/s$, $\mathrm{sd}(x,r) = \mathrm{sn}(x,r) / \mathrm{dn}(x,r)$ is Jacobi elliptic function. Substituting to Eq.(3) $z = L$, $\varphi = \varphi_t$, we obtain the implicit equation for the director deviation on the surface $z = L$

$$\sin\varphi_t = \frac{a}{s}\,\mathrm{sd}(s, r). \tag{4}$$

Note, that the index r of Jacobi elliptic function is close to 1, especially for the strong fields when the condition $\xi_H >> 1$ is matched and the director in the interior of the cell is virtually parallel to $\boldsymbol{H}$. In this case we can expand Jacobi functions in series, in particular $\mathrm{sn}(x,r) \approx \tanh(x)$[10], and Exp.(4) takes more simple form

$$\frac{\sin\varphi_t}{\sin 2(\alpha-\varphi_t)} = \tfrac{1}{2}\xi\frac{\tanh\xi_H}{\xi_H}. \tag{5}$$

Moreover, the numerical calculations of the director angle derived from the Eq.(4) and Eq.(5) show, that (5) can be useful in all region of H giving the error in the value of the actual twist angle φ_t less than 0.5deg (Fig.2).

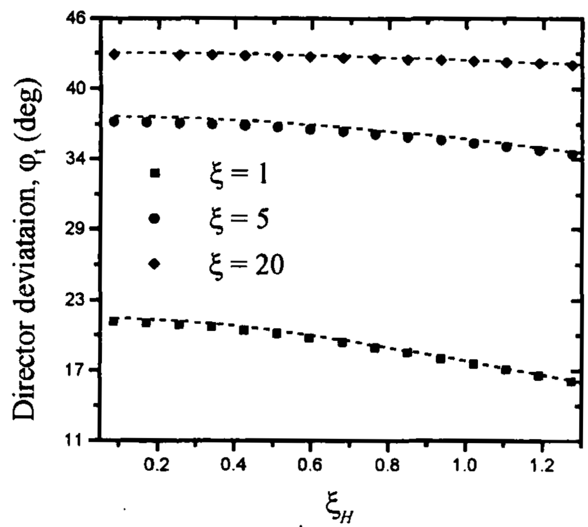

FIGURE 2. Director deviation φ_t *vs* applied field H. Exact solution calculated using Eq.4 for: ■ $\xi = 1$, ● $\xi = 5$, ◆ $\xi = 20$, $\alpha = \pi/4$. Corresponding dashed lines - approximate solutions given by Eq.5. Even under the small fields H the difference between approximate and exact solutions is less than 0.5deg.

Optical measurements of the deviation angle φ_t should take into account possible non perfect validity of the adiabatic theorem (Mauguin limit) since strong fields can result in strong director distortions and lead to the coupling of the ordinary and extraordinary light waves.

We consider the optical transmission of a twisted nematic cell in the magnetic field when it is placed between a polarizer and analyzer and a light beam is incident normal to the cell. The x axis is along the transmission axis of polarizer (along the rubbing direction) and the z axis is normal to the cell plates. After passing through the analyzer the field is given by

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \hat{P}_{\mathrm{A}} \hat{P}_{\mathrm{cell}} \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \tag{6}$$

where $\hat{P}_{\mathrm{A}}$ and $\hat{P}_{\mathrm{cell}}$ are Jones matrix of the analyzer and that of the cell, respectively. The Jones matrix of the cell is in the principal coordinate system, in which the x axis is along the entrance LC director.

