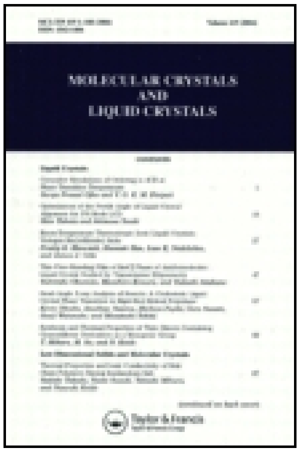


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# Influence of Light Induced Molecular Conformational Transformations and Anchoring Energy on Cholesteric Liquid Crystal Pitch and Dielectric Properties

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# INFLUENCE OF LIGHT INDUCED MOLECULAR CONFORMATIONAL TRANSFORMATIONS AND ANCHORING ENERGY ON CHOLESTERIC LIQUID CRYSTAL PITCH AND DIELECTRIC PROPERTIES.

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Abstract The cholesteric liquid crystal (CLC) pitch and director orientation are obtained as the functions of the anchoring energy W of a director and its pretilt angles $\Delta\vartheta_1$, $\Delta\vartheta_2$ on the cell orienting surfaces. If the anchoring energy is strong enough, the monotonic change of the CLC twisting ability due, for example, to the light-induced molecular conformational transformations causes jumps of the CLC pitch and mean values of dielectric susceptibility tensor $\langle\varepsilon_{ij}\rangle$. Values of jumps of $\langle\varepsilon_{ij}\rangle$ components are determined by anchoring energy W and pretilt angles $\Delta\vartheta_1$, $\Delta\vartheta_2$ that may be used for experimental estimations of W, $\Delta\vartheta_1$, $\Delta\vartheta_2$.

## INTRODUCTION

Liquid crystals are often used as cells of various thickness. The cell bounding planes are properly treated providing a definite orientation of the director at these planes as well, as in the cell volume if the liquid crystal is nematic [1-3]. In cholesteric liquid crystals (CLC) the director orientation in a cell depends on twisting ability of cholesteric molecules (or optically active dopant) and as a result the director characteristic spiral twisting with a certain pitch is formed. Usually it doesn't make a distinction between pitch values of infinite CLC and CLC in a cell except for the case of absolutely rigid anchoring of the director with the cell surfaces. In the last case, as it is known, the whole number of half-pitches must be located on the cell thickness.

In the present work we consider the CLC cells, in which the anchoring energy of the director with the cell bounding planes is finite, and investigate the influence of the anchoring energy value as well as nonplanarity of the director boundary conditions on the pitch value and the director orientation in a cell volume. Besides, one should take into account that long-lived metastable states of molecules with conformation different from that of the initial molecules can be formed in a liquid crystal under the action of light of definite frequency [4-5]. Such phototransformed molecules have polarizability, twisting ability and other physical parameters different from that of the CLC molecules and can be considered as light-induced impurities . Changing the intensity of incident light and, therefore , the light-induced impurity concentration one can control the twisting ability of a cholesteric. It will be shown that in the cell with a sufficiently rigid anchoring of the director with cell bounding planes a monotonous change of cholesteric twisting ability can lead to a discontinuous change of a pitch and the mean values of components of the CLC dielectric susceptibility tensor. The relations connecting the value of jumps with parameters characterizing the anchoring energy of the director and its orientation on the cell bounding planes are obtained.

## PITCH AND DIRECTOR ORIENTATION IN A CELL

Let's suppose that we have a plane-parallel CLC cell with a thickness 2L. We choose the origin of coordinates in the middle of the cell and direct OZ-axis perpendicular to the bounding planes. The CLC surface free energy we take as [6]

$$F_s=-\frac{W}{2}\int dS_1(\vec{d}\vec{e}_1)^2 - \frac{W}{2}\int dS_2(\vec{d}\vec{e}_2)^2 \ , \ W>0 \qquad (1)$$

where $\vec{d}$ is the CLC director, and $\vec{e}_1,\vec{e}_2$- are the unit vectors of easy orientation of the director on the bounding cell planes. In a spherical system of coordinates with polar axis along OZ we have $e_i = \{\cos\phi_i \sin\vartheta_i, \ \sin\phi_i \sin\vartheta_i, \cos\vartheta_i\}$, $d=\{\cos\phi\sin\vartheta, \sin\phi\sin\vartheta, \cos\vartheta\}$.

