# Determination of the binding energy of nematics with crystalline substrates from measurements of electro-optical effects

L. M. Blinov and A. A. Sonin

*Crystallography Institute, USSR Academy of Sciences*

(Submitted 6 March 1984)
Zh. Eksp. Teor. Fiz. **87**, 476–482 (August 1984)

Two electro-optical effects, Freedericksz transition and the flexoelectric effect, are investigated in 5CB and MBBA nematic liquid crystals with leucosapphire or lithium-niobate substrates whose van der Waals forces orient the nematic homotropically. The Freedericksz transition threshold is seen to be raised by the stabilizing effect of the dispersive forces of the anisotropic substrates. Calculations from the electro-optical measurements yield a coupling energy $W \sim 10^{-4}$ erg/cm$^2$ between the nematics and the crystalline substrates and a surface polarization $p_s \sim 10^{-4}$ dyn$^{1/2}$ for a homotropic MBBA layer. The values of $W$ calculated from measurements of the two electro-optic effects are in satisfactory agreement.

## INTRODUCTION

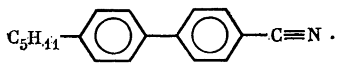
Progress in the technology of liquid-crystal devices is determined to a considerable degree by the level of understanding of the processes that take place at the interface of the liquid crystal and its bounding surface. An important parameter that describes the interaction of a liquid crystal with a solid substrate is the binding energy $W$, which characterizes the work done to deflect the liquid-crystal molecules from their equilibrium position through a certain angle. Knowing $W$ we can assess the total action of the orienting forces of the solid substrate (steric, dipole, van der Waals, as well as specific forces of chemical origin) on a liquid crystal. One of the simplest methods of determining $W$ in nematic liquid crystals (NLC) is to calculate it from measurements of electro-optical effects, viz., the Freedericksz transition and the flexoelectric effect.[1] The presently known studies aimed at determining $W$ by this method[2,3] were made on samples of homotropically oriented NLC, with the orientation achieved by treating glass substrates with surface-active media (SAM). Thus, the nematic was in contact not with the substrate substance itself, but with an SAM of rather complicated structure: furthermore, the molecules of the orientant, by penetrating into the NLC volume, could in principle alter its properties, e.g., the electric conductivity or the diamagnetic anisotropy. The values of $W$ calculated from different electro-optical effects in accord with the existing theory were therefore contradictory.

We made the first attempt to determine, from electro-optical experiments, the binding energy of nematics with pure crystalline substrates whose dispersion forces produce a homotropic orientation of the NLC molecules.

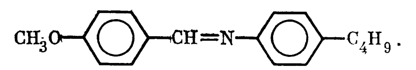
## EXPERIMENT

It was established theoretically and experimentally that orientation of nematics on cleaved solid-crystal surfaces is caused predominantly by the dispersion interaction and is determined by the symmetry of the crystal surface.[4–6] Low-symmetry surfaces having a syngony 1, for example, stabilize the homotropic orientation of the NLC.[6] In that study, optically polished slabs of single crystals of leucosapphire $Al_2O_3$ and lithium niobate $LiNbO_3$ were used, having a symmetry 1 and faces parallel to the optical axes were used ($X$ cuts). The measurements were made on two NLC with different anisotropy of the dielectric constant $\varepsilon_a$:

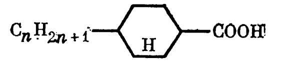
1. 4-amyl-4′cyanobiphenyl (5CB) with $\varepsilon_a \approx 13$:



2. 4-methoxybenzylidene-4′-butylaniline (MBBA) with $\varepsilon_a' \approx -0.6$:



