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Anchoring transition induced by *trans-cis* isomerization in photosensitive substrate

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A molecular model describing the effective anchoring energy of a liquid crystal (LC) system, composed of 4-n-pentyl-4′-cyanobiphenyl (5CB) molecules deposited on a photosensitive azobenzene layer consisting of 6Az10PVA molecules, is proposed. This model takes into account the interaction between the surface polarization in the LC phase and the surface electric field, arising from the surface charge density. Within the framework of this molecular model, the mechanism responsible for the anchoring transition in the LC phase from homeotropic to planar alignment and vice versa, caused by *trans-cis* and *cis-trans* conformational changes in the monolayer 6Az10PVA after laser radiation, is described. It is shown that using experimental data for the voltage across the 6Az10PVA+5CB film, obtained by the surface potential technique, the charge separation during the conformational changing, caused by the laser irradiation, may lead to an anchoring transition induced by *trans-cis-trans* isomerization in the photosensitive azobenzene monolayer. The calculated values of the isothermal surface pressure diagram π-A showed that the surface area A per LC molecule is noticeably higher for the *cis* configuration, which reflects a less efficient packaging than in the *trans* state.

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I. INTRODUCTION

The photoalignment method, which uses photoswitchable surfactants (azodendrimers), provides an excellent opportunity to control the anchoring transitions of liquid crystal (LC) systems applied to photosensitive surfaces. Some organic materials, such as azobenzene, undergo *trans-cis* isomerization during laser beam transmission, and are therefore useful as a photoactive interface for LC systems [1–5]. Since azodendrimers are spontaneously adsorbed on various solid surfaces, they can be used as photoactive surfaces.

The photoisomerization process, taking place during the *trans-cis* or *cis-trans* isomerization, due to the vertical component of the dipole moment of the surface azobenzene monolayer, may result in changes of the surface charge density caused by the charge separation [6]. The effect of changes in the surface charge density during *trans-cis* and *cis-trans* conformational transitions in azobenzene layers adsorbed on metal electrodes in contact with the LC phase, during the laser beam transmittance across this system, was studied by the Maxwell-displacement-current (MDC) [7] and surface potential (SP) [6,7] techniques. It has been observed, by means of both the SP and MDC methods [6,7], that the azobenzene monolayer, composed of molecules of poly(vinyl alcohol) bearing azobenzene side chains (6Az10PVA), which in the initial state exhibits the *trans* conformation, with the transmittance of a He-Ne laser beam (632 nm in the wavelength) undergo the *trans-cis* isomerization. By putting this azobenzene monolayer in contact with the LC film, composed of 4-n-pentyl-4′-cyanobiphenyl (5CB) molecules, one can expect the change, during the laser beam transmittance, of the surface alignment of the LC molecules (see Fig. 1). Such an orientation transition, in turn, can be induced by a change in the surface charge density caused by charge separation, which leads to the conformational change in this azobenzene monolayer.

It should be noted here that the role of the *trans-cis* conformational transition in the formation of a hydrodynamic flow in a microsized LC channel, when heated by a laser beam focused on the boundary of an LC channel, containing a monolayer of azobenzene, has been investigated [8]. It has been shown that the charge separation during the conformational changing caused by the laser irradiation may lead to the change of the surface alignment of LC molecules, for instance, from homeotropic to planar and vice versa. For example, in the case of an initially homeotropic alignment of the director along the lower boundary of the microsized channel corresponding to the *trans* conformational state, after laser radiation focused on the lower boundary of the LC channel, a small domain with a planar alignment of the director corresponding to the *cis* conformational state should appear in the frame of the laser spot. In this case, we are dealing with a sharper

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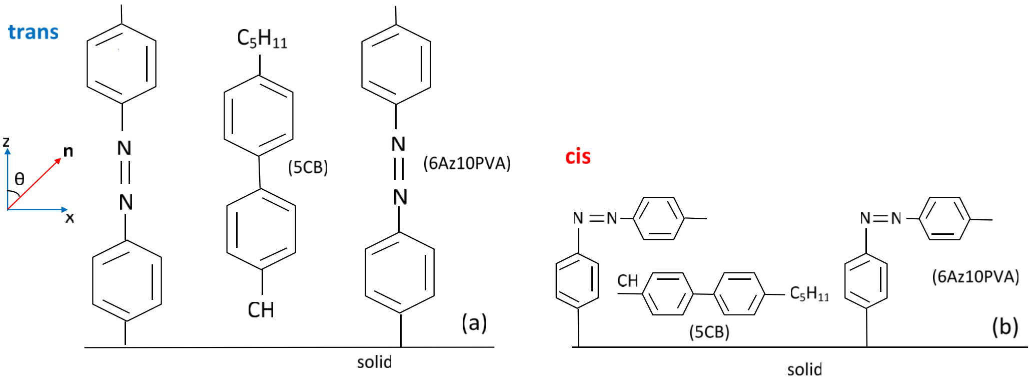

FIG. 1. Schematic representation of the surface orientation of LC molecules by a monolayer of azobenzene: homeotropic (a) in *trans* state and planar (b) in *cis* state.

reorientation of the director field along the lower boundary of the LC channel, especially near the boundaries of the laser spot, and the formation of both the director gradient $\nabla\hat{\mathbf{n}}$ and the local temperature gradient ∇T around the laser spot. Taking into account the fact that the interaction of $\nabla\hat{\mathbf{n}}$ and ∇T leads to the formation of a hydrodynamic flow $\mathbf{v}$ [9], it is possible to shed light on the role of the orientational defect caused by the conformational transition on the formation of $\mathbf{v}$ in the microsized LC channel. However, to do this, it is necessary to understand the mechanism responsible for the transition of LC molecules from homeotropic alignment to planar and vice versa, induced by *trans-cis* and *cis-trans* conformational changes in photosensitive azobenzene layer, after laser radiation.

In this paper, we investigate the effect of the charge separation during the *trans-cis* and *cis-trans* conformational changes in the surface azobenzene 6Az10PVA monolayer on a polar LC film consisting of 5CB molecules, within the framework of a molecular model that takes into account the interaction between the surface polarization and the electric field built up across the LC film. All the necessary values of the electric field $V_{\rm Az10PVA+5CB}$ in systems formed by the azobenzene layer and the LC film (6Az10PVA+5CB), which were used to calculate the values of surface charge densities (σ_{trans} and σ_{cis}), were obtained by the MDC and SP methods.

The outline of this paper is as follows: The effective anchoring energy described in the framework of the molecular model, taking into account the interaction between surface polarization and the surface electric field, is given in Sec. II. The investigation of the effect of the charge separation during the *trans-cis* and *cis-trans* conformational changes in the surface azobenzene 6Az10PVA monolayer on the polar LC film (consisting of 5CB molecules), based on the above-mentioned molecular model, using the experimental data for the voltage $V_{\rm 6Az10PVA+5CB}$ across the azobenzene layer and the LC (6Az10PVA+5CB) film, provided by the surface potential technique, is given in Sec. III. Our conclusions are summarized in Sec. IV.

II. MOLECULAR MODEL

In order to elucidate the role of the charge separation during the *trans-cis* or *cis-trans* conformational changes in the surface azobenzene monolayer, sandwiched between the LC film and metal electrodes, we use the molecular model which takes into account interactions between the surface polarization and surface electric field. The interaction of the LC film with the surface azobenzene monolayer leads to the change of the molecular orientation in the LC film. Our 2D LC layer system is composed of axially symmetric molecules, the hydrophilic heads of which are uniformly distributed on the azobenzene surface and the hydrophobic tails are directed away from the interface. This allows us to consider the model of axially symmetric molecular rods, the hydrophilic heads of which are uniformly distributed on the surface and the hydrophobic tails are directed away from the solid surface and tilted at the average equilibrium angle $\theta_{\rm eq}(A)$ with respect to the unit vector $\hat{\mathbf{k}}$ directed perpendicular to the interface. Here A is the surface area per LC molecule. The unit vector $\hat{\mathbf{i}}$ is directed parallel to the interface with the distance x, whereas z is the distance away from the LC-azobenzene interface [see Fig. 1(a)]. We use the molecular model that takes into account the interaction between the surface polarization and the surface electric field arising from the surface charge density σ. In the simplest case that electric field can be written in the form $\mathbf{E} = E_0\hat{\mathbf{k}} = \sigma/\epsilon_0\bar{\epsilon}\hat{\mathbf{k}}$, where $\bar{\epsilon} = \frac{\epsilon_\parallel + 2\epsilon_\perp}{3}$ is the average dielectric permittivity, and $\epsilon_\parallel$ and $\epsilon_\perp$ are the dielectric constants parallel and perpendicular to the director $\hat{\mathbf{n}}$, respectively. Thus, the electric field $\mathbf{E}$ has an orienting effect on the LC monolayer at a distance of the order of the Debye screening length λ_D [10]. As a result, the corresponding dielectric energy per unit area can be written as

$$\begin{aligned} f_{\rm el} &= \int_0^d F_{\rm el}(z)dz = -\frac{1}{2}\epsilon_0\epsilon_a \int_0^d (\mathbf{E}\cdot\hat{\mathbf{n}})^2 dz \\ &= -\frac{1}{2}w_{\rm el}\cos^2\Delta_\theta, \end{aligned} \tag{1}$$

