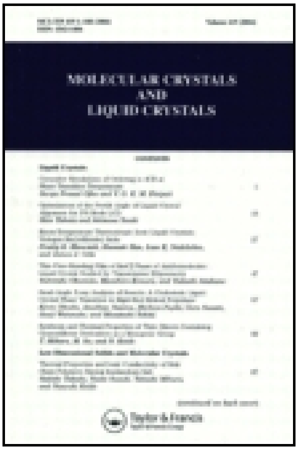


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Measures of the Molecular Tilt Angle and Optical Anisotropy n Ferroelectric Liquid Crystals

V. A. Baikalov [a] , L. A. Beresnev [a] & L. M. Blinov [b]
[a] Organic Intermediates & Dyes Institute, 117333, Moscow, Leninsky Prosp. 59
[b] Institute of Crystsllography of USSR Acad. Sci., 117333, Moscow, Leninsky Prosp. 59

Version of record first published: 17 Oct 2011.

To cite this article: V. A. Baikalov , L. A. Beresnev & L. M. Blinov (1985): Measures of the Molecular Tilt Angle and Optical Anisotropy n Ferroelectric Liquid Crystals, Molecular Crystals and Liquid Crystals, 127:1, 397-406

To link to this article: http://dx.doi.org/10.1080/00268948508080854

Mol. Cryst. Liq. Cryst., 1985, Vol. 127, pp. 397–406
0026-8941/85/1274–0397/$15.00/0

Printed in the United States of America

Measures of the Molecular Tilt Angle and Optical Anisotropy in Ferroelectric Liquid Crystals†

V. A. BAIKALOV, L. A. BERESNEV
Organic Intermediates & Dyes Institute.

and

L. M. BLINOV
*Institute of Crystallography of USSR Acad. Sci., 117333, Moscow,
Leninsky Prosp. 59.*

(*Received July 19, 1984*)

A pulse electro-optical technique is described which allows the molecular tilt angle and optical anisotropy of ferroelectric liquid crystals to be measured. The technique provides high accuracy and reproducibility of the measurement and is insensitive to the non-homogeneity of a liquid crystalline layer. The temperature behaviour of the tilt angle and the optical anisotropy is studied for two "classical" substances (DOBAMBC and HOBACLPC) and several ferroelectric mixtures.

INTRODUCTION

Ferroelectric liquid crystals have some serious advantages over nematic substances from the point of view of their application in fast electro-optical devices. The main peculiarities of ferroelectric liquid crystals are[1] lamellar (smectic) structures, the tilt of long molecular axes with respect to the normal of smectic planes and chirality of the molecules forming the liquid crystalline compound. The spontaneous polarization could also be induced in an achiral smectic C matrix using a chiral mesogenic or nonmesogenic impurity.[2]

---

†Paper presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

Of the paramount importance from both the fundamental and practical points of view is the molecular tilt angle θ, since the values of the polarization P_s depends directly upon it: this has been shown both theoretically and experimentally.[3,4] Therefore, measuring θ in tilted smectic phases, especially in ferroelectric (chiral) ones, and the investigation of its dependence on the molecular structure, temperature and the composition of mixtures is necessary for constructing new materials for electro-optical devices.

Published data on the tilt angles for smectic phases are rather scarce and, as a rule, refer to the well known smectic C phase of only a limited number of compounds. This is due mainly to the difficulties in the experimental technique for measuring θ. Methods used were optical conoscopy and X-ray diffraction,[5] suitable only for achiral (i.e., non-ferroelectric) smectics, the visual electro-optical technique[4,6] for measuring θ in liquid crystalline ferro-electrics, measurements of the guest-host effect for smectics C containing dyes as impurities,[7] and the ellipsometry technique, applied to freely suspended smectic C films consisting of only several molecular layers.[8]

TECHNIQUES

In this paper, a pulse electro-optical technique is proposed, which is based on some peculiarities of the linear electro-optical effect in chiral tilted smectics (fig. 1). Because of the spontaneous polarization the direction $\vec{n}$ is inclined by the angle θ to the left of the normal OZ if the electric field of a given polarity ($-\vec{E}$ in fig. 1) is applied to a sample. For the other polarity of the field ($+\vec{E}$ in fig. 1) the plane of the molecular tilt together with the director turns by 180° around the OZ-axis and the director is inclined by the angle θ to the right of the normal OZ. Therefore this sample is analogous to a uniaxial optical plate with two possible directions for its optical axis corresponding to different polarities of the external field. These directions are separated by an angle of 2θ and both lie in the plane perpendicular to the field, which coincides with the YZ-plane of cells for homogeneous initial molecular orientation.