Both substances, in cells with crystalline substrates, gave good homotropic orientation that was independent of the relative arrangement of the optical axes of the upper and lower bearing surfaces. The time of formation of a homotropic texture on the initial planar one, due to the flow of the NLC when the cell was filled, was several hours. Figure 1 illustrates the establishment of the homotropic orientation of the 5CB molecules (dark field), viewed through crossed polarizers for $LiNbO_3$ substrates. For comparison we investigated also the orientation of a nematic mixture of the fourth and six homologs (1:1 by weight) of $n$-alkyl-trans-cyclohexanocarboxylic acids:



with $\varepsilon_a \approx 0.17$, in which the benzene rings that have delocalized electrons are replace by cyclohexane rings. No homogeneous homotropic textures were obtained in this case. The required presence of delocalized electrons in the NLC molecules and the absence of a significant dependence of the character of the orientation on the sign of $\varepsilon_a$ of the nematic indicate that the homotropic orientation of the NLC was produced on the NLC on the crystalline substrate is the result of dispersion interaction.

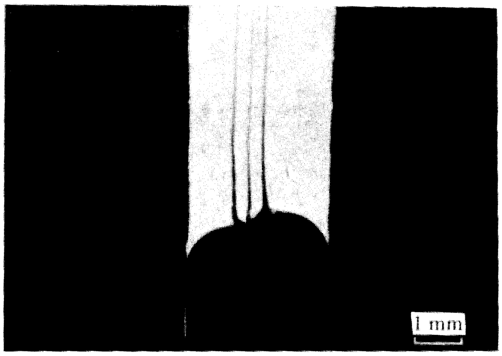


FIG. 1. Reorientation of 5CB molecules from a flow-produced planar texture into a homotropic structure under the action of the dispersion forces of a crystalline ($LiNbO_3$) substrate (crossed polarizers).

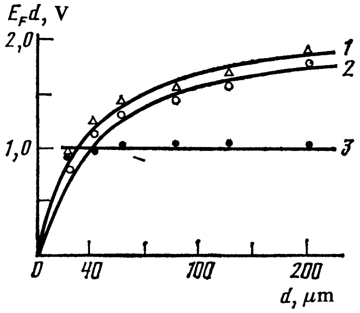


FIG. 2. Freedericksz-transition threshold $E_F d$ vs thickness for a homotropic 5CB layer (points—experiment, curves—calculation): 1—$Al_2O_3$ substrates, 2—$LiNbO_3$, 3—glass treated with lecithin.

The Freedericksz transition and the flexoelectric effect were investigated by the standard polarization-optics procedure, viz., we measured the light transmission by the liquid-crystal cell in crossed polarizers as a function of the voltage between the electrodes. The light source was an He-Ne laser ($\lambda = 0.6328$ μm. Aluminum-foil electrodes were inlayed in the end faces of the cell at 45 ° to the optical axis of the substrate surfaces. The electrodes governed simultaneously the thickness of the liquid-crystal layer, which could be varied in steps of 20 μm. The distance between the electrodes was measured with an ocular micrometer accurate to 10 μm, and was varied in the range 1.0–3.0 mm. The Freedericksz transition was measured in a alternating electric field at 60-Hz voltage from a GZ-33 generator. The flexoelectric effect was measured in a dc field. Since the geometry of the experiments was the same, the Freedericksz transition was measured in 5CB ($\varepsilon_a > 0$) and the flexoelectric effect in MBBA ($\varepsilon_a < 0$). These substances are close in their electronic structure, so that the binding energies $W$ determined in two independent experiments were expected to be of the same order of magnitude.

The liquid-crystal layer thickness was varied in the range from 20 to 200 μm. In this range, 5CB always gave a good homotropic orientation independent of the ratio of the interelectrode distance $l$ to the nematic-layer thickness $d$. For MBBA, the quality of the homotropic orientation depended on the ratio $l/d$. With increase of the latter, the homotropic texture was established for ever increasing cell thicknesses. Thus, for example, at $l = 1.0$ mm the homotropic texture was highly unstable even at $d \approx 150$ μm, while for $l = 2.0$ mm orientation was established already at $d = 200$ μm. Obviously, the so-called spontaneous Freedericksz transition, i.e., loss of homotropic orientation on account of the disequlibrium of the initial boundary conditions for NLC with $\varepsilon_a < 0$, took place in MBBA.

In the investigation of the Freedericksz transition, the threshold voltage $U_F$ was determined by measuring the abrupt increase of the cell transmission, at an error $\Delta U_F \approx 10\%$. From the measured $U_F$ we calculated the product of the threshold field strength by the liquid-crystal layer thickness: $E_F d = U_F d/l$.

The dependences of $E_F d$ on $d$ for leucosapphire and lithium niobate substrates are shown in Fig. 2. Obviously, the product $E_F d$ increases with increasing cell thickness, thus pointing to the presence of a finite binding energy between the NLC and the substrates.

Calibration measurements of the thickness dependence of $E_F d$ were performed for 5CB with substrates of ordinary glass coated with a layer of lecithin (see Fig. 2). It is clearly seen that in this case, within the limits of experimental error, $E_F d$ is independent of $d$, just as in Ref. 2. This indicates that experiments aimed at determining $W$ can be performed in our electrode geometry. That $E_F d$ is independent of $d$ was observed also in measurements of the Freedericksz transition using crystal substrates coated with lecithin. In this case the value of $E_F d$ is the same as in the experiment with glass substrates coated with lecithin. The experimental value of $E_F d$ for 5CB on lecithin-coated substrate is equal to the value calculated for an infinitely strong bond. The higher value obtained in measurements of the Freedericksz transition threshold for crystal substrates is attributed to the stabilizing effect of the van der Waals forces in the NLC surface layers. Indeed, the average volume density $q$ of the dispersion forces, with allowance for delay, can be estimated from the equation[10]

$$\bar{q} = \frac{2}{d} \int_{\delta}^{d/2} \frac{B}{z^4} dz \approx \frac{2B}{3\delta^3 d}, \tag{1}$$

where $B$ is the Hamacker constant, $\delta$ is the minimum size for the validity of the macroscopic theory of van der Waals forces, $z$ is the coordinate, and $d$ is the thickness of the liquid-crystal cell. The experimental value is $B = 10^{-19}$ erg/cm.[10] Assuming $\delta$ to be the distance over which the effect of delay is already substantial ($\delta \sim 500$ Å, Refs. 10 and 11), we obtain $\bar{q} \approx 0.1$ erg/cm$^3$, i.e., $\bar{q}$ is of the same order as the Freedericksz-transition threshold field in the case of tight binding of the nematic to the substrate. The van der Waals forces of the substrates can thus renormalize the Freedericksz-transition threshold, as indicated theoretically in Ref. 4.

In measurements of the flexoelectric effect, the average birefringence $\overline{\Delta n}$, which is produced in a nematic layer by longitudinal bending deformation, was calculated from the formula[12]

$$J/J_0 = \sin^2(\pi d \overline{\Delta n}/\lambda), \tag{2}$$

where $J_0$ is the intensity of the light passing through the liquid-crystal cell at $U = 0$, $J$ is the intensity at $U \neq 0$, and $\lambda$

is the wavelength of the incident light. To calculate $\overline{\Delta n}$ we used not only the points of the extrema of $J/J_0$ for which $\overline{\Delta n}d/\lambda = k/2\,(k = 0, 1, 2, \ldots)$, but also intermediate values of $J/J_0$. The apparatus was therefore graduated beforehand to ensure satisfaction of Malus' law.

The dependences of $\overline{\Delta n}$ on $E^2$ at different thicknesses of the liquid-crystal layer for $LiNbO_3$ substrates are shown in Fig. 3. Obviously, the extremal points fit satisfactorily straight lines. Figure 4 shows plots of $\overline{\Delta n}/E^2d^2$ against the thickness for $Al_2O_3$ and $LiNbO_3$ substrates. It is clearly seen that $\overline{\Delta n}/E^2d^2$ decreases with increasing $d$, and this also points to the presence of a finite binding energy between the molecules of the nematic and the solid substrates. Just as in the case of the Freedericksz transition, the flexoelectric effect was measured for MBBA using glass substrates treated with lecithin. In this case $\overline{\Delta n}/E^2d^2$ is independent of $d$ within the limits of experimental eror ($\sim 15\%$), likewise in agreement with the results of Ref. 2. Values of $\overline{\Delta n}/E^2d^2$ lower than measured for pure crystalline substrates are attributed to the stabilization of the homotropic orientation by the action of the van der Waals forces and to large values of the surface polarization of the nematic in contact with the solid crystal.

Thus, when lecithin-treated glass substrates are used measurements of the Freedericksz transition and of the flexoelectric effect yield, just as in Ref. 2, different binding energies if the Rapini potential[13] is used in the calculation of $W$. At the same time, for pure crystalline substrates the results of the two independent measurements agree.

### DISCUSSION OF RESULTS

Let us estimate the binding energy of nematics with crystalline substrates as deduced from our experiments. Since the van der Waals forces decrease quite rapidly with distance,[10,14] we shall assume that they act only in the immediate vicinity of the substrates, and the dispersion-interaction energy will be taken into account together with the energy of the steric and other short-range binding forces.

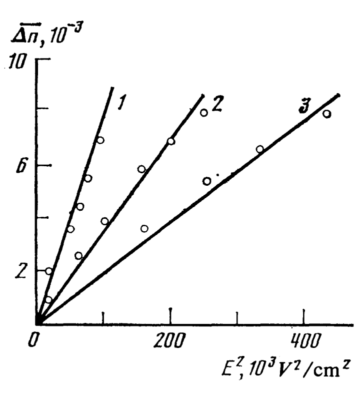


FIG. 3. Average birefringence $\overline{\Delta n}$ vs $E^2$ for homotropic MBBA layer in contact with an $LiNbO_3$ substrate at different layer thicknesses: 1—$d = 140\,\mu m$, 2—$80\,\mu m$, 3—$40\,\mu m$.

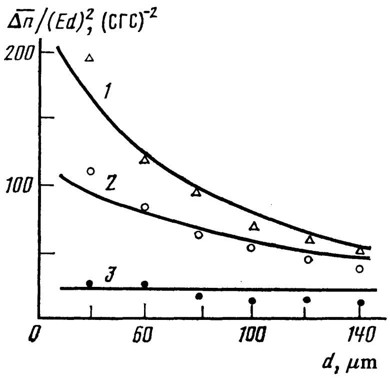


FIG. 4. Thickness dependence of $\overline{\Delta n}/E^2d^2$ for a homotropic MBBA layer (points—experiment, curves—calculation): 1—$Al_2O_3$ substrate, 2—$LiNbO_3$, 3—glass treated with lecithin.

We apply the theory of the Freedericksz transition to the case of a finite binding energy of the NLC with the substrates.[15] We assume that our experimental points are satisfactorily described by the relation[15]

$$\frac{\xi E_F}{dE_{F0}} = \operatorname{ctg}\left(\frac{\pi}{2}\frac{E_F}{E_{F0}}\right), \tag{3}$$

where $\xi = \pi K_{33}/W$ is the characteristic length that determines the influence of the substrate on the NLF orientation in a certain region next to the wall, $K_{33}$ is the nematic elastic constant, and $E_{F0}$ is the threshold field of the Freedericksz transition in the case of tight binding ($W \rightarrow \infty$). The values of $E_{F0}d$ and $\xi$ are chosen by least squares. This calls for satisfaction of the condition

$$\Phi_1 = \sum_{i=1}^{n} [d_i E_{Fi}(d_i, \xi, E_{F0}d) - E_{Fi}d_i]^2 \rightarrow \min, \tag{4}$$

where $n$ is the number of experimental points, $E_{Fi}d_i$ are the experimental values of the Freedericksz transition threshold, $d_i E_{Fi}(d_i, \xi, E_{F0}d)$ are calculated by numerically solving Eq. (3) with $\xi$ and $E_{F0}d$ chosen to minimize the functional (4). For leucosapphire substrates we get $E_{F0}d = 2.3$ V and $\xi = 6.7 \cdot 10^{-3}$ cm, while for lithium niobate we get $E_{F0}d = 2.2$ V and $\xi = 7.2 \cdot 10^{-3}$ cm. In the calculation of $W$ for 5CB we chose $K_{33} = 1.6 \cdot 10^{-6}$ dyn ($T_{NI} - T = 10$ °C).[16] The values of $W$ for the two crystalline substrates are listed in Table I.

We find thus from measurements of the thickness dependences of the Freedericksz-transition threshold that the binding energy of 5CB with the crystalline substrates at homotropic orientation of the director is of the order of $10^{-4}$ erg/cm², and $W$ for $Al_2O_3$ substrates is somewhat larger than for $LiNbO_3$. The theoretical thickness dependences of $E_Fd$ calculated from (3) are shown in Fig. 2 (solid curves). The experimental data agree satisfactorily with the theory.

The average birefringence produced in an NLC layer under flexoelectric deformation is obtained from the following theoretical relation[17]:

$$y = a(1+bx)^{-2}. \tag{5}$$

We use here the notation

$$y = \frac{\overline{\Delta n}}{E^2d^2}, \quad a = \frac{1}{24} n_0 \left(1 - \frac{n_0^2}{n_e^2}\right)\left(\frac{e_{33}+p_s}{K_{33}}\right)^2,$$

$$b = \frac{W}{2K_{33}}, \quad x = d,$$

TABLE I. Values of binding energy and of surface polarization of homotropic NLC layers calculated from measurements of the Freedericksz transition and of the flexoelectric effect.

| Substrate material | Liquid crystal material | | |
|---|---|---|---|
| | 5CB | MBBA | |
| | W, erg/cm | W, erg/cm | $P_s$, dyn$^{1/2}$ |
| $Al_2O_3$ | $7{,}5\cdot10^{-4}$ | $1{,}5\cdot10^{-4}$ | $5{,}0\cdot10^{-4}$ |
| $LiNbO_3$ | $6{,}5\cdot10^{-4}$ | $7{,}5\cdot10^{-5}$ | $4{,}6\cdot10^{-4}$ |

where $n_o$ and $n_e$ are respectively the refractive indices for the ordinary and extraordinary rays, $e_{33}$ is the flexoelectric coefficient, and $p_s$ is the surface polarization of the homotropic NLC layer, i.e., the polarization per unit area of the bearing surface. We shall assume that our experimental points $x_i$ and $y_i$ are satisfactorily described by Eq. (5), so that the coefficients $a$ and $b$ can be determined by least squares from the condition

$$\Phi_2=\sum_{i=1}^{n}[y_i-a(1+bx_i)^{-2}]^2\rightarrow \min. \tag{6}$$

Numerical solution of (6) yields $a = 326.6$ dyn$^{-1}$ and $b = 100$ cm$^{-1}$ for leucosapphire substrates and $a = 138.0$ dyn$^{-1}$ and $b = 50$ cm$^{-1}$ for lithium niobate. In the estimates of $W$ and $p_s$ we used for MBBA the values $n_o = 1.54$, $n_e = 1.86$ (Ref. 18), $K_{33} = 7.5\cdot10^{-7}$ dyn (ref. 12), and $e_{33} = -4.0\cdot10^{-4}$ dyn$^{1/2}$ (Ref 19) ($T_{NI} - T = 20$ °C). The values of $W$ and $p_s$ for the two crystalline substrates are also listed in Table I. The values of $W$ obtained by measuring the flexoelectric effect in MBBA are somewhat smaller (within one order of magnitude) than those calculated from the experimental data on the Freedericksz transition for 5CB. This can be attributed to the destabilizing action of the surface polarization on the homotropic MBBA layer, and also to the fact that the elastic constants of 5CB are larger than those of MBBA. The surface-polarization values obtained from measurements of the flexoelectric effect, $p_s \sim 10^{-4}$ dyn$^{1/2}$, coincide with the values of $p_s$ measured by independent methods, viz., in a semiconductor + homotropic MBBA layer system[20] and in a Langmuir film + glass system.[21] The theoretical dependences of $\overline{\Delta n/E^2d^2}$ on $d$ shown in Fig. 4, calculated from Eq. (5), agree satisfactorily with the experimental data.

The value of $W$ for MBBA can be additionally estimated if one know the homotropic NLC layer critical thickness $d_c$ at which the spontaneous Freedericksz transition takes place. Under the conditions of our experiment $d_c$ is of the order of $10^{-2}$ cm, we find therefore from the formula $d_c = 2K_{33}/W$ (Ref. 8) that $W\sim10^{-4}$ erg/cm$^2$.

Our experiments show thus that the dispersion forces of crystalline substrates influence the course of volume electrooptic effects in NLC. In particular, they renormalize the Freedericksz-transition threshold. The binding energy of nematics with clean crystalline substrates, determined from measurements of the Freedericksz transition and from the flexoelectric effect, are in good agreement.

The authors thank A. V. Kaznacheev and E. I. Kats for helpful discussions.

[1] S. A. Pikin, Strukturnye prevrashcheniya v zhidkikh kristallakh (Structural Transitions in Liquid Crystals), Nauka, 1981.

[2] M. I. Barnik, L. M. Blinov, T. B. Korkishko, B. A. Umanskii, and V. G. Chigrinov, Zh. Eksp. Teor. Fiz. **85**, 176 (1983) [Sov. Phys. JETP **58**, 102 (1983)].

[3] A. S. Vasilevskaya, A. V. Kaznachev, and A. S. Sonin, Abstracts, 5th Conf. of Socialist Countries on Liquid Crystals, Odessa, 1983, Vo. I, part II, p. 64.

[4] E. I. Kats, Zh. Eksp. Teor. Fiz. **70**, 1394 (1976) [Sov. Phys. JETP **43**, 726 (1976)].

[5] A. A. Sonin, L. M. Blinov, S. G. Yudin, and N. N. Davydova, Ref. 3, p. 88.

[6] A. A. Sonin, T. V. Korkishko, V. G. Chigrinov, and L. M. Blinov, Ref. 3, p. 190.

[7] A. N. Chuvyrov, Kristllografiya **25**, 326 (1980) [Sov. Phys. Crystallography **25**, 188 (1980)].

[8] A. V. Kaznacheev and A. S. Sonin, Fiz. Tverd. Tela (Leningrad) **25**, 917 (1983) [Sov. Phys. Solid State **25**, 528 (1983)].

[9] A. A. Sonin and A. V. Kaznacheev, ibid. **26**, 807 (1984) [**26**, 486 (1984)].

[10] J. N. Israelachvili and D. Tabor, Proc. Roy. Soc. Lond. **A331**, 19 (1972).

[11] E. Dubois-Violette and P. G. de Gennes, J. Colloid. Inter. Sci. **57**, 403 (1976).

[12] L. M. Blinov, Elektro- i magnitooptika zhidkikh kristallov (Electro- and Magneto-Optics of Liquid Crystals), Nauka, 1978.

[13] A. Rapini and M. Papoular, J. Phys. (France) Coll. C4, 30 (1969).

[14] I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Usp. Fiz. Nauk **73**, 381 (1961) [Sov. Phys. Usp. **4**, 153 (1961).

[15] V. F. Chigrinov, Kristallografiya **27**, 404 (1982) [Sov. Phys. Crystallography **27**, 245 (1982)].

[16] P. R. Karat and N. V. Madhusudana, Mol. Cryst. Liquid Crystl. **36**, 51 (1976).

[17] A. Dershanski, A. G. Petrov, and M. D. Mitov, J. Phys. (France) **39**, 273 (1978).

[18] R. Chang. Mol. Cryst. Liquid Cryst. **30**, 155 (1975).

[19] J. Dozov, G. Durand, Ph. Marinot-Lagarde, and J. Penchev, Ref. 3, p. 10.

[20] A N. Lachinov and A. N. Chuvyrov, Ref. 3, p. 191.

[21] L. M. Blinov, Usp. khim. **52**, 1263 (1983).

Translated by J. G. Adashko