where $w_{\rm el} = \epsilon_0\epsilon_a \int_0^d E^2(z)dz = \sigma^2\epsilon_a d/\bar{\epsilon}^2\epsilon_0$, d is the layer thickness, $\Delta_\theta = \theta_s - \theta_0$, $\theta_s = \theta_{\rm eq} = \cos^{-1}(\hat{\mathbf{n}}_s\cdot\hat{\mathbf{k}})$ is the angle between the surface director and the substrate normal, $\theta_0 = \cos^{-1}(\hat{\mathbf{n}}_0\cdot\hat{\mathbf{k}})$ denotes the polar angle of the easy axis $\hat{\mathbf{n}}_0$, and $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$ is the dielectric anisotropy of the LC layer.

It should be noted that in the nematic phase, both the splay and bend deformations caused by an electric field lead to a flexoelectric $f_{\rm pol}$ contribution to the dielectric energy $f_{\rm el}$. Taking into account the fact that in our case the value of the surface electric field $E_0 \sim \sigma$ is small, the flexoelectric contribution $f_{\rm pol}$ is proportional to $(e_1+e_3)E_0$, where both flexoelectric coefficients e_i $(i=1,3)$ are estimated as $\sim$pC/m. Thus, in our case, the flexoelectric contribution of $f_{\rm pol}$ to $f_{\rm el}$ can be neglected [6].

The additional contribution to the effective anchoring energy should be accounted by adding the term $-\int_0^d \mathbf{P}_s\cdot\mathbf{E}dz$, where

$$\begin{aligned}\mathbf{P}_s &= n_s\Delta_z(A)\hat{\mathbf{n}} = n_s\Delta_z(A)(\sin\Delta_\theta\hat{\mathbf{i}}+\cos\Delta_\theta\hat{\mathbf{k}})\\ &= \frac{1}{Ad}(\mu_z\cos\Delta_\theta + 4\pi\epsilon_0\alpha E_s)(\sin\Delta_\theta\hat{\mathbf{i}}+\cos\Delta_\theta\hat{\mathbf{k}}) \quad (2)\end{aligned}$$

is the spontaneous polarization from the noncentrosymmetry at the LC/solid interface [7]. Here n_s is the film surface density given by $n_s = 1/Ad$, $\Delta_z(A) = \mu_z\cos\Delta_\theta + 4\pi\epsilon_0\alpha E_s$ is the total magnitude of the depolarized dipole moment of the 5CB molecules on the azobenzene surface, μ_z is the z component of the molecular dipole moment corresponding to the tail of the 5CB molecule on the azobenzene surface, α is the electronic polarizability, and E_s is the depolarizing field [7,11]. The depolarizing field due to a single point dipole of moment μ_i in the plane $z=0$ is given by [7,11]

$$\mathbf{E}_s^i = -\frac{\mu_i}{4\pi\epsilon_0 a^3}\hat{\mathbf{k}} = -\left(\frac{3}{4}\right)^{3/2}\frac{\mu_i}{4\pi\epsilon_0}\frac{1}{A^{3/2}}\hat{\mathbf{k}}, \quad (3)$$

where a is a distance between the nearest neighbors, and A is the surface area per 5CB molecule. Summing for the infinite array, the total field $\mathbf{E}_s = \sum_{i=-\infty}^{+\infty}\mathbf{E}_s^i$ is given by [12]

$$\begin{aligned}\mathbf{E}_s &= -\frac{\mu}{4\pi\epsilon_0 a^3}\sum_{u=-\infty}^{+\infty}\sum_{v=-\infty}^{+\infty}\sqrt{1/(u^2+v^2-uv)^3}\,\hat{\mathbf{k}}\\ &= -\frac{11.0342\mu}{4\pi\epsilon_0 a^3}\hat{\mathbf{k}} = -\frac{7.167\mu}{4\pi\epsilon_0}\frac{1}{A^{3/2}}\hat{\mathbf{k}}. \quad (4)\end{aligned}$$

Here the double summation has been evaluated by Topping [13] as 11.0342 and $\mu = \mu_i$ $(i=1,\dots,n)$, where n is the number of dipoles on the azobenzene surface. Hence, the following expression for the $\Delta_z(A)$ is obtained [7]:

$$\begin{aligned}\Delta_z(A) &= \mu_z\mathcal{F}(A)\cos\Delta_\theta\\ &= \mu_z\left[1-\frac{10.27\alpha}{A^{3/2}}\left(1+\frac{\epsilon_w-1}{\epsilon_w+1}\right)\right]\cos\Delta_\theta. \quad (5)\end{aligned}$$

