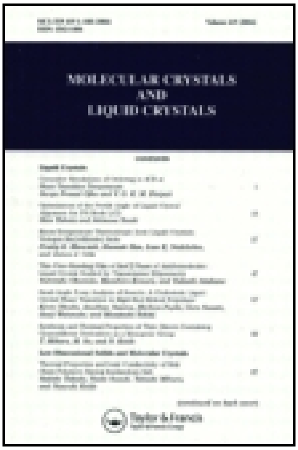

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Kerr-Effect in the Isotropic Liquid Phase of Nematogens[†]

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Kerr-Effect in the Isotropic Liquid Phase of Nematogens†

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The existence of strong fluctuations of the orientational order in the isotropic phase of nematics determines the nature of electro-optical effects near to T_c the temperature of the phase transition of the isotropic liquid into the liquid crystalline state. Electric birefringence in the isotropic phase of liquid crystals differing in the value and direction of the dipole moment of the molecules was investigated. The relaxation phenomena manifest using a radio frequency sinusoidal electric field in the isotropic phase of nematogens in the vicinity of T_c are discussed. Two ranges of dispersion of the Kerr effect were detected experimentally: a low frequency range ($f = 10^5$ to 10^6 Hz) and a high frequency range (for $f > 10^6$ Hz). The first range has been related to supermolecular relaxation processes and characterizes the rotational mobility of the fluctuation 'swarm' (i.e., the nucleus of the mesophase) in the isotropic phase. The second range was due to the relaxation of the dipole orientation of the molecule forming the dielectrically anisotropic 'swarm'. It was established that the high frequency dependence of the Kerr constant corresponds to the type of dispersion of the dielectric anisotropy of the same substances in the liquid-crystalline state. This dependence has been related to the exclusion of the molecular dipole mechanism of rotation of the polar molecules about the short transverse axis from the polarization of the liquid.

INTRODUCTION

The existence of distinct fluctuations of the orientational order in the isotropic phase of liquid crystals is of considerable importance in the equilibrium[1–3] and relaxation[4–9] properties of mesogenic liquids near to T_c the temperature of their transition into the liquid crystalline state. Electric birefringence (Kerr effect) is the most effective method

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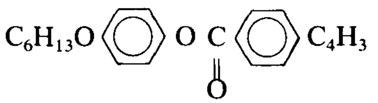
for the study of relaxation phenomena in the vicinity of T_c. Many recently published papers deal with the investigation of free relaxation of the Kerr effect induced by a pulsed laser field.[4,5,9] Under these conditions the orientational mechanism related to the existence of permanent dipole moments of the molecules does not provide any contribution to the Kerr effect because a high-frequency laser field (optical frequencies) is used as the orientational factor. The purpose of the present paper is to study the relaxation phenomena in a radio-frequency sinusoidal electric field when the dipole-orientational mechanisms may be of considerable importance in the relaxation processes.

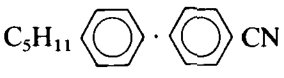
We investigated two nematic liquid crystals for which the directions of the permanent dipole moment μ forming an angle β with the long axis of the molecule differ greatly.[7,10]

N 21



Cr 29°C N 49°C I
$\mu = 2.3$ D; $\beta = 59°$

5 CB



Cr 24°C N35°C I
$\mu = 5$D; $\beta = 0°$

In accordance with the molecular structure and the β values these two liquids are characterized by a macroscopic dielectric anisotropy $\Delta\epsilon$ that differs in sign: it is negative for N 21 and positive for 5 CB. In the isotropic-liquid state N 21 is also characterized by a negative electric birefringence, whereas for 5 CB the Kerr effect is positive in sign.

EXPERIMENTAL

The previously described method of electric birefringence measurements[11,12] was used. A He-Ne laser, at the wavelength λ of 632.8 nm, was used as the light source. The measurements were carried out under applied A.C. fields at a frequency f of between 2.10^5 and 2.10^7 Hz and for field strengths E of up to 3.10^3 V.cm^{-1}. The sample temperature was maintained to within ±0.1°C. In order to exclude the possibility of heating the substance with the high-frequency electric field pulses of sinusoidal voltage, at a frequency of 10 pulses per second with duration of 2 ms, were used.

Under the influence of the sinusoidal electric field, $E = E_0 \cos 2\pi ft$ a birefringence, Δn, appears in the Kerr cell such that,

$$\Delta n = \frac{1}{2}\left[\overline{\Delta n} + \widetilde{\Delta n} \cdot \cos(4\pi ft - \delta)\right] \qquad (1)$$

where the constant component $\overline{\Delta n}$ and the amplitude of the variable component $\widetilde{\Delta n}$ of induced anisotropy may depend on the frequency f in the range of dispersion of the Kerr effect. The light flux, Φ proportional to Δn^2 was transformed into the electric signal with the aid of the photomultiplier, i.e.,

$$\Phi \sim \Delta n^2 = \overline{\Delta n^2} + \frac{1}{2}\widetilde{\Delta n}^2 + 2\overline{\Delta n} \cdot \widetilde{\Delta n} \cos(4\pi ft - \delta) + \frac{\widetilde{\Delta n}^2}{2} \cos(8\pi ft - 2\delta) \qquad (2)$$

In Eq. (2) the component independent of time t is determined from the first two terms. The change in this component of the light flux Φ_f measured at various electric field frequencies f permits the experimental study of the frequency dependence of the total value of $\overline{\Delta n^2} + 1/2\widetilde{\Delta n}^2$.

RESULTS AND DISCUSSION

The Kerr effect was also measured by the method of birefringence compensation using a rotational elliptical compensator.[12] Since for this method only the constant anisotropy component, $\overline{\Delta n}$ is compensated, in this case, in the study of the frequency dependence of birefringence, the dispersion of $\overline{\Delta n}$ is fixed. Hence, the use of two methods for the measurement of dispersion of the Kerr effect makes it possible to separate the frequency dependent Φ_f into two parts. The first is related to the dispersion of the constant component of electric birefringence $\overline{\Delta n}$ and the second depends on the dispersion of the amplitude of the variable component $\widetilde{\Delta n}$. The dependence of Φ_f/Φ_0 (where $\Phi_0 \equiv \Phi_{f\to 0}$) on frequency f was determined for N 21 and 5 CB in the temperature range $\Delta T = T - T_c = (0 - 5)$°C. Figure 1 shows the results obtained at $\Delta T = 0.3$°C. In the frequency range investigated the two following dispersion ranges were characteristic of both substances: the first range was for frequencies of 10^4

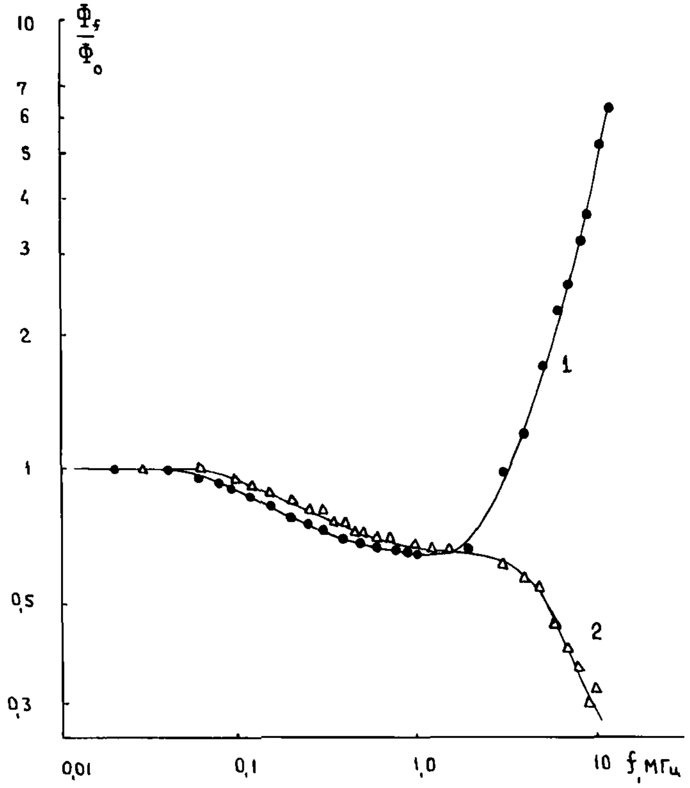


FIGURE 1. Relative change in the light flux Φ_f/Φ_0 versus field frequency f at $\Delta T = T - T_c = 0.3°C$ for 1) N 21 and 2) 5 CB.

to 10^6 Hz and the second range above 3.10^6 Hz. The experimental data show that regardless of the sign of the electric birefringence the low frequency dispersion leads to a decrease in the absolute value of the measured effect. In contrast, for the high frequency range the dispersion types for these substances differed greatly. For N 21, at frequencies exceeding 3.10^6 Hz, the effect increased sharply but remained negative in sign. For 5 CB, in the same frequency range, a decrease in the positive electric birefringence was observed. Figures 2 (curve 5) and 3 (curve 4) show the results of an independent measurement of $(\Delta n)_f/(\Delta n)_0$ for N 21 and 5 CB using the compensation method. In the frequency range up to 10^6 Hz, the electric birefringence remains constant for both substances and a dispersion was observed only if $f > 3\ 10^6$ Hz, which corresponds to the high-frequency dispersion range in Figure 1. Hence, it is possible to assume that the high-frequency dependence of the observed effect is due to the dispersion in $\overline{\Delta n}$, whereas the low-frequency dependence results from the dispersion in $\tilde{\Delta n}$.

The existence of strong fluctuations of the orientational order in the isotropic phase of nematics determines the nature of electro-optical effects in the pretransitional temperature region for the isotropic liquid to the liquid-crystalline phase transition.[1-3] Electric birefringence near to T_c depends on the orientation of dielectrically anisotropic fluctuations ('swarms') in the electric field. Hence, in terms of molecular theory the low frequency dispersion range may be interpreted as the relaxation of orientation of these 'swarms' of locally on average colinearly oriented molecules.

The size of 'swarms' varies greatly with increasing temperature and this is reflected in the marked temperature dependence of low frequency dispersion range of the electric birefringence (Figure 2, curves 1–4, and Figure 3, curves 1–3).

In the framework of these concepts the low-frequency dispersion of Δn may be described using the Peterlin-Stuart equation[13] for the dispersion of the Kerr effect in an assembly of non interacting dielectrically anisotropic particles having no permanent dipole moments, i.e.

$$\Delta n(t) = (\Delta n)_f \left[1 + \frac{\cos(4\pi f t - \delta)}{\sqrt{1 + 4\pi^2 f^2 \tau_1^2}}\right] \tag{3}$$

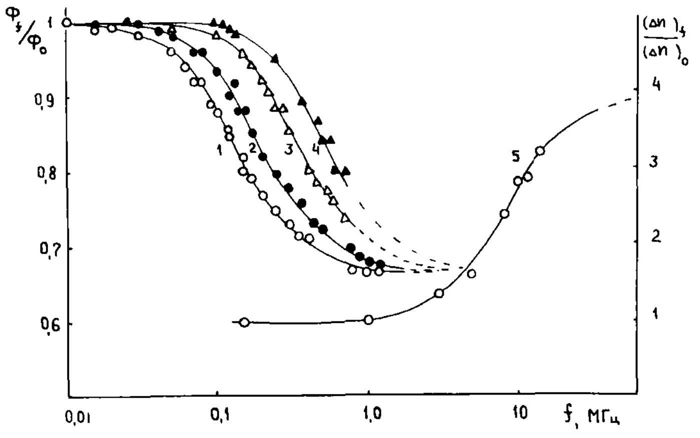


FIGURE 2. Relative change in the light flux Φ_f/Φ_0 at $\Delta T = 0.2°C$ (1), 0.7°C (2), 2.0°C (3), 3.2°C (4), and in electric birefringence $(\Delta n)_f/(\Delta n)_0$ at $\Delta T = 0.2°C$ (5), as a function of field frequency f for N 21. Solid lines are theoretical curves 1–4 according to Eq. (5) and curve 5 according to Eq. (6).

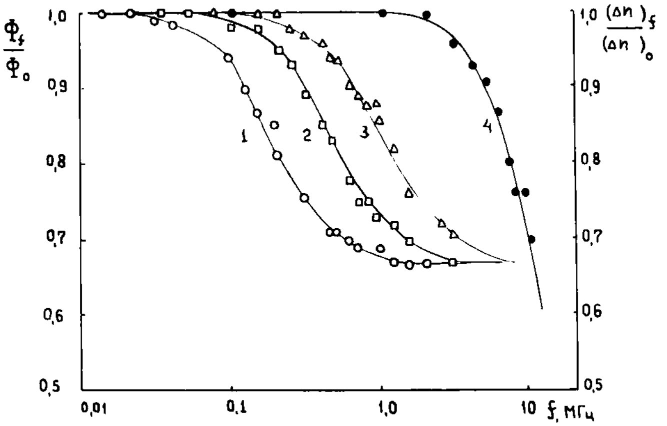


FIGURE 3. Relative change in the light flux Φ_f/Φ_0 at $\Delta T = 0.3°C$ (1), 2.3°C (2), 4.4°C (3), and in electric birefringence $(\Delta n)_f\,(\Delta n)_0$ at $\Delta T = 0.5°C$ (4) as a function of field frequency f for 5 CB. Solid lines are theoretical curves 1–3 according to Eq. 5 and curve 4 according to Eq. 6.

where τ_1 is the relaxation time of a dielectrically anisotropic particle in the sinusoidal electric field. This τ_1 is two times longer than the free orientational relaxation time of the particles after the field is switched off. Eq. (3) may also be obtained[14] by using the concepts of the relaxation of the order parameter Q induced in the isotropic phase by a sinusoidal electric field.[15]

Applying Eq. (3) the expression for the light flux Φ may be written as follows:

$$\Phi(t) \sim \left\{(\Delta n)_f \cdot \left[1 + \frac{\cos(4\pi f t - \delta)}{\sqrt{1 + 4\pi^2 f^2 \tau_1^2}}\right]\right\}^2 \qquad (4)$$

The constant component Φ_f, at a frequency f, is determined from the equation

$$\frac{\Phi_f}{\Phi_0} = \frac{2}{3}\left[\frac{(\Delta n)_f}{(\Delta n)_0}\right]^2 \cdot \left(1 + \frac{1}{2}\,\frac{1}{1 + 4\pi^2 f^2 \tau_1^2}\right) \qquad (5)$$

Eq. (5) may be used for the quantitative description of the experimental data plotted in Figures 2 and 3.

The experimental points corresponding to the low frequency dispersion of the electric birefringence are given approximately by Eq. 5, i.e., Figures 2 (curves 1–4) and 3 (curves 1–3). This fact permitted the determination of the relaxation times τ_1 at various temperatures.

The values of τ_1 obtained for N 21 and 5 CB are plotted in Figure 4 as a function of temperature. It should be noted that the values of τ_1 found for 5 CB agree in the order of magnitude with the literature data[9] for this liquid crystal obtained in the investigation of the free relaxation by using a pulsed laser field.

As has been repeatedly shown[2,7,8,16] the value of $(\Delta n)_f$ contained in Eq. (3) is directly determined by the dielectric anisotropy, $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ of the nematic sample. It is well known that the relaxation of the longitudinal component of the dielectric permittivity $\epsilon_{\parallel}$, resulting from the exclusion of the rotation mechanism of polar molecules about the short transverse axis from the dipole polarization of the liquid crystal, leads to a drastic increase in the negative dielectric anisotropy ($\epsilon_{\perp} > \epsilon_{\parallel}$) of N 21.[8] The same molecular relaxation mechanism is responsible for the decrease in the positive ($\epsilon_{\parallel} > \epsilon_{\perp}$) dielectric anisotropy of 5 CB.[10] The experimental data shown in Figures 1–3 suggest that the frequency dependence of $(\Delta n)_f$ in the range of $f > 10^6$ Hz is consistent with the radio-frequency character of changes in $\Delta\epsilon$ for the substances investigated.

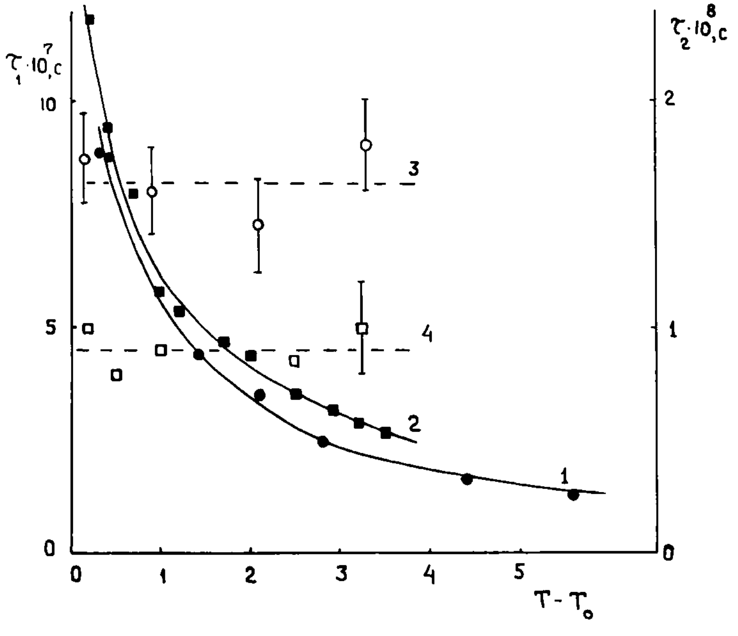


FIGURE 4. Relaxation times τ_1 for (1) 5 CB (2) N 21 and τ_2 for (3) N 21 and (4) 5 CB as a function of temperature where $\Delta T = T - T_c$.

This is directly demonstrated by experimental data in Figure 5. This figure shows the results of investigations of the frequency dependence of dielectric anisotropy $\Delta\epsilon$ (Figure 5a) of the substances discussed in this paper and of several other liquid crystals.[17–19] The results of the high-frequency dependence of Kerr constants $K = \Delta n/E^2$ (E is the electric field strength) at a temperature $T - T_c < 1°C$ studied by the authors previously and in the present work for the same substances are shown in Figure 5b.

Comparison of Figures 5a and 5b shows that for each substance the type of the radio-frequency dependence of the Kerr constant K in the isotropic phase is very similar to the curve of dispersion of dielectric anisotropy $\Delta\epsilon$ for the same substance in the nematic phase. The resemblance between the dispersion curves for $\Delta\epsilon$ and those for K (or Δn) is not restricted to their general shape but also includes the agreement of the changes in the signs of $\Delta\epsilon$ and K with changing frequency. This fact indicates the coincidence of molecular mechanisms responsible for the dispersion of dielectric anisotropy of the mesophase and the high frequency dispersion of the Kerr effect in the isotropic phase. In both phenomena this mechanism is the relaxation of the dipole orientation related to the rotation of the molecule about its transverse axis. It is known that in the mesophase one relaxation time τ_ε corresponds to this relaxation process. Hence, the frequency dependence of $(\Delta n)_f$ (or K), just as for the case of dispersion of dielectric anisotropy of the mesophase discussed here, may be described by the Debye equation

$$(\Delta n)_f = (\Delta n)_{f=\infty} + \frac{(\Delta n)_0 - (\Delta n)_{f=\infty}}{1 + 4\pi^2 f^2 \tau_2^2} \tag{6}$$

The quantitative agreement between the experimental frequency dependences of $(\Delta n)_f$ and the theoretical curve 6 (Figures 2 and 3) makes it possible to determine the times of high-frequency dispersion of the Kerr effect: $\tau_2 = (0.9 \pm 0.2) \times 10^{-8}$ s for 5 CB and $\tau_2 = (1.6 \pm 0.2) \times 10^{-8}$ s for N 21. Within experimental error in the determination of τ_2 the temperature dependence of τ_2 is not observed in the temperature range investigated (Figure 4). The comparison of the frequency dependences of $\Delta\epsilon$ and K (Figure 5) for all the samples discussed here shows that all these dependencies may be represented by Debye curves (Eq. 6) and the relaxation time τ_ε exceeds several times the relaxation time τ_2 for the same substance. This result appears to be quite reasonable because the degree of orientational order in the isotropic phase near to T_c is much lower[16] and, correspondingly,

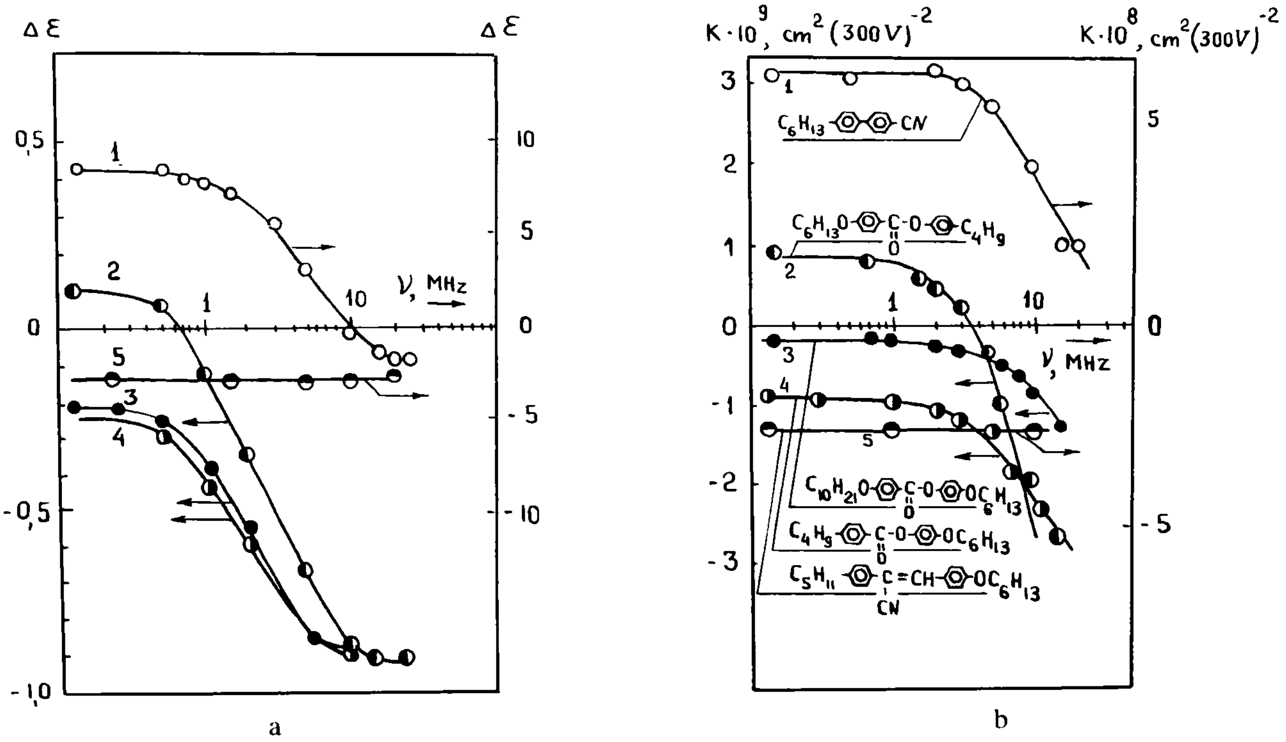


FIGURE 5. Frequency dependence of a) dielectric anisotropy Δε at temperatures T − T_c = −3°C for several nematics, and b) Kerr constant *K* in the isotropic phase for the same substances at the temperature T − T_c < 1°C.

the rotational mobility of dipolar molecules is higher than in the nematic phase.

Hence, this method of studying the Kerr effect made it possible to detect and investigate in a single experiment two dispersion ranges of electric birefringence in the isotropic phase of liquid crystals near to T_c. The first range (10^4 – 10^6 Hz) is related to supermolecular relaxation processes and characterises the rotational mobility of the 'swarm' as a whole, within the Peterlin-Stuart framework, in the isotropic phase. The second range ($f > 10^6$ Hz) is actually the dispersion range of the dielectric anisotropy of the 'swarm' as a fluctuation nucleus of the nematic order in the isotropic phase of the nematogen. The finite time τ_2 of the establishment of the dielectric anisotropy of the 'swarm' is not caused by the rotational motion of the 'swarm' as a whole but is due to the relaxation of the dipole orientation of the molecules forming the 'swarm.'

References

1. V. N. Tsvetkov, *Zhurn. Eksp. Teor. Fiz.*, **14**, 35 (1944).
2. V. N. Tsvetkov and E. I. Rjumtsev, *Dokl. Akad. Nauk SSSR*, **175**, 382 (1967).
3. E. I. Rjumtsev and V. N. Tsvetkov, *Optika i spektroskopiya*, **26**, 607 (1969).
4. G. K. L. Wong and Y. R. Shen, *Phys. Rev. Lett.*, **30**, 895 (1973).
5. J. Prost and J. R. Lalanne, *Phys. Rev.*, **A8**, 2090 (1973).
6. M. Shadt, *J. Chem. Phys.*, **67**, 210 (1977).
7. E. I. Rjumtsev, T. A. Rotinian and V. N. Tsvetkov, *Dokl. Akad. Nauk SSSR*, **254**, 854 (1980).
8. E. I. Rjumtsev, T. A. Rotinian, A. P. Kovshik, S. A. Onishchuk and V. N. Tsvetkov, *Dokl. Akad. Nauk SSSR*, **260**, 77 (1981).
9. H. J. Coles, *Mol. Cryst. Liq. Cryst.* (*Lett*)., **49**, 67 (1978).
10. P. G. Cummins, D. A. Dunmur and D. A. Laidler, *Mol. Cryst. Liq. Cryst.*, **30**, 109 (1975).
11. S. N. Penkov, *Optika i spektroskopiya*, **10**, 787 (1961).
12. V. N. Tsvetkov, I. P. Kolomietz, A. V. Lezov and A. S. Stepchenkov, *Vysokomol. Soedin.*, **A25**, 1327 (1983).
13. A. Peterlin and H. