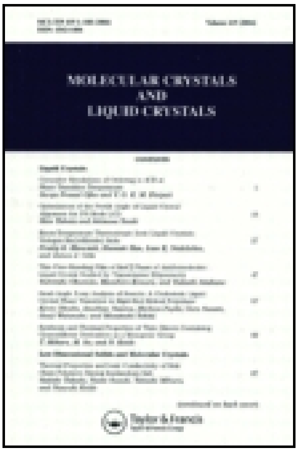

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Anchoring Energy of Liquid Crystals

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Version of record first published: 15 May 2012.

To cite this article: A. K. Dadivanyan, O. V. Noah, Yu. M. Pashinina, V. V. Belyaev, V. G. Chigrinov & D. N. Chausov (2012): Anchoring Energy of Liquid Crystals, Molecular Crystals and Liquid Crystals, 560:1, 108-114

To link to this article: http://dx.doi.org/10.1080/15421406.2012.663185

Mol. Cryst. Liq. Cryst., Vol. 560: pp. 108–114, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.663185

Anchoring Energy of Liquid Crystals

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The liquid crystals anchoring theory is considered on the molecular level. Earlier calculations of mesogenic molecules interaction energy with graphite and PE surface give results being one-two orders higher than experimentally obtained values. To explain the experimental values of anchoring energy we proposed its dependence on the interaction between liquid crystal layers. In our calculations we have simulated the mesogen molecules by virtual rod-like molecules. The molecules orientation was given by polar and azimuthal angles towards the directors of neighboring liquid crystal layers. Obtained values of polar and azimuthal anchoring energy as well as their dependences on the order parameter are in good agreement with experimental data.

Keywords Atom-atom potentials; interaction energy; liquid crystals; mesogens; polar and azimuthal anchoring energy

Electronic paper, LC TV sets, LC monitors and other optical LC-based devices properties are considerably defined by both polar and azimuthal anchoring energy of liquid crystals with the carrier surface. Nowadays there is no satisfactory statistic theory explaining both the experimental dependence of these characteristics on order parameter and their experimentally obtained values.

On the basis of atom-atom potential method we took an attempt to create such theory by calculating the interaction energy of mesogen molecules with graphite and polyethylene surfaces [1,2] which appeared to be one order higher than polar and two orders higher than azimuthal anchoring energy [3]. Similar results were obtained in experimental work [4].

In this work we supposed the anchoring energy dependence not only on the mesogen molecules interaction with a surface, but on the interaction between liquid crystal layers. The molecules orientation was defined by polar angle θ and azimuthal angle φ (Fig. 1).

In our calculations we have simulated the mesogen molecules by virtual rod-like molecules. C atoms and CH, CH_2, CH_3 groups have been replaced by the model C^* atoms [5]. The model atoms number is equal to *N*. The adequacy of such replacement was shown in [5–7]. The distance between atoms was selected by such way, that the model molecule length was equal to the length of the mesogen molecule, and the number of atoms and groups was equal to that in the mesogen molecule. It was supposed that mesogen molecules are

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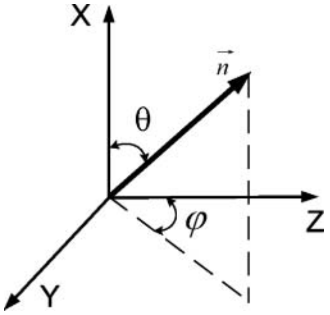

Figure 1. The molecule orientation coordinate system.

located on the cones surfaces and can move on the surface (Fig. 2). Molecules orientation is characterized by angles θ_i, θ_j, φ_i, φ_j.

Polar anchoring energy (E_θ) is defined by the difference of surface interaction energies between layers at $\theta = 0^\text{o}$, $\varphi = 0^\text{o}$ and $\theta = 90^\text{o}$, $\varphi = 0^\text{o}$ and azimuthal (E_φ) is defined by their difference at $\theta = 90^\text{o}$, $\varphi = 90^\text{o}$ and $\theta = 90^\text{o}$, $\phi = 0^\text{o}$ divided into the surface area s.

The interaction energy was calculated by atom-atom potentials method. For the calculation it was necessary to know the distance between atoms for various mutual layers orientations R_{ijl}.

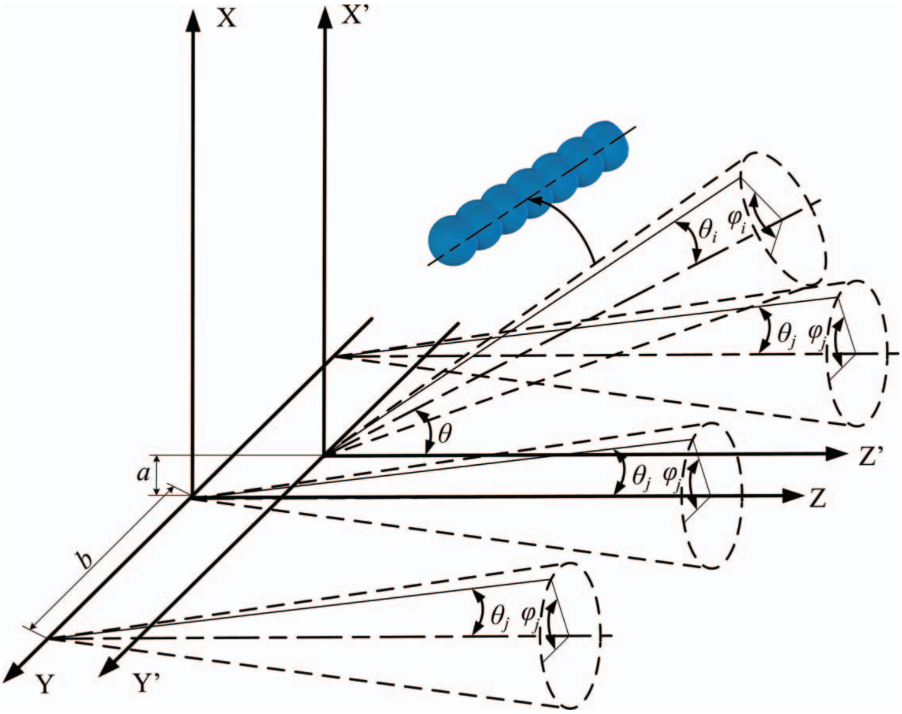

Figure 2. Mutual orientation of the mesogen molecule and the surface.

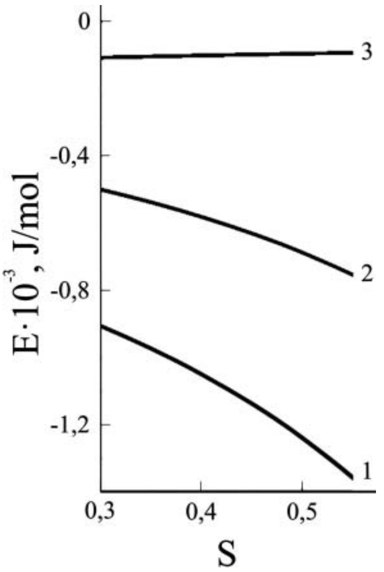

Figure 3. Dependence of the interaction energy between the mesogen molecule and the LC-layer on the order parameter S for $\theta = 90^\circ$, $\varphi = 0^\circ$ (1), $\theta = 90^\circ$, $\varphi = 90^\circ$ (2), $\theta = 0^\circ$, $\varphi = 0^\circ$ (3).

For R_{ijl} values in static coordinate system the next equations have been obtained: for $\theta = 90^{\text{o}}$, $\varphi = 0^{\text{o}}$:

$$\begin{aligned} R_{ijl}^2 &= (a + r_i \sin\theta_i \cos\varphi_i - r_j \sin\theta_j \cos\varphi_j)^2 \\ &\quad + (r_i \sin\theta_i \sin\varphi_i - bl - r_{ij} \sin\theta_j \sin\varphi_j)^2 + (r_i \cos\theta_i - r_j \cos\theta_j)^2 \end{aligned}$$

for $\theta = 90^{\text{o}}$, $\varphi = 0^{\text{o}}$:

$$\begin{aligned} R_{ijl}^2 &= (a + r_i \cos\theta_i - r_j \sin\theta_j \cos\varphi_j)^2 \\ &\quad + (r_i \sin\theta_i \sin\varphi_i - bl - r_{ij} \sin\theta_j \sin\varphi_j)^2 + (r_i \sin\theta_i \cos\theta_i - r_j \cos\theta_j)^2 \end{aligned} \quad (1)$$

for $\theta = 0^{\text{o}}$, $\varphi = 90^{\text{o}}$:

$$\begin{aligned} R_{ijl}^2 &= (a + r_i \sin\theta_i \cos\varphi_i - r_j \sin\theta_j \cos\varphi_j)^2 \\ &\quad + (r_i \cos\theta_i - bl - r_j \sin\theta_j \sin\varphi_j)^2 + (-r_i \sin\theta_i \sin\varphi_i - r_j \cos\varphi_j)^2 \end{aligned}$$

Here above b is the distance between the molecules of a layer, l is a number of a molecule in the j-th layer.