The CLC volume free energy is taken in the form [7]

$$F_v = \frac{1}{2}\int dV\{K_1(\mathrm{div}\,\vec{d})^2 + K_2([\vec{d}\,\mathrm{rot}\vec{d}] + \frac{2\pi}{p_0})^2 + K_3([\vec{d}\,\mathrm{rot}\vec{d}])^2\} \quad (2)$$

where $p_0$ is the pitch in an infinite CLC. Its value is determined by twisting ability of CLC molecules or optically active dopant.

We consider the vectors of easy orientation are fixed at the surfaces of the bounding cell planes and independent of the position of point at these surfaces (but, generally speaking, $\vartheta_1 \neq \vartheta_2$, $\phi_1 \neq \phi_2$ ) The angle coordinates of CLC director in the cell volume depend only on the coordinate Z: $\vartheta = \vartheta(z)$, $\phi = \phi(z)$. To find the dependencies $\vartheta(z)$, $\phi(z)$, one should minimize the CLC free energy $F=F_v+F_s$ over the angles $\vartheta$ and $\phi$.

After minimization we obtain the following equations for $\vartheta(z)$ and $\phi(z)$

$$\frac{\partial^2\vartheta}{\partial z^2} - \sin 2\vartheta\left(\sin^2\vartheta\,\frac{\partial\phi}{\partial z} - \frac{2\pi}{p_0}\right)\frac{\partial\phi}{\partial z} - \frac{1}{4}\sin 4\vartheta\left(\frac{\partial\phi}{\partial z}\right)^2 = 0\ , \quad (3)$$

$$(\sin^4\vartheta + \frac{1}{4}\sin^2 2\vartheta)\,\frac{\partial^2\phi}{\partial z^2} + (4\sin^3\vartheta\cos\vartheta + \frac{1}{2}\sin 4\vartheta)\,\frac{\partial\vartheta}{\partial z}\,\frac{\partial\phi}{\partial z} - \frac{2\pi}{p_0}\sin 2\vartheta\,\frac{\partial\vartheta}{\partial z} = 0 \quad (4)$$

and boundary conditions

$$\frac{\partial\vartheta}{\partial z} + (-1)^i\,\frac{W}{K}\,[\cos\vartheta\cos\vartheta_i + \sin\vartheta\sin\vartheta_i\cos(\phi-\phi_i)][\sin\vartheta\cos\vartheta_i - \cos\vartheta\sin\vartheta_i\cos(\phi-\phi_i)]=0, \quad (5)$$

$$\left[\frac{\partial\phi}{\partial z} - \frac{2\pi}{p_0}\right]\sin^2\vartheta + (-1)^i\,\frac{W}{K}[\cos\vartheta\cos\vartheta_i + \sin\vartheta\sin\vartheta_i\cos(\phi-\phi_i)]\sin\vartheta\sin\vartheta_i\sin(\phi-\phi_i)=0, \quad (6)$$

where $i=1,2$ and if $i=1$ one should put $Z=-L$, if $i=2$, then

Z=L. Here for simplicity we also put $K_1 = K_2 = K_3 = K$

Let us consider the case when the boundary conditions are close to the planar ones. Then, supposing that $\vartheta_{1,2} = \frac{\pi}{2} - \Delta\vartheta_{1,2}$, we have $\Delta\vartheta_1 \ll 1, \Delta\vartheta_2 \ll 1$. Putting for the angle of the director in a cell volume, $\vartheta = \frac{\pi}{2} - \Delta\vartheta$, we'll probably have $\Delta\vartheta \ll 1$. Taking this into account we linearize Eq.(3), (4) and obtain

$$\frac{\partial^2 \phi}{\partial z^2} = 0 \tag{7}$$

$$\frac{\partial^2 \Delta\vartheta}{\partial z^2} - \frac{4\pi}{p_0}\Delta\vartheta \frac{\partial\phi}{\partial z} + \Delta\vartheta\left(\frac{\partial\phi}{\partial z}\right)^2 = 0 \tag{8}$$