To determine the two directions of the optical axis we used linearly polarized light of a He-Ne laser and a square-wave form external voltage applied across the cell electrodes. The values of the angle $\alpha_1 = +\theta$ and $\alpha_2 = -\theta$ are read out from a limb of the cell rotating around the OX axis. The two values correspond to those positions of the cell where the amplitudes of the response of a photomultiplier

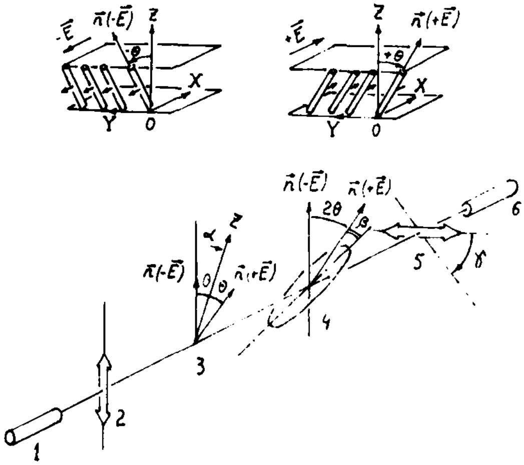


FIGURE 1 Top: switching the director $\vec{n}$ in a ferroelectric liquid caused by a change in polarity of an external field applied along the OX axis. Bottom: an experimental set-up for measuring the tilt angle θ and optical anisotropy. 1-He-Ne laser, 2-polarizer, 3-liquid crystal cell, 5-analyser, 6-photomultiplier.

detecting transmitted light pass through two minima for corresponding voltage polarities (crossed nicols). For these angles the light electric vector coincides with either direction $\vec{n}(-\vec{E})$ or $\vec{n}(+\vec{E})$.

The molecular tilt angle θ is considered to be equal to one half the angle between the two positions (fig. 2, $\alpha_1 = +\theta$ and $\alpha_2 = -\theta$). If the cell is fixed at the position $\alpha = \theta$ but an analyser is rotated, the angle $\gamma = 2\theta + \beta$ could be determined. This is the angle between those positions of the analyser where the response passes through an absolute minimum for both voltage polarities. Such positions of an analyser correspond to the directions of the principal axis of a polarization ellipse at the exit of a cell. Therefore, for a known cell thickness d the phase delay between the ordinary (refraction index n_0) and extraordinary (index n_e) beams can be determined using the expressions

$$\phi \approx 2\pi(n_e - n_0)d/\lambda \tag{1}$$

$$\mathrm{tg}\,2\beta = \mathrm{tg}\,4\theta \cdot \cos\phi \tag{2}$$

So, from (1) and (2) the optical anisotropy $\Delta n = n_e - n_0$ can be calculated for various wavelengths λ.

From a practical point of view, the values Δn and θ are of critical importance as they allow the optimum thickness to be calculated for

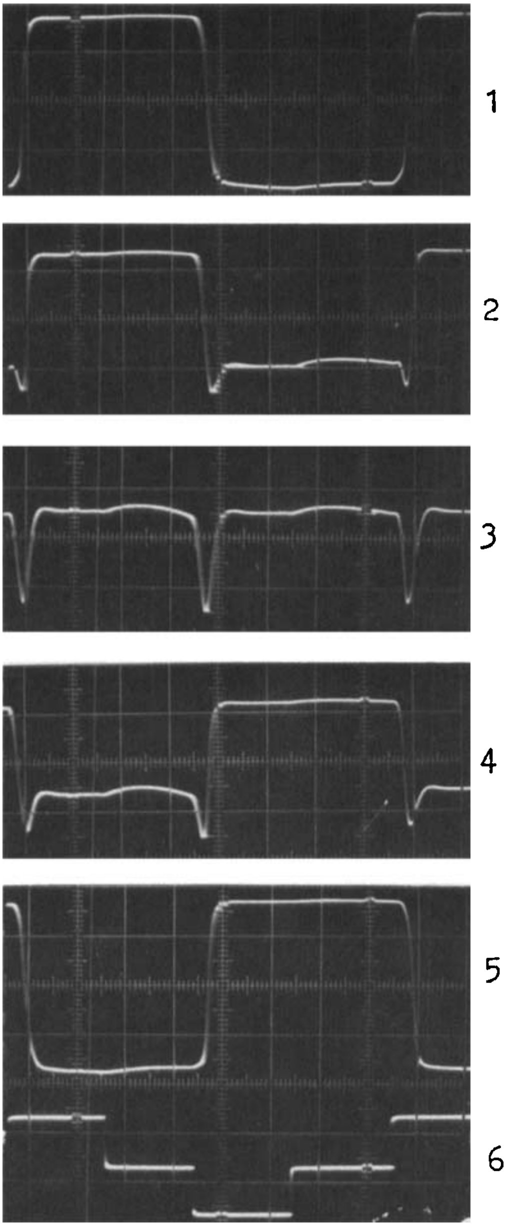


FIGURE 2 Oscillograms of the electrooptical response of a ferroelectric liquid crystals on square-wave pulses for various α at $\gamma = 0$: 1) $\alpha = +\theta$, 2) $0 < \alpha < \theta$, 3) $\alpha = 0$, 4) $-\theta < \alpha < 0$, 5) $\alpha = -\theta$); and for various γ at $\alpha = \theta$: 1) $\gamma = 0$, 2) $0 < \gamma < (2\theta + \beta/2)$, 3) $\gamma = (2\theta + \beta/2)$ 4) $(2\theta + \beta/2) < \gamma < 2\theta + \beta$ 5) $\gamma = 2(+ \beta)$; 6) oscillogram of square-wave pulses (X-axis: 1mS/div, Y-axis: 10V/div).

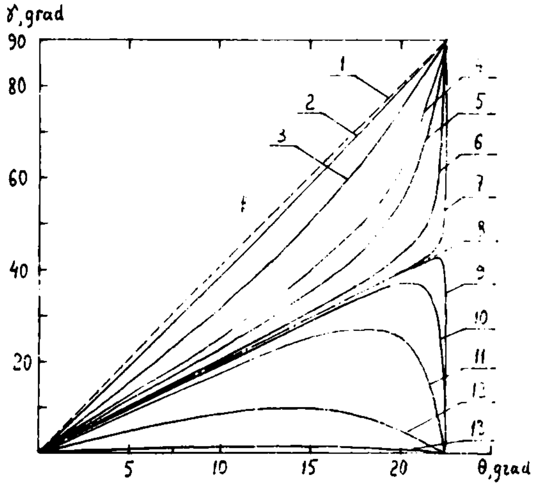


FIGURE 3 The calculated $\theta-\gamma$ diagram for various values of $\cos\phi$. 1) $\cos\phi=1$ ($\phi=180°$); 2) $-0.9(154.2°)$; 3) $-0,5(120°)$; 4) $-0.3(107.5°)$; 5) $-0.1(06.7°)$; 6) $-0.02(91.2°)$; 7 $-0.001(90,05°)$; 8) $0(90°)$; 9) $+0.001(89.9°)$; 10) $+0.02(88.9°)$; 11) $+0.1(84.3°)$; 12 $+\ 0.5(60°)$; 13) $+0.9(25.8°)$.

an electro-optical cell to be a "uniaxial plate" with a well defined phase delay. For example, to switch the light polarization plane between two directions perpendicular to each other we may choose a substance with the tilt angle $\theta=22,5°$ and the cell thickness according to the condition $d=\lambda(N+\frac{1}{2})/\Delta n$, $N=0,1,2\ldots$ ($\lambda/2$-plate). Fig. 2 shows typical oscillograms of the electro-optical response for the cell and analyzer rotated according to fig. 1.

For the sake of convenience, the calculated values γ as functions of θ are shown in Fig. 3, the phase delay ϕ being a parameter. Though the θ-values measured with this technique are independent of cell thickness the latter was determined on an empty cell using an interferometric method[9].

It should noted that the principal peculiarity of this technique, based on signal "minimization" by rotating a cell and analyzer, results in measured θ-values independent of the mosaic structure of a liquid crystalline layer with the planar molecular orientation.