According to R_{ijl} values the energy values E have been calculated (Fig. 3).

The interaction energy E of an upper layer molecule and lower layer molecules has been calculated by atom-atom potentials method and presented as a sum of values of the interaction energy between atoms of this molecule and atoms of low layer molecules E_{ijl}

$$E = \sum_{ijl} E_{ijl}, \tag{2}$$

$$E_{ijl} = \frac{A}{R_{ijl}^{6}} + \frac{B}{R_{ijl}^{12}}, \tag{3}$$

where $A = -5{,}31 \cdot 10^{3}\ \mathrm{J{\cdot}mol^{-1}{\cdot}\mathring{A}^{6}}$, $\mathrm{B} = 11{,}5 \cdot 10^{9}\ \mathrm{J{\cdot}mol^{-1}{\cdot}\mathring{A}^{12}}$ [5].

The average E values were calculated according to θ_{i}, φ_{i}, θ_{j}, φ_{j} angles, with φ_{i} и φ_{j} angles considered to be equally probable.

A $\overline{\cos^2\theta_k}$ value can be presented in terms of the order parameter S by equation:

$$S = \frac{3}{2}\left(\overline{\cos^2\theta_k} - \frac{1}{3}\right)$$

where $k = i, j$.

Energy defining equations include $\overline{\cos^{m+n}\theta_k}$ and $\overline{\sin^{p+q}\theta_k}$ values, where $k = i,\ j$. In this case we suggested, that $\cos^{m+n}\theta_k \sin^{p+q}\theta_k = \cos^{m}\theta_k \cos^{n}\theta_k \sin^{p}\theta_k \sin^{q}\theta_k$. Such assumption is well grounded, as investigations of hydrocarbons intermolecular interaction [8] showed that realization probabilities of the most probable states are one order higher than probabilities of other 90% realizations, and we can propose that in practice only a small number of states can be realized in the interval of deviations from the most probable value ($\theta \pm 10^{0}$).

In order to calculate the anchoring energy the difference of interaction energy values at various angles should be divided into upper molecule and lower layer anchoring area *s*.

The dependences of both polar and azimuthal anchoring energy on order parameter S are presented in Figs 4 and 5. As shown in figures here above both polar and azimuthal

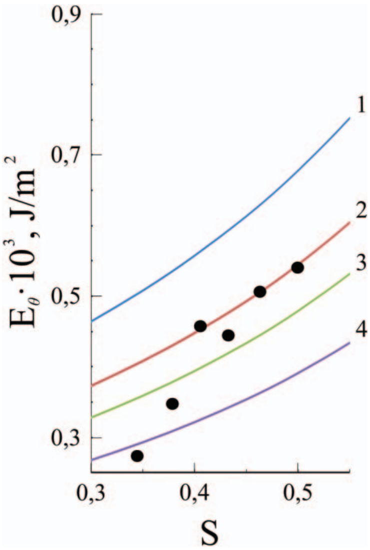

Figure 4. Polar anchoring energy E_θ dependence on the order parameter S at different model molecule length. 1 – $N = 40$; 2 – $N = 50$; 3 – $N = 6\ 0$; 4 – $N = 70$, N is a C atoms number in mesogen molecule, dots are experimental data [3].

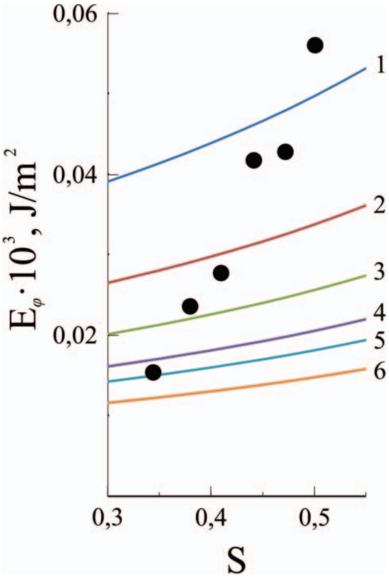

Figure 5. Azimuthal anchoring energy E_ϕ dependence on the order parameter S at different model molecule length. 1 – $N = 20$; 2 – $N = 30$; 3 – $N = 40$; 4 – $N = 50$; 5 – $N = 60$; 6 – $N = 70$, N is a C atoms number in mesogen molecule, dots are experimental data [3].

anchoring energy increase with increase of the order parameter S, and azimuthal anchoring energy is one order less than polar. That is consistent with experimental data [2].

One order difference of polar and azimuthal anchoring energy is shown in Fig. 6, where dependences of energy on θ at $\phi = 0°$ and on ϕ at $\theta = 0°$ at order parameter $S = 1$ are given. It is shown in Fig. 6 that the absolute energy value decreases continuously with θ

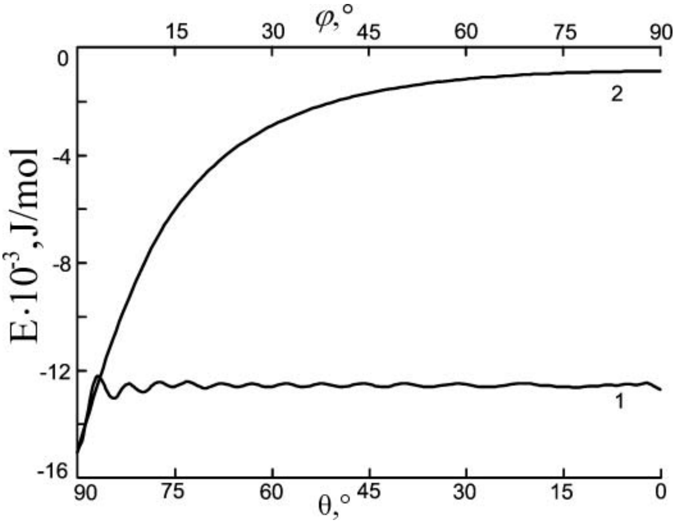

Figure 6. Dependence of the anchoring energy of the model molecule and the LC layer on their mutual orientation.

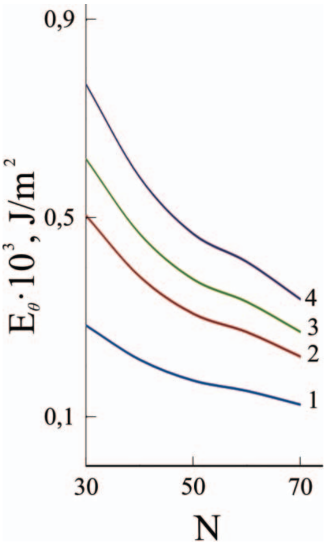

Figure 7. Dependence of the polar anchoring energy E_θ on the molecule length (N is a number of atoms in the LC molecule) at different order parameter values. 1 – $S = 0$; 2 – $S = 0.3$; 3 – $S = 0.4$; 4 – $S = 0.5$.

increasing, because of the continuous increase of interatomic distance with θ increasing. On the contrary with increasing of the φ angle value the absolute interaction energy value decreases at first and then periodically changes because of periodic increase and decrease of interatomic distance starting from some φ value.

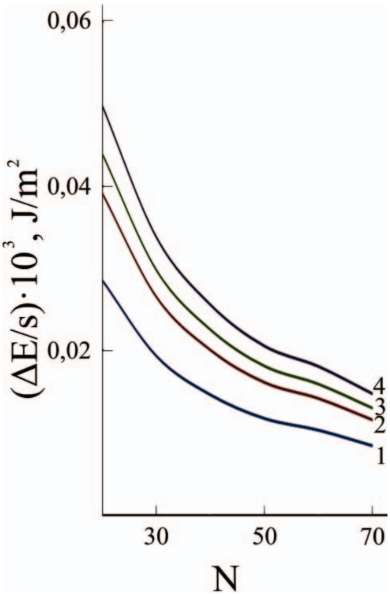

Figure 8. The dependence of the azimuthal anchoring energy E_ϕ on the molecule length (N is a number of atoms in the LC molecule) at different order parameter values. 1 – $S = 0$; 2 – $S = 0.3$; 3 – $S = 0.4$; 4 – $S = 0.5$.

The data obtained allowed to determine the dependence of the polar (Fig. 7) and azimuthal (Fig. 8) anchoring energy on the molecule length at different order parameter values. The higher is the order parameter value, the stronger is the dependence.

Thus in this work an assumption about the anchoring energy dependence on the interaction between liquid crystal layers permits to obtain the dependences of polar and azimuthal anchoring energy on the order parameter. Both polar and azimuthal anchoring energy values are shown to depend on the mesogen molecule length and to increase with increasing of the order parameter. The obtained results are in good agreement with experimental data.

Acknowledgment

The project is supported by the Ministry of Education and Science of Russian Federation contracts ##02.740.11.5218, 14.740.11.0977, REBR grants #10-07-00385-a, 10-03-90028-Bel_a and by Hong-Kong grants CERG 612409, CERG 612310.

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