Here μ_z is the z component of the molecular dipole moment corresponding to the tail of the 5CB molecule on the azobenzene surface, ϵ_w is the dielectric constant of 6Az10PVA, $a = (\frac{2A}{\sqrt{3}})^{1/2}$, A is the molecular area in Å^2, and α is the electronic polarization given by [10] $|4\pi\epsilon_0|$ (Å^3). By integrating over the z component of the $-\mathbf{P}_s\cdot\mathbf{E}$, one has $-\int_0^d \mathbf{P}_s\cdot\mathbf{E}dz = -[\sigma\Delta_z(A)/\overline{\epsilon}\epsilon_0 A]\cos^2\Delta_\theta$.

Thus, the total energy per unit area, which plays the role of the effective anchoring energy $f_{\rm eff}(\sigma)$, and depends on the surface charge density σ, is given by [6,14]

$$\begin{aligned}f_{\rm eff}(\sigma) &= -\tfrac{1}{2}w_{\rm eff}\cos^2(\theta_s-\theta_0) + \text{const.}\\ &= -\tfrac{1}{2}(\alpha_1\sigma^2+\alpha_2\sigma)\cos^2\Delta_\theta + \text{const.}, \quad (6)\end{aligned}$$

where $w_{\rm eff}(\sigma) = \alpha_1\sigma^2+\alpha_2\sigma$ is the effective anchoring energy strength [6], $\alpha_1 = (\epsilon_a d)/(\overline{\epsilon}^2\epsilon_0)$, $\alpha_2 = 2\Delta_z(A)/(\overline{\epsilon}\epsilon_0 A)$, and σ is the surface charge density corresponding to the *trans* or *cis* conformational state, respectively. The coefficient α_1 has dimension in m, while the coefficient α_2 has dimension in D/m^2.

It should be noted that in addition to the existing functional dependence for $f_{\rm eff}(\sigma)$, there are an extra two contributions to the effective anchoring energy, first, due to the elastic force, which can be written in the case of a 2D LC system in the form [15]

$$f_{\rm elast} = \int_0^{\lambda_{\rm ex}} F_{\rm elast}(z)dz, \quad (7)$$

and, second, in the Rapini and Papoular form [16] w_0, due to the van der Waals interaction. Here $F_{\rm elast} = \frac{1}{2}[K_1(\nabla\cdot\hat{\mathbf{n}})^2 + K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2]$, and K_1 and K_3 are the splay and bend elastic constants, respectively, whereas $\lambda_{\rm ex}$ is an extrapolation length [15]. Since we are interested in the dependence of the effective anchoring energy only on the surface charge density σ, the last two contributions to $f_{\rm eff}(\sigma)$ can be considered as the initial reference level and are not taken into account in further calculations.

The surface pressure π-A isothermal diagram $\pi(A) = -\partial f_{\rm eff}(A)/\partial A$ can be written as [6]

$$\begin{aligned}\pi(A) &= -\frac{\partial f_{\rm eff}(A)}{\partial A} = \frac{1}{2}\frac{\partial w_{\rm eff}(A)}{\partial A}\cos^2\Delta_\theta\\ &= \frac{1}{2}\frac{\partial\alpha_2(A)}{\partial A}\sigma\cos^2\Delta_\theta. \quad (8)\end{aligned}$$

To calculate the effective anchoring energy $f_{\rm eff}(A_i,\sigma_i)$ and surface pressure $\pi(A_i,\sigma_i)$ $(i = trans, cis)$ we need both the values of the surface charge densities σ_i and the area A_i per 5CB molecules corresponding to *trans* and *cis* conformational states. In the next section these data will be estimated based on the experimentally obtained values of the voltage V across the azobenzene+LC film during the *trans-cis* and *cis-trans* conformational transitions in the azobenzene monolayer deposited on the metal electrode, caused by the transmittance of the laser beam, as well as the area A per LC molecule.

III. CALCULATIONS AND DISCUSSION

To understand how adequately the molecular model proposed above describes the effect of charge separation during the *trans-cis* and *cis-trans* conformational changes in the surface monolayer of azobenzene deposited on a metal electrode on the anchoring energy of the LC film, we must take into account the interaction between the surface polarization in the LC phase and the surface electric field, arising from the surface charge density. As a result, we must understand the mechanism responsible for the transition of LC molecules from homeotropic to planar alignment and vice versa, caused by *trans-cis* and *cis-trans* conformational changes in the photosensitive azobenzene layer after laser radiation; i.e., we must examine the magnitude of the change in the surface charge density $\Delta\sigma = \sigma_{trans} - \sigma_{cis}$, as well as the voltage change $V(trans)$ and $V(cis)$ across the 6Az10PVA+5CB film, corresponding to the *trans* and *cis* conformational states of the azobenzene monolayer.