In order to evaluate the effects of a non perfect validity of the adiabatic theorem, we use the first order perturbation approximation of the Berreman's 4×4 matrix method[11]. It allows to obtain the light propagation matrix $\hat{P}_{\mathrm{cell}}$ in the form[12]

$$\hat{P}_{\mathrm{cell}} = \exp\left[i\pi \tfrac{L}{\lambda}\left(n_o + n_e\right)\right] \begin{Bmatrix} \exp\left(\frac{1}{2} i\delta\right)\cos\varphi_t & t - \exp\left(-\frac{1}{2} i\delta\right)\sin\varphi_t \\ t^* + \exp\left(\frac{1}{2} i\delta\right)\sin\varphi_t & \exp\left(-\frac{1}{2} i\delta\right)\cos\varphi_t \end{Bmatrix}, \tag{7}$$

where $\delta = 2\pi(n_e\text{-}n_o)L/\lambda$, n_e, n_o are extraordinary and ordinary refractive indices,

$$t = \int_0^L \exp\left(i\delta \frac{z}{L}\right) \frac{\partial\varphi}{\partial z} dz \tag{8}$$

is the parameter which describes coupling between ordinary and extraordinary light waves.

Typically $\delta >> 1$ and variation of the director is smooth on the scales L/δ. Thus, using the method of the stationary phase[13] we obtain the asymptotic expansion of the integral (8)

$$t \approx (i\delta)^{-1} L\left(\exp(i\delta)\partial\varphi/\partial z\big|_{z=L} - \partial\varphi/\partial z\big|_{z=0}\right). \tag{9}$$

From the distribution of the director given by Exp.(3) we obtain $L\partial\varphi/\partial z\big|_{z=0} = a/\mathrm{dn}\left(sz/L\right)\big|_{z=0} = a$. Taking into account the boundary conditions and Exp.(5) we can obtain the derivative of the director angle at the surface $z = L$: $L\partial\varphi/\partial z\big|_{z=L} = \frac{1}{2}\xi \sin 2\left(\alpha - \varphi_t\right) = \sin\varphi_t\, \xi_H/\tanh\xi_H$. Finally, the expression (8) for the parameter t takes the form

$$t = (i\delta)^{-1}\left(\exp(i\delta)\sin\varphi_t\, \xi_H/\tanh\xi_H - a\right). \tag{10}$$

In the experimental conditions one must search for the analyzer setting giving the extremum of the light intensity (under the fixed position of the polarizer). This conditions writes

$$\tan(2\alpha_A) = 2\frac{\cos\varphi_t\{T+\sin\varphi_t\}}{\cos 2\varphi_t - 2T\sin\varphi_t - |t|^2}, \tag{11}$$

where $T = \mathrm{Re}[t\exp(i\delta/2)]$.

The position of the analyzer, which gives the maximum of intensity behind the analyzer and the actual director deviations on the exit surface are plotted in figure 3 for the different values of anchoring ξ. It is seen, that the maximum (minimum) of intensity is found not for the parallel (perpendicular) directions of the analyzer and the director on the exit plate as it is in the hypothesis of validity of the adiabatic theorem, especially for strong director anchoring.

Nevertheless, we can show that for the anchoring energies up to 5×10^{-4} erg/cm^2 the adiabatic theorem holds good for all values of magnetic field H.

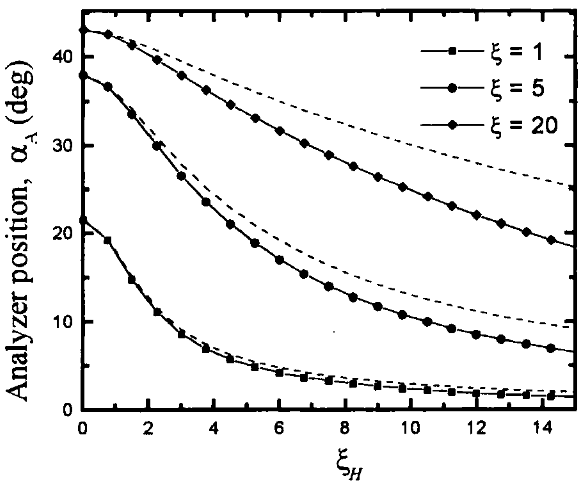

FIGURE 3. Position of analyzer giving the maximum transmitted intensity for different values of anchoring: ■ $\xi = 1$, ● $\xi = 5$, ◆ $\xi = 20$. Corresponding dashed lines - actual director angle φ_t. For calculations we use $\delta = 50$, $\alpha = \pi/4$. It is seen that deviation from the adiabatic theorem is negligible for small anchoring energies for all values of field.