RESULTS

Fig. 4 shows our reference data on $\theta(T)$ obtained with the well known

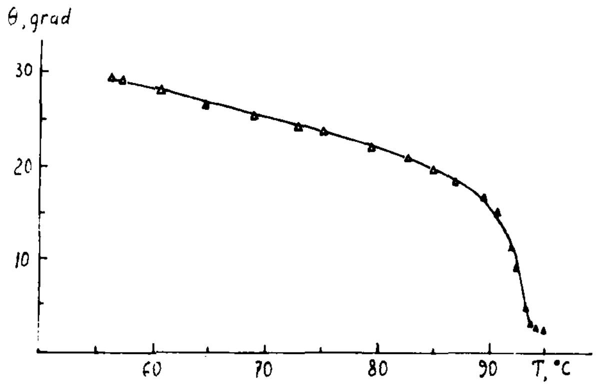
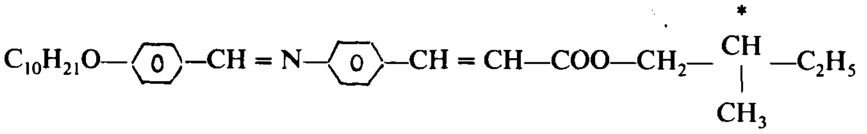


FIGURE 4 Temperature behaviour of the molecular tilt angle for DOBAMBC.

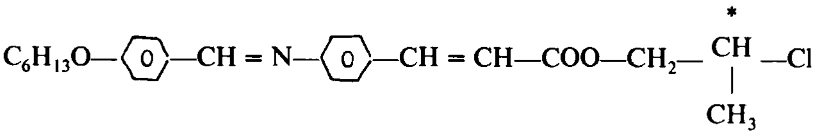
substance l-p-decyloxybenzylidene-p’-amino-2methyl-butyl cinnamate (DOBAMBC)



$$C_{10}H_{21}O-\langle O\rangle-CH=N-\langle O\rangle-CH=CH-COO-CH_2-\overset{*}{\underset{\displaystyle CH_3}{CH}}-C_2H_5$$

Our results well agree with previously obtained data (see, e.g., ref. 4).

The measurements of the θ(T) function for the other “classical” ferroelectric compound HOBACLPC (L-p-hexyloxybenzylidene-p′-amino-2-chloropropyl cinnamate)



$$C_6H_{13}O-\langle O\rangle-CH=N-\langle O\rangle-CH=CH-COO-CH_2-\overset{*}{\underset{\displaystyle CH_3}{CH}}-Cl$$

reveal some peculiarities. First, the absolute values of the tilt angle in the chiral smectic C (S_c^*) phase are rather high (18–20°) as compared with the previously published data.[6] Second, the technique allows the measurements of the θ-angles to be carried out not only in the S_c^* phase but in some more ordered tilted smectic phases[10] as well. At the phase transition point (66°C for HOBACLPC) there is no anomaly in the θ angle temperature behaviour despite the rather sharp increase in switching times measured as described in[11] and the anomaly in the pryro-electric response.[12] The switching times for the S_c^* phase of HOBACLPC agree with known data.[13]

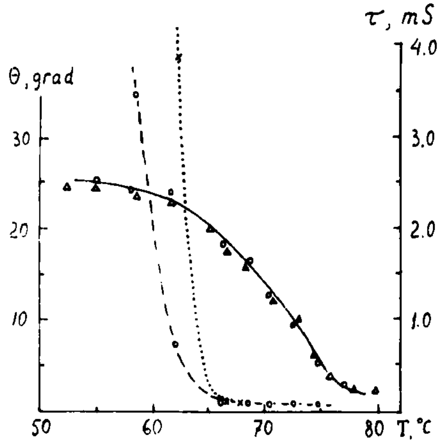


FIGURE 5 Temperature behaviour of the tilt angle θ and switching time τ for the director of HOBACLPC; cell thickness $d = 4.1$ μm pulse voltage 5V (×), 20V (○), 40V (△).