We will consider the 6Az5PVA monolayer, exhibiting the *trans* conformation in the initial state, which with the trans-

TABLE I. The measured data on the voltage V across both 6Az10PVA+5CB and 6Az10PVA films on Al electrode [7], during the *trans-cis* and *cis-trans* conformational changes in the 6Az10PVA monolayer caused by the laser beam (632 nm in the wavelength), at $T = 300$ K, and the calculated values of σ.

	trans	*cis*	*trans*	*cis*
6Az10PVA+5CB layer (*trans* form):				
σ $(\times 10^{-3})$ (C/m^2)	9.75	4.94	2.5	1.66
V (mV)	87.5	58.0	32.5	19.5
6Az10PVA monolayer (*trans* form):				
σ $(\times 10^{-3})$ (C/m^2)	−6.3	−1.49	−7.74	−1.09
V (mV)	−106	−25	−131	−18.5
	cis	*trans*	*cis*	*trans*
6Az10PVA+5CB layer (*cis* form):				
σ $(\times 10^{-3})$ (C/m^2)	11.25	6.37	7.48	2.15
V (mV)	131.5	75	88	31
6Az10PVA monolayer (*cis* form):				
σ $(\times 10^{-3})$ (C/m^2)	−6.7	−0.77	−5.9	−1.49
V (mV)	−113	−13	−100	25

mittance of a He-Ne laser beam (632 nm in the wavelength) undergoes the *trans-cis* isomerization [6]. The orientational transitions of 5CB molecules caused by the conformational change in the surface 6Az5PVA monolayer deposited on the Al electrode using the experimental data for the voltage V across the 6Az10PVA+5CB film, were provided by the surface potential method [6,7]. This measurement technique, developed by Iwamoto Laboratory in the 2000s [7,17], provides a direct experimental approach to determining the voltage V both across the 6Az10PVA+5CB and 6Az10PVA films. It is shown that the charge separation during change of conformation, caused by the laser irradiation, may lead to the change of the surface charge densities σ_{trans} and σ_{cis}, corresponding to *trans* and *cis* conformational states. Using the values of the voltage V across the 6Az10PVA+5CB film, which were measured across 6Az10PVA+5CB and 6Az10PVA films, the surface charge density σ_i ($i = trans, cis$) can be calculated by using the following form [6],

$$\sigma_i = \epsilon_w \epsilon_0 \frac{V_i}{L} \ (i = trans, cis), \tag{9}$$

where ϵ_0 is the dielectric permittivity of free space, ϵ_w is the dielectric constant of the 6Az10PVA monolayer, and $L \sim l_{5\mathrm{CB}} + l_{6\mathrm{Az10PVA}}$ or $L \sim l_{6\mathrm{Az10PVA}}$ is the film thickness for both the 6Az10PVA+5CB and 6Az10PVA films on the metal electrodes, respectively. In the following we use the experimental data for the dielectric constant of 6Az10PVA $\epsilon_w \sim 3.0$ [18], whereas the values of the lengths of the 5CB and 6Az10PVA molecules are equal to $l_{5\mathrm{CB}} \sim 2.0$ nm and $l_{6\mathrm{Az10PVA}} \sim 4.5$ nm, respectively.

The sequences of the surface potential values $V(trans)$ and $V(cis)$, and the conformational state changes in both the azobenzene 6Az10PVA+5CB and azobenzene 6Az10PVA films, caused by the charge separation, taking place during the *trans-cis* and *cis-trans* isomerizations, are measured using the surface potential signals and are collected in Table I. The isomerization involves a decrease of the distance between the pair carbon atoms in the azobenzene layer from about 0.9 nm in the *trans* form (case A) to 0.55 nm in the *cis* form (case B). The *trans* planar isomer, which has a rod-shaped configuration [see Fig. 1(a)], is transformed to the bent-shaped *cis* conformation [see Fig. 1(b)] in which the $-N \equiv N$ group is in a plane perpendicular to the phenylene groups. Likewise, *cis*-azobenzene has a very small dipole moment (0–0.2 D), while the dipole moment of the *trans* compound is 4.0–4.5 D [19]. This large conformational change induced by isomerization is reversible. In case A, it was observed that the initial state of the surface azobenzene monolayer, which exhibits the *trans* conformation with the molecular area $A \sim 0.4$ nm^2, with the transmittance of a He-Ne laser beam, undergoes the *trans-cis*, *cis-trans*, *trans-cis*, and *cis-trans* sequence of the isomerizations, at the different values of voltages V across both the 6Az10PVA+5CB and 6Az10PVA films. In case B, the initial state of the surface azobenzene monolayer exhibits the *cis* conformation ($A \sim 1.2$ nm^2), and with the transmittance of the laser beam undergoes the inverse, to case A, sequence of the photoisomerization changes.

It should be pointed out that the voltage V across the 5CB film on the 6Az10PVA monolayer, caused by the laser illumination, generates a positive charge density range in the interval $1.66 \times 10^{-3}\ \mathrm{C/m^2} \leqslant \sigma \leqslant 11.25 \times 10^{-3}\ \mathrm{C/m^2}$, whereas the voltage V across the 6Az10PVA film on the Al electrode generates a negative charge density range in the interval $-7.74 \times 10^{-3}\ \mathrm{C/m^2} \leqslant \sigma \leqslant -0.77 \times 10^{-3}\ \mathrm{C/m^2}$. The surface charge density in $\sigma \sim 10^{-3}\ \mathrm{C/m^2}$ corresponds to a surface ion concentration $n_{\mathrm{surf}} = \frac{\sigma}{e} = 6.25 \times 10^{15}\ \mathrm{m^{-2}}$, which is in agreement with the experimental data $n_{\mathrm{surf}} \approx 10^{15}$–$10^{16}\ \mathrm{m^{-2}}$ [10]. Here e is the proton charge.

To find out the effect of charge separation during the conformational *trans-cis* or *cis-trans* changes on the anchoring transition in the LC film deposited on the azobenzene monolayer, additional information for the $\epsilon_\parallel$, $\epsilon_\perp$, and α is needed. In the following, we use the calculated $\epsilon_\parallel = 18$, $\epsilon_\perp = 8$, $\bar{\epsilon} = 11.3$, and $\epsilon_a = 10$ from molecular dynamics simulation of 5CB at $T = 300$ K [20], using the conventional potential energy function composed of intra- and intermolecular contributions. Taking into account that the electronic polarizability of a C-H bond is $\sim 0.65 \times 4\pi\epsilon_0$ (Å^3) [10], the upper bonds for α can be taken as $\sim 1.95 \times 4\pi\epsilon_0$ (Å^3) [12]. Figure 2 shows the dependence of the effective anchoring energy strength $w_{\mathrm{eff}}(\sigma)$ of the LC (5CB) system deposited on the azobenzene monolayer, both for *trans* ($A \sim 0.4$ nm^2) (triangles down) and for *cis* ($A \sim 1.2$ nm^2) (triangles up) conformational states in the 6Az10PVA monolayer film. In the framework of the molecular model, based on the surface polarization mechanism, such changing of the anchoring energy can be explained by changing of the surface charge density, for instance, from σ_{trans} to σ_{cis} (see Fig. 2), taking place during the laser irradiation.

It should be noted that in the case of the *trans* conformational state in the azobenzene monolayer, a homeotropic orientation of the director field ($\hat{\mathbf{n}}_s \parallel \hat{\mathbf{k}}$) is realized in the LC system deposited on this azobenzene layer, while in the case of the *cis* conformational state in the azobenzene monolayer, a planar orientation of the director field ($\hat{\mathbf{n}}_s \parallel \hat{\mathbf{i}}$) is realized in the LC system deposited on the same azobenzene layer. In the case when $w_{\mathrm{eff}}^{trans} = w_{\mathrm{eff}}^{cis}$, we are dealing with the change of the surface charge density from $\sigma_{trans} = 2.3 \times 10^{-3}\ \mathrm{C/m^2}$

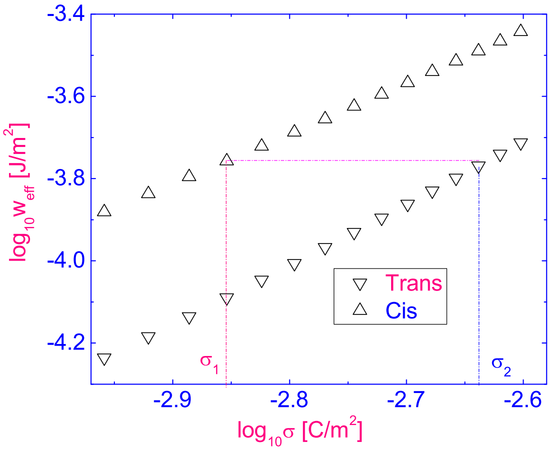

FIG. 2. The surface charge density σ dependencies of $w_{\mathrm{eff}}(\sigma)$, calculated using Eq. (6), at $T = 300$ K, for *cis* (triangles up), with $\sigma_1 = \sigma_{cis}$, and *trans* (triangles down), with $\sigma_2 = \sigma_{trans}$ conformational states.

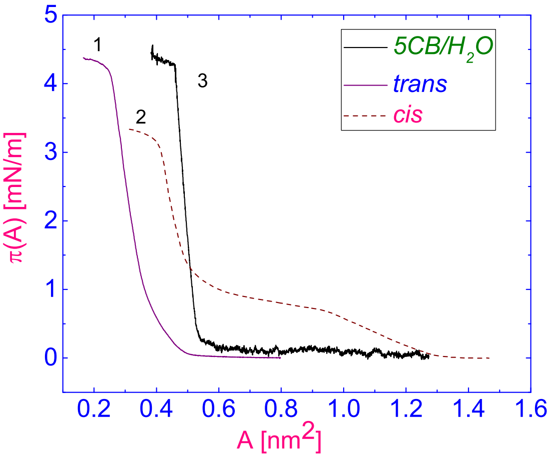

FIG. 3. The calculated surface pressure $\pi(A)$ vs molecular area A for the 5CB layer on the azobenzene monolayer, for *trans* (curve 1) and *cis* (curve 2) conformational states 6Az10PVA, and measured $\pi(A)$ vs A (see Ref. [17]), for the 5CB layer at the air/water interface.

to $\sigma_{cis} = 1.41 \times 10^{-3}$ C/m^2. Such change of the surface charge density in $\Delta\sigma = \sigma_{trans} - \sigma_{cis} \sim 8.9 \times 10^{-4}$ C/m^2 can be caused by the charge separation, taking place during the conformational change in the surface 6Az10PVA layer. In order to examine the magnitude of the changing surface charge density $\Delta\sigma$, one should consider data for changing of the voltage V across the 6Az10PVA+5CB film on metal electrodes. The surface charge density $\sigma_{trans} \sim 2.3 \times 10^{-3}$ C/m^2 (see Fig. 2), corresponding to the *trans* conformational state of the surface azobenzene monolayer, may be realized at $V \sim 31$ mV (see Table I, corresponding to 6Az10PVA+5CB layer in *trans* form), whereas the surface charge density $\sigma_{cis} \sim 1.66 \times 10^{-3}$ C/m^2, corresponding to the *cis* conformational state of the surface 6Az10PVA monolayer, may be realized at $V \sim 19.5$ mV (see Table I, corresponding to 6Az10PVA+5CB layer in *cis* form). So, our analysis shows that the *trans-cis* conformational changes, during the photoisomerization in the azobenzene monolayer, caused by the laser irradiation, may lead to the change of the surface alignment of liquid crystalline molecules, such as 5CB, having contact with that solid substrate. Thus, the molecular model based on the mechanism of surface polarization can adequately describe the orientation transition in the LC system deposited on the azobenzene monolayer caused by conformational changes in this monolayer.

The surface pressure π-A isothermal ($T = 300$ K) diagram during the lateral compression of the 5CB film spread on the azobenzene monolayer, calculated using Eq. (8), for both the *trans* and *cis* conformational states of 6Az10PVA, is shown in Fig. 3. To produce the *trans* form, the monolayer of 6Az10PVA was spread in the absence of light and the *cis* form was produced by irradiating the spread layer with the laser radiation. The two molecular configurations produce qualitatively different isotherms. In the case of the *trans* conformational state of the 6Az10PVA monolayer, the surface pressure $\pi(A)$ shows a steep increase at a molecular area $A \sim 0.4$ nm^2 (curve 1), and saturates at $\pi(trans) \sim 4.3$ mN/m, whereas the *cis* conformational state shows that a steep increase occurs at $A \sim 1.2$ nm^2 (curve 2), and saturates at $\pi(cis) \sim 3.3$ mN/m. So, the surface area per molecule is markedly higher for the *cis* configuration, which reflects the less efficient packing possible with the *trans* state. The existence of the higher collapse pressure for the *trans* isomer compared to the *cis* isomer suggests that the intermolecular interactions are stronger in the *trans* monolayer.

It should be noted here that the calculated isotherms $\pi(A)$-A, shown by curves 1 and 2 in Fig. 3, agree well with the measured curve 3 of the same isotherm of the monolayer 5CB spread on the water surface (see Ref. [17]).