For this purpose let us estimate t for the conditions realized in experiment i.e. $\alpha = \pi/4$. In this case Eq.(5) can be solved analytically and gives

$$\sin\varphi_t = \tfrac{1}{2}\left(\sqrt{2+q^2}-q\right), \tag{12}$$

where $q = \xi_H/(\xi\tanh\xi_H)$. Substituting (12) to (10) one can get

$$t \approx (i\delta)^{-1}(\xi_H/\tanh\xi_H)\sin\varphi_t\left(\exp(i\delta)-1/\cosh\xi_H\right). \tag{13}$$

Thus, for the small anchoring energies, $\xi \ll 1$, we have

$$t \sim \xi/\delta = W\lambda/(2\pi K_2\Delta n). \tag{14}$$

For typical LC parameters ($\Delta n = 0.1$, $K_2 = 3.6\times10^{-7}$erg/cm, $\lambda = 0.5\mu$m) we obtain from (14) that for $W < 5\times10^{-4}$erg/cm^2 the parameter $t < 0.1$ and may be neglected with respect to the unity, i.e. the adiabatic theorem holds good for all values of field.

Further, the parameter t given by the Exp.(14) does not depend on the cell thickness. Thus, under the small anchoring the polarization of the incident light wave follows the director for all cell thicknesses.

For larger anchoring energies the optical coupling of the extraordinary and ordinary light waves leads to the non-perfect validity of the adiabatic theorem and should be taken into account.

The facts above are easily understood if we note that the decreasing of the cell thickness or increasing of field lead to the decreasing of the twist angle φ_t. The less the anchoring is, the effective this angle decreases and leads to the decreasing of the director variation in the cell bulk, i.e. to the conditions favorable to the validity of the adiabatic theorem.

2. EXPERIMENT

Experiments were performed for the liquid crystal 5CB (K15, EM Industries) at fixed temperature 25^{0}C. The cell thickness (measured by interference method) was $L = 65\mu$m. The rubbed polyimide layer was used to provide the strong planar anchoring on a reference plate. The tested plate covered with polyvinylcinnamate-F material was irradiated by polarized UV light with the angle α = 45deg with respect to the rubbing direction. The intensity of UV light in the plane of the samples was about 5mW/cm^2. The different irradiation times t_{exp} were used in order to study the dependence of anchoring coefficient on the time of UV irradiation. After irradiation the cell was filled with liquid crystal in the isotropic phase at 70^{0}C and cooled to the room temperature.

The cell was then arranged between polarizers so that the rubbing direction was parallel to the first polarizer. The beam from weak He-Ne laser passing through the first polarizer was normally incident on the cell. The magnetic field up to 8kG was applied parallel to the rubbing direction e_t. The α_A was measured by rotating the analyzer to find the extinction position for the passing through the cell extraordinary light wave of the laser beam.

Figure 4 shows the measured and calculated dependencies $\alpha_A(H)$. α_A was determined with accuracy of 1deg. Fitting of the experimental data with Exp.(11) resulted in $W \sim 10^{-2}$ - 10^{-4} erg/cm^2. We used $K_2 = 3.6\times10^{-7}$dyne, $\chi_a = 1.76\times10^{-7}$. Note that the experimental conditions such as chosen cell thickness, magnetic field strength allow measurements up to 10^{-2} erg/cm^2.

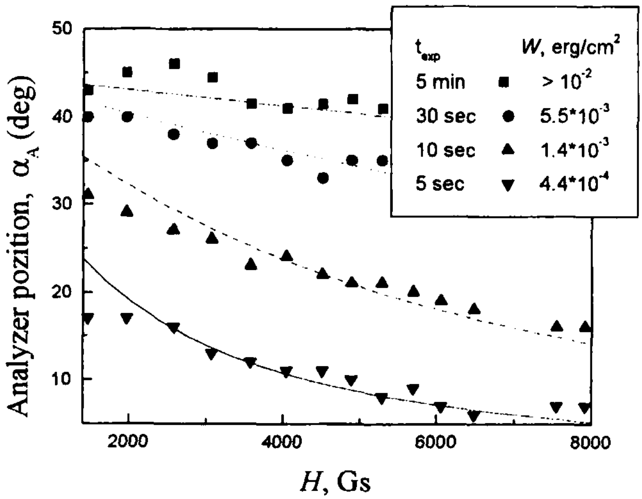

FIGURE 4. Position of the analyzer α_A giving the minimum of the light intensity behind the cell as a function of the applied magnetic field H (polarizer setting is fixed) and corresponding fitting curves.

We also used an independent wedge cell method to compare the results of anchoring energy measurements. This method is based on the measurements of the analyzer angle α_A as a function of the cell thickness L. For this purpose the wedge cell is assembled with one reference and one tested substrates with the tested and reference easy axes making an angle $\alpha = \pi/4$.

The deviation of the director φ_t in this case can be found from the Exp.(4) putting here $H = 0$. As a result we obtain

$$W = \frac{K_2}{L}\frac{2\sin\varphi_t}{\sin 2(\alpha - \varphi_t)} \tag{15}$$

The light intensity behind the analyzer is given by[5]

$$T = \tfrac{1}{2}\left(1 + T_c\cos 2\alpha_A + T_s \sin 2\alpha_A\right) \tag{16}$$

where $u = \left(\dfrac{\pi\Delta n L}{\lambda\varphi_t}\right)^2$, $T_c = \left\{\dfrac{u-1}{u+1}\sin^2\theta + \cos^2\theta\right\}\cos 2\varphi_t + \dfrac{\sin 2\theta}{\sqrt{u+1}}\sin 2\varphi_t$,

$T_s = \left\{\dfrac{u-1}{u+1}\sin^2\theta + \cos^2\theta\right\}\sin 2\varphi_t - \dfrac{\sin 2\theta}{\sqrt{u+1}}\cos 2\varphi_t$, $\theta = \varphi_t\sqrt{u+1}$.

Thus, the position of analyzer which gives the minimum of intensity writes

$$\alpha_A = \tfrac{1}{2}\arctan\left(T_s/T_c\right) \tag{17}$$

The experiment was performed under the same conditions as in the determination of the anchoring coefficient by magnetic field method: the same materials and exposure times were used. The wedge angle was 3×10^{-4} rad; the cell thickness L changed in the range 0-50μm.

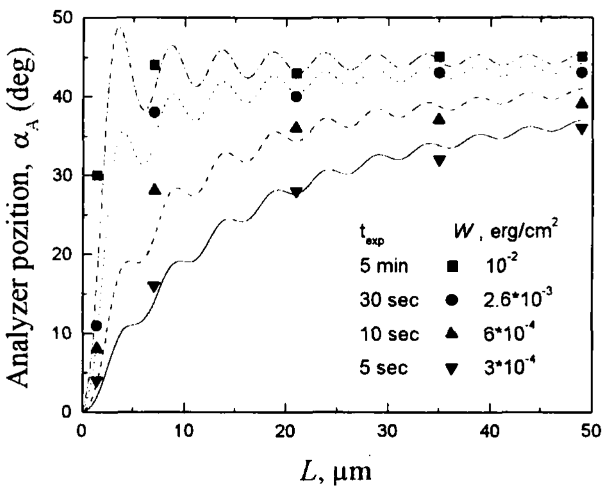

FIGURE 5. Position of the analyzer α_A giving the minimum of the light intensity behind the cell as a function of the cell thickness L and the fitting curves.

Figure 5 shows the measured and calculated dependencies $\alpha_A(L)$. It is seen that both methods gives the same order of anchoring magnitude. However, the magnetic field method is more precise for the determination of the azimuthal anchoring coefficient. First, we measure deviation angle at the definite cell thickness (measurements in a wedge cell involve the whole cell, so that we need to have large irradiated areas and to control the wedge thickness). Second, in the wedge cell the director tends to have twisted structure because of anisotropy in elastic constants[14]; this influence the total deviation of the director.