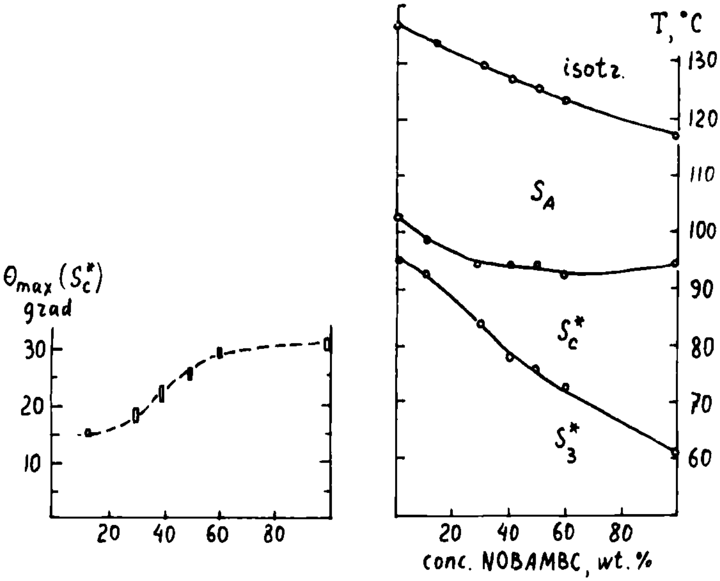
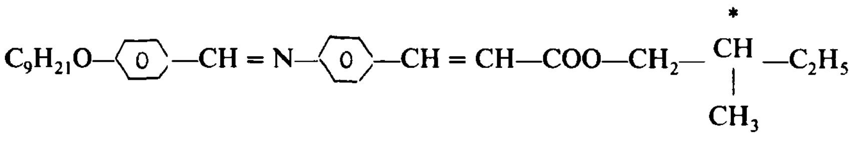
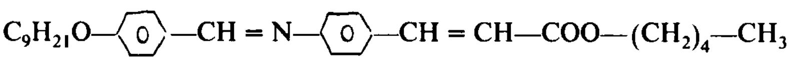


FIGURE 6 Phase diagram (below) and the corresponding dependence of maximum tilt angle in the S_c^* phase upon composition of NOBAPC-NOBAMBC mixtures.

To illustrate further our technique, in fig. 6 the maximum tilt angle in the S_c phase is shown as a function of composition for mixtures of a ferroelectric liquid crystal NOBAMBC (a homologue of DOBAMBC)

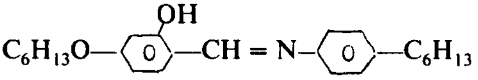


with its achiral isomer p-nonyloxybenzylidene-p′-aminopentyl cinnamate (NOBAPC)



The phase diagram of the mixtures (fig. 6) and the temperature behaviour θ(T) of pure NOBAMBC (fig. 7) are also shown. The rather strong concentration dependence of θ_{max} for these mixtures must be taken into account when one calculates the reduced value of the spontaneous polarization P_s/θ and discusses different models for dipolar ordering.[14]

Fig. 8 shows temperature dependencies for both the tilt angle $\theta(T)$ and optical anisotropy $\Delta n(T)$ for a mixture of an achiral p-hexyloxy-p'-hexyl-salicilydenaniline (HOHSA)



having the S_c phase with a chiral non-mesogenic substance

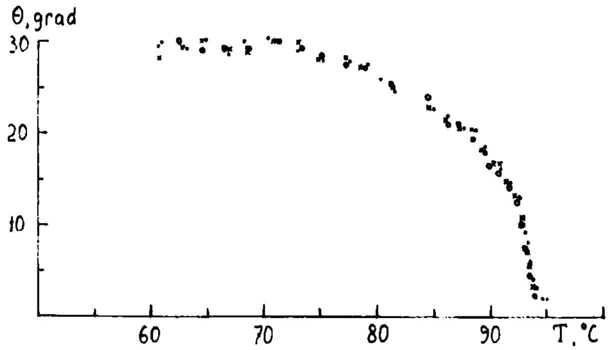


FIGURE 7 Temperature behaviour of the tilt angle θ(T) for NOBAMBC at various voltages (○-20V, ×-40V, ●-50V).

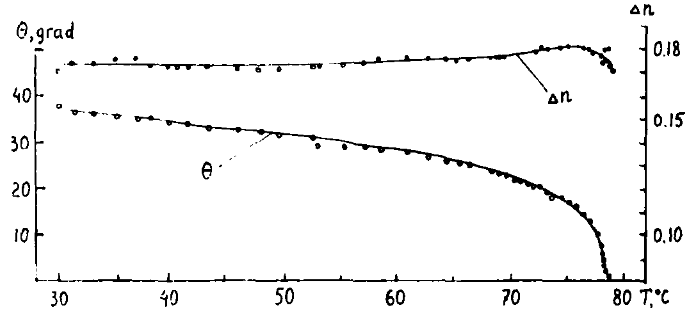
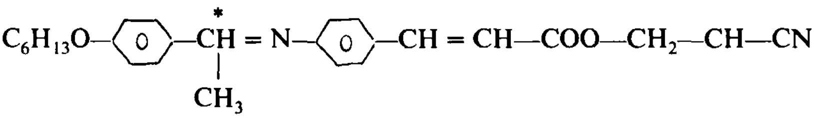


FIGURE 8 Tilt angle θ and optical anisotropy Δn as functions of temperature for a mixture of HOHSA and 5% of HOBACNP; cell thickness $d = 8.6\mu m$, voltage U = 50V.