In the wide region of the molecular area, the MDC signals allow us to determine the dipole moment $\Delta_z(A)$ of the cyanobiphenyl molecules at the LC-solid interface [7]. It has been found from MDC measurement of 5CB molecules at the air-water interface [7] that with decreasing of the molecular area the z component of the molecular dipole moment μ_z, corresponding to the tail of the 5CB molecule on the water surface, increases from zero, at the molecular area $0.6 \leqslant A/\mathrm{nm}^2 \leqslant 1.2$, up to 4.5 D per molecule, at the molecular area $0.2 \leqslant A/\mathrm{nm}^2 < 0.6$. Physically, this means that the initial dipole moment of the 5CB molecule ($\Delta \sim 5$ D) is fully compensated, due to interaction with the water molecules, at the molecular area $0.6 \leqslant A/\mathrm{nm}^2 \leqslant 1.2$, and that compensation is decreased up to 4.5 D per molecule, with decreasing of the molecular area. When the same tendency is true for the case of the 6Az10PVA+5CB system, the value of the total molecular dipole moment $\Delta_z(A_{trans})$, corresponding to the z component of the 5CB molecule on the azobenzene monolayer, in the *trans* conformational state is greater than the value of $\Delta_z(A_{cis})$ corresponding to the *cis* conformational state. Thus, using the expression (5), one can calculate the tilt angle $\theta_s = \cos^{-1}[\frac{\Delta_z(A)}{\mu_z \mathcal{F}(A)}]$, which consists of the director $\hat{\mathbf{n}}_s$ with respect to the solid substrate, while the easy axis $\hat{\mathbf{n}}_0$ is directed perpendicular to the LC/solid interface. At the molecular area $A_{trans} \sim 0.4$ nm^2, the z component of the total dipole moment, $\Delta_z(A_{trans})$, is greater than $\Delta_z(A_{cis})$, at the molecular area $A_{cis} \sim 1.2$ nm^2. This means that in our case of the 6Az10PVA monolayer, which exhibits the *trans* conformational state with the molecular area $A_{trans} \sim 0.4$ nm^2, the dipole moment $\Delta_z(A_{trans})$ is equal to 4.0–4.5 D, while the dipole moment $\Delta_z(A_{cis})$ of the *cis* conformational state, with the molecular area $A_{cis} \sim 1.2$ nm^2, is equal to 0.0–0.2 D. Using the expression (5), one can find that in the *trans* conformational state $\cos\theta_s(trans) \sim 1$, or θ_s is close to 0 (homeotropic alignment), while in the *cis* conformational state $\cos\theta_s(cis) \sim 0$, or θ_s is close to $\frac{\pi}{2}$ (planar alignment).

IV. CONCLUSIONS

In this paper, the molecular model to describe the effective anchoring energy that takes into account the interaction between the surface polarization in the LC phase and the surface electric field, arising from the surface charge density, is proposed. Within the framework of the proposed molecular model, the mechanism responsible for the anchoring transition of LC molecules from homeotropic to planar alignment and vice versa, caused by the *trans-cis* and *cis-trans* conformational changes in the photosensitive azobenzene layer after laser radiation, is described. It is shown, using the experimental data for the voltage across the 6Az10PVA+5CB film, provided by the surface potential technique, that the charge separation during the conformational changes, caused by the laser irradiation, may lead to the change of the surface alignment of liquid crystalline molecules. It is shown that this molecular model, based on the surface polarization mechanism, can adequately describe the orientational transition in the LC system deposited on the azobenzene photosensitive monolayer.

In turn, the calculated values of the isothermal surface pressure diagram π-A showed that the surface area A per LC molecule is noticeably higher for the *cis* configuration, which reflects a less efficient packaging than in the *trans* state. It is also shown that the strong dipole interaction between the hydrophilic tail of 5CB molecules and 6Az10PVA molecules in the *cis* conformational state orients the surface director $\hat{\mathbf{n}}_s$ close to the LC/solid interface (planar), while the strong dipole interaction between the hydrophilic head of 5CB molecules and 6Az10PVA molecules in the *trans* conformational state orients the surface director $\hat{\mathbf{n}}_s$ close to the normal (homeotropic) to the metal electrode.

It should be noted here that the qualitatively similar behavior of the calculated and measured isotherms $\pi(A)$ during the lateral compression of the 5CB film on the azobenzene monolayer in the *trans* conformational state and on the water surface shows that in both these cases, the homeotropic alignment of the 5CB film on these substrates is realized.

In conclusion, despite the fact that certain successes have been achieved based on molecular models describing the effective energy of LC system deposited on the photosensitive azobenzene layers [21,22], it is still too early to talk about developing a mechanism on a molecular scale that allows us to describe the switching of the alignment of the adjacent LC layer from homeotropic to planar alignment.

We believe that the present study not only shows some useful routes for understanding the nature of the surface charge density changes due to photoisomerization in Langmuir films, but also for analyzing the surface potential at the metal-organic interface.

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