Note, that Bryan-Brown and Sage [6] perform the same measurements of the anchoring coefficient of the liquid crystal E7 on the polyvinylcinnamate surface using ½π - twisted 20.8μm cell. They found that the anchoring energy saturates at a value 4×10^{-3}erg/cm^2. Their method has several drawbacks, however. First, for low anchoring parameters ($WL/K_2 < 1$) the twist angle is zero since the anchoring strength is less than that required to induce the twist deformation. Thus, we can not measure $W < K_2/L$. Second, they did not take into account non-validity of the adiabatic theorem for the light propagation in the twisted nematic cell. This gives the significant error in the determination of the actual twist angle and leads to the incorrect values of the calculated anchoring energy.

3. CONCLUSIONS

To conclude, we emphasize the basic advantages of the geometry proposed for the anchoring parameters determination by magnetic field method. Why the initially twisted configuration of the director in the cell is better than the homogeneous? First, it makes possible application of field along the reference easy axis and guarantee the director on the reference substrate be parallel to the reference easy axis; hence, we do not need to adjust both polarizers in order to measure the analyzer angle giving the minimum of intensity. Second, in the geometry proposed the increase of the applied field decreases the twist angle. For small anchoring energies (up to 5×10^{-4}erg/cm^2) this leads to the propagation of light in the Mauguin regime, i.e. the position of analyzer gives actual twist angle φ_t for all values of the applied field.

We also perform a systematic measurements of the azimuthal anchoring coefficient of liquid crystal K15 onto the photosensitive polyvinylcinnamate surface. Anchoring energies were found to depend on the exposure and change in the range 10^{-2} - 10^{-4} erg/cm^2.

Acknowledgments
The authors are very thankful to S.B.Kwon and O.D. Lavrentovich for useful discussions. The research described in this publication was made possible in

part by Grant No. 2.4/923 from the Ukrainian State Found for Fundamental Studies Support and Grant No. UE1-315 of CRDF Cooperative Grants Program awards between the US and Ukraine.

References

[1.] A.Rapini, M.Papolar, J.Phys. Collod. **30**, 54 (1969)
[2.] Y.Sato, K.Sato, T.Uchida, Jpn.J.Appl.Phys., **31**, 579 (1992)
[3.] M.Jiang, Z.Wang, R.Sun, K.Ma, R.Ma, X.Huang, Jpn.J.Appl.Phys., **33**, 1242 (1994)
[4.] V.Vorflusev, H.Kitzerow, V.Chigrinov, Jpn.J.Appl.Phys., **34**, 1137 (1995)
[5.] T.Akahane, H.Kaneko, M.Kimura, Jpn.J.Appl.Phys., **35**, 4434 (1996)
[6.] G.P.Bryan-Brown, I.C.Sage, Liq.Cryst., **20**, 825 (1996)
[7.] A.Dyadyusha, T.Marusii, Yu.Reznikov, V.Reshetnyak and A.Khizhnyak, JETP Lett., 56, **17** (1992)
[8.] P. Shannon, W. Gibbons, Shao-Tang Sun, Nature, **368**, 532, (1994)
[9.] P.G.deGennes, J.Prost, The Physics of Liquid Crystals, Clarendon Press, Oxford (1993)
[10.] M.Abramowtz, I.A.Stegan, Handbook of Mathematical Functions, National bureau of standards (1964)
[11.] D.W.Berreman, J.Opt.Soc.Am., **62**, 502 (1972)
[12.] G.Barbero, E.Miraldi, C.Oldano, M.L.Rastello, P.T.Valabrega, J.Phys. (France), **47**(8), 1411 (1986)
[13.] F.W.J.Olver, Asymptotics and special functions, NewYork-London, Academic Press (1974)
[14.] O.D.Lavrentovich, Phys.Rev.A, **46**(2), R722 (1992)