HOBACPC (p-hexyloxybenzylidene-p'-amino-2-cyanopropyl cinnamate)



$$C_6H_{13}O\text{—}\langle O \rangle\text{—}\underset{\displaystyle CH_3}{\overset{*}{C}H} = N\text{—}\langle O \rangle\text{—}CH = CH\text{—}COO\text{—}CH_2\text{—}CH\text{—}CN$$

The temperature dependence $\Delta n(T)$ is rather weak and some decrease of Δn with decreasing temperature can be accounted for by a decrease in the anisotropy of molecular polarizability or the orientational order parameter (or both) due to the tendency of the molecules to have the zig-zag form at lower temperatures[5]. In this case the value of Δn is independent of the amplitude of the external square-wave field, while there is a marked influence of the field on the θ and γ values in ferroelectric liquid crystals with a high value of the spontaneous polarization.[15] The latter can be explained by an electro-clinic effect.[16]

In conclusion, a pulse electro-optical technique is described which allows the molecular tilt angle and optical anisotropy to be measured for ferroelectric liquid crystals. This technique is insensitive to the structure in homogeneities and provides accurate and reproducible measurements.

We are grateful to Drs. B. M. Bolotin, N. B. Etyngen, A. I. Pavluchenko and G. V. Purvanetskas for supplying the liquid crystals investigated and to Mrs. N. S. Ivanova for technical assistance.

References

1. R. B. Meyer, L. Leibert, L. Strzeleki, P. Keller, *J. Phys. (Paris) Lett.* **36**, L-69 (1975).

2. L. A. Beresnev, L. M. Blinov, L. M. Baikalov, E. P. Pozhidyev, G. V. Purvanetskas, A. I. Pavluchenko, *Mol. Cryst. Liq. Cryst.*
3. S. A. Pikin and V. L. Indenbom, *Uspekhi Fiz. Nank* **125**, 251 (1978).
4. B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov, N. I. Chernova, Pisma v ZhETF, **25**, 80 (1977) (*JETP Lett.* **25**, 70 (1977)).
5. R. Bartolino, J. Doucet, G. Durand, *Ann. Phys.* **3**, 389 (1978).
6. P. Martinot-Lagarde, *J. Phys. (Paris)* **37**, C3-129 (1976).
7. G. Pelzl, P. Kolbe, U. Preukschas, S. Diele, D. Demus, *Mol. Cryst. Liq. Cryst.* **53**, 167 (1979).
8. Ch. Rosenblatt, R. Pindak, N. A. Clark, R. B. Meyer, *Phys. Rev. Lett.* **42**, 1220 (1979).
9. L. M. Blinov, V. A. Kizel, V. G. Rumjantsev, V. V. Titov, *J. Phys. (Paris)* **36**, C1-69 (1975).
10. J. Doucet, P. Keller, L. M. Levelut, P. Porquet, *J. Phys. (Paris)* **39**, 48 (1978).
11. L. A. Beresnev, V. A. Baikalov, J. M. Blinov, *Zh. Tekhn. Fiz.* **52**, 2109 (1982).
12. L. A. Beresnev, L. M. Blinov, G. V. Purvanetskas, *Pis'ma v ZhETF* **31**, 37 (1980).
13. N. A. Clark, S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
14. L. A. Beresnev, E. P. Pozhidayev, L. M. Blinov, *5th Conf. of Soc. Countries on Liquid Crystals* Odessa, USSR, 1983. Abstract, v. 1, part 2, C13.
15. L. A. Beresnev, E. P. Pozhidayev, L. M. Blinov, A. L. Pavluchenko, N. B. Etyngen, *Pis'ma v ZhETF* **35**, 430 (1982).
16. S. Garoff and R. B. Meyer, *Phys. Rev. Lett.* **38**, 848 (1977); *Phys. Rev. A* **19**, 338 (1979).