Solving Eq.(7) we have

$$\phi(z) = \frac{2\pi}{p} z + C \tag{9}$$

where p is the CLC pitch in a cell

Substituting Expr.(9) into Eq.(8) we obtain:

$$\Delta\vartheta(z) = B\exp(\alpha z) + D\exp(-\alpha z), \tag{10}$$

$$\alpha = \frac{2\pi}{p}\left(2\frac{p}{p_0} - 1\right)^{1/2}$$

Here B,C,D are the constants of integration. The values of these constants as well as the CLC pitch value p can be found from the four boundary conditions (5) and (6).

First we find a pitch p and a constant C. For this purpose we substitute solutions (9),(10) into (6) at i=1,2 and neglect the small terms of the second order with respect to $\Delta\vartheta, \Delta\vartheta_1, \Delta\vartheta_2$. Considering that the OX-axis is directed so that the easy orientation vector $\vec{e}_1$ is in the plane XOZ, i.e.the angle $\phi_1 = 0$, and denoting $\phi_2 = \phi_0$, we obtain the following system of equations instead of (6):

$$\begin{cases} \left|\frac{2\pi}{p} - \frac{2\pi}{p_0}\right| + \frac{W}{2K}\sin 2[\phi(L) - \phi_0] = 0 \\ \left|\frac{2\pi}{p} - \frac{2\pi}{p_0}\right| - \frac{W}{2K}\sin 2\phi(-L) = 0 \end{cases} \tag{11}$$

Then, taking into account (9), we find that

$C=\frac{\phi_0}{2}+k\,\frac{\pi}{2}$, where k is the integer and the pitch p is the solution of the equation

$$\frac{W}{2K}\sin\left(\frac{4\pi L}{p}-\phi_0\right)=(-1)^{k+1}\left|\frac{2\pi}{p}-\frac{2\pi}{p_0}\right| \qquad (12)$$

In the general case this equation should be solved numerically. Here we consider only those cases when the solution of Eq.(12) may be presented in an analytical form. We denote the nondimensional parameter $\frac{WL}{K}=\sigma$ and let the anchoring energy of the director with the cell surface be rather small so that for the cell which has the thickness $2L>p_0$ the condition $\sigma \ll 1$ is satisfied. In this case a pitch in the cell should be close to the pitch $p_0$ in an infinite CLC and then in equation (12) we can put $\frac{2L}{p}=\frac{2L}{p_0}+\tilde{\alpha}$, where $\tilde{\alpha} \ll 1$. As a result, neglecting small terms ~ $\tilde{\alpha}^2$, $\Delta\vartheta_1^2$, we obtain

$$p = p_0\left[1+(-1)^k\,\sigma\,\frac{p_0}{4\pi L}\sin\left(\frac{4\pi L}{p_0}-\phi_0\right)\right], \qquad (13)$$

where p must also satisfy one of the conditions $p > 8L$ or $\frac{8L}{5+4r} \le p < \frac{8L}{3+4r}$ if $k=2m$, and $\frac{8L}{3+4r} < p < \frac{8L}{1+4r}$, if $k=2m+1$; $r=0,1,2,...$

If the anchoring energy of the director is relatively large so that the condition $\frac{Wp_0}{K} \gg 1$ is satisfied, then the value p is close to the pitch value $p_\infty$ in a cell with absolutely rigid boundary conditions ($W=\infty$). In this case substituting in equation (12) $\frac{2L}{p}=\frac{2L}{p_\infty}+\beta$ where $\beta \ll 1$, we obtain

$$p = p_\infty\left[1+\frac{1}{\sigma}\left(1-\frac{p_\infty}{p_0}\right)\right], \qquad (14)$$

Here $p_\infty = \frac{4L}{n}$, where n is the whole number of half-pitches of the CLC spiral locating on the cell thickness and in Expr.(12) k=n. In obtaining Expr.(14) small terms ~ $\beta^2$, $\Delta\vartheta_1^2$ are neglected and for simplicity we put $\phi_0=0$.

As $p_\infty$ assumes discrete values mostly close to $p_0$ then the function $p(p_0)$ determined by Expr.(14) is discontinuous. At some critical value $p_0=p_0^{cr}$ there occurs a jump of a pitch in a cell from the value determined by (14), in which we put $p_\infty=\frac{4L}{n}$, to that determined by the same expression, but with $p_\infty=\frac{4L}{n+1}$ or $p_\infty=\frac{4L}{n-1}$ depending on the fact whether we increase or decrease a cholesteric twisting ability. From the condition of continuity of CLC full free energy we find that

$$p_0^{cr}=\frac{8L}{2n\pm1} \tag{15}$$

where the sign + corresponds to the $n\to n+1$ transition (with increasing the number of half-pitches locating on the cell thickness) and the sign '−' corresponds the $n\to n-1$ transition (with decreasing the number of half-pitches).

In particular, using Expr.(14), (15) it is easy to obtain the expression for the anchoring energy W through the pitch critical values corresponding to the $n\to n\pm1$ transitions. This expression can be used for determining W on the experiment.

To find the constants B and D determining the value of $\Delta\vartheta(z)$, we substitute Expr. (9), (10) into boundary conditions (5) and obtain the following system of two inhomogeneous equations

$$[-\alpha+\frac{W}{k}\cos^2\phi(-L)]\exp(-\alpha L)B+[\alpha+\frac{W}{k}\cos^2\phi(-L)]\exp(\alpha L)D=$$
$$=\Delta\vartheta_1\frac{W}{k}\cos\phi(-L)$$
$$[\alpha+\frac{W}{k}\cos^2(\phi(L)-\phi_0)]\exp(\alpha L)B+[\alpha+\frac{W}{k}\cos^2(\phi(L)-\phi_0)]\exp(-\alpha L)D=$$
$$=\Delta\vartheta_2\frac{W}{k}\cos(\phi(L)-\phi_0), \tag{16}$$

where $\phi(\pm L)$, $\alpha$ − are determined by formulas (9), (10), correspondingly. Solving the system of equations (16) one can obtain the expressions for B and D and, therefore, find a final expression for $\vartheta(z)$.

Thus, formulas (9),(10),(12) and (16) determine a pitch and orientation of CLC director in the cell. It is seen that with an accuracy to small terms ~ $\Delta\vartheta_1^2$, $\Delta\vartheta_2^2$ a director describes in CLC cell a spiral with a constant pitch whose value depends on the director anchoring energy with the bounding cell planes. The degree of deviation of the director from the plane perpendicular to a pitch axis (the plane XOY) due to nonplanarity of the boundary conditions depends on the distance of the CLC point to the cell planes. Let the director anchoring energy be such that the parameter $\sigma \ll 1$ or the condition $n \gg \sigma \gg 1$ is satisfied, where n is the whole number of half-pitches locating on the cell thickness at absolutely rigid anchoring. Then from (10) and (16) we obtain that the angle $\vartheta(z)$ characterizing the degree of deviation of the director from the plane XOY is determined by the expression

$$\Delta\vartheta(z) = \frac{\sigma\cos\phi(-L)}{\alpha L\,\mathrm{sh}(2\alpha L)}[\Delta\vartheta_1 \mathrm{ch}\alpha(z-L) + (-1)^k \Delta\vartheta_2 \mathrm{ch}\alpha(z+L)] \quad (17)$$

were for the case $\sigma \ll 1$ we have $\alpha = \frac{2\pi}{P_o}$ with an accuracy to small terms $\sim\sigma^2$ and for the case $n \gg \sigma \gg 1$ the expression for $\alpha$ is more complex, but $\alpha \sim \frac{n}{L}$.

If the inequality $\sigma \gg n \gg 1$ is satisfied, then neglecting small terms $\sim \frac{n}{\sigma}\Delta\vartheta_1$, we have for $\Delta\vartheta(z)$ the following expression

$$\Delta\vartheta(z) = \frac{1}{\mathrm{sh}(2\alpha L)}[-\Delta\vartheta_1 \mathrm{sh}(\alpha(z-L)) + (-1)^n \Delta\vartheta_2 \mathrm{sh}(\alpha(z+L))] \quad (18)$$

From (17) and (18) it follows that the degree of deviation of the CLC director from the XOY plane, which is conditioned by the pretilt of the director at the cell surface, is decreased at the moving away from the orienting planes ( $z \to 0$).

## JUMP OF DIELECTRIC SUSCEPTIBILITY TENSOR COMPONENTS

The tensor of CLC dielectric susceptibility can be written through the components of CLC director in the following way[7]

$$\varepsilon_{ij}=\varepsilon_{\perp}\delta_{ij}+\varepsilon_a d_i d_j , \qquad (19)$$
$$\varepsilon_a=\varepsilon_{\parallel}-\varepsilon_{\perp},$$

where $\varepsilon_{\perp}$, $\varepsilon_{\parallel}$ - are the main values of the tensor $\varepsilon_{ij}$.

Substituting in (21) the director cartesian components we obtain the components of the tensor $\varepsilon_{ij}$ averaged over the cell thickness in the form

$$\langle\varepsilon_{xx}\rangle=\varepsilon_{\perp}+\varepsilon_a\langle\cos^2\Delta\vartheta(z)\cos^2\phi(z)\rangle, \qquad (20)$$
$$\langle\varepsilon_{yy}\rangle=\varepsilon_{\perp}+\varepsilon_a\langle\cos^2\Delta\vartheta(z)\sin^2\phi(z)\rangle,$$
$$\langle\varepsilon_{zz}\rangle=\varepsilon_{\perp}+\varepsilon_a\langle\sin^2\Delta\vartheta(z)\rangle,$$

where $\langle\varepsilon_{ij}\rangle=\frac{1}{2L}\int_{-L}^{L}\varepsilon_{ij}dz$

Substituting expressions for $\Delta\vartheta(z)$ and $\phi(z)$ found above into formula (20) it is possible to obtain the dependence of the tensor components $\langle\varepsilon_{ij}\rangle$ on the CLC twisting ability at arbitrary values of the director anchoring energy.

We consider the most interesting case of large anchoring energies when a pitch in a cell changes discontinuously with changing of CLC twisting ability. Then, assuming that $\frac{Wp_o}{K}\gg 1$, we should substitute expressions (9) and (18) ( the latter is valid at $\sigma\gg n\gg 1$ ) into formula (20) taking into account the formula (14) for a pitch in a cell. As a result it is easily seen that the values of $\langle\varepsilon_{ij}\rangle$ components as well as the CLC pitch reveal the jumps at values of cholesteric twisting ability $p_o=p_o^{cr}$ (formula (15)).

The values of the jumps are different for longitudinal and transversal components of the $\langle\varepsilon_{ij}\rangle$ tensor and are determined by the following expressions

$$\Delta\langle\varepsilon_{xx}\rangle=\langle\varepsilon_{xx}(n)\rangle-\langle\varepsilon_{xx}(n+1)\rangle=\langle\varepsilon_{yy}(n)\rangle-\langle\varepsilon_{yy}(n+1)\rangle=$$

$$=\frac{1}{2}\varepsilon_a\left(\frac{1}{\sigma n}-\frac{\Delta\vartheta_1^2+\Delta\vartheta_2^2}{8\pi n^2}\right), \qquad (21)$$

$$\Delta\langle\varepsilon_{zz}\rangle=\langle\varepsilon_{zz}(n)\rangle-\langle\varepsilon_{zz}(n+1)\rangle=(-1)^n 4\varepsilon_a\Delta\vartheta_1\Delta\vartheta_2\exp(-\pi n), \qquad (22)$$

Here $\langle \varepsilon_{ij}(n) \rangle$ corresponds to the value of CLC pitch determined by formula (14) with $p_\infty = \frac{4L}{n}$. In deriving formula (21) small terms $\sim \frac{\Delta\vartheta_i^2}{\sigma}$, $\Delta\vartheta_1\Delta\vartheta_2 \exp(-\pi n)$ are neglected, in deriving formula (22) terms $\sim \frac{\Delta\vartheta_i^2}{\sigma}\exp(-\pi n)$ are neglected and for simplicity we put $\phi_0 = 0$. One should also remember, that $\varepsilon_a$ depends on the light-induced impurity concentration and is taken at such concentration value, which corresponds to the CLC twisting ability $p_0 = p_0^{cr}$.

If the inequality $n \gg \sigma \gg 1$ is satisfied then in formulas (20) one should use Expr. (17) for $\vartheta(z)$. The values of jumps are determined by the expressions similar to (21), (22), but the right-hand part of the latter should be multiplied by $(\frac{2\sigma}{\pi n})^2$.

As it follows from the above expressions, the jumps in the values of $\langle \varepsilon_{ij} \rangle$ that appear during the changing of the CLC twisting ability are result of both the finiteness of the director anchoring energy with the cell bounding planes and the presence of pretilt angles of the director on these planes. As the result, the jumps in both longitudinal ($\langle \varepsilon_{zz} \rangle$) and transversal components ($\langle \varepsilon_{xx} \rangle$, $\langle \varepsilon_{yy} \rangle$) of the tensor $\langle \varepsilon_{ij} \rangle$ take place even if the boundary conditions for the director are absolutely rigid ($\sigma = \infty$). But if the director orientation on the bounding planes is planar ( $\vartheta_1 = \vartheta_2 = \pi/2$ ), then only the jumps of the transversal tensor components take place. In this case for arbitrary values of an integer n ($n \geq 1$, but $\sigma \gg n$ ), instead of expr.(21), we'll have:

$$\Delta\langle \varepsilon_{xx} \rangle = \Delta\langle \varepsilon_{yy} \rangle = \frac{\varepsilon_a (1+2n)}{4\sigma n(n+1)} \qquad (23)$$

If planar boundary conditions are absolutely rigid ( $\sigma = \infty$), then the averaged dielectric susceptibility tensor remains a continuous function of the CLC twisting ability.

It should be noted that, as follows from Expr. (21)-(23), the value of $\langle \varepsilon_{ij} \rangle$ jumps decreases as the CLC twisting ability increases. Besides, the effects of discontinuous change of the pitch and $\langle \varepsilon_{ij} \rangle$ are considered above at the condition $\frac{Wp_o}{K} \gg 1$ . If this condition is broken as the CLC twisting ability decreases then the effect of discontinuity must disappear.

Thus, the above expressions for $\Delta\langle \varepsilon_{xx} \rangle$, $\Delta\langle \varepsilon_{zz} \rangle$ make it possible to estimate the director anchoring energy W and the values of angles $\Delta\vartheta_1$, $\Delta\vartheta_2$ of the director pretilt on the bounding cell planes using experimental values of jumps $\Delta\langle \varepsilon_{ii} \rangle$. Note, that a discontinuous change of the averaged values $\langle \varepsilon_{ii} \rangle$ must appear, for example, in studying the dependence of CLC cell electrical capacity or phase retardation of light passing through the cell on intensity of light initiating the molecular phototransformations. We also note, that the phenomenon of discontinuous change of cell electrical capacity was observed in [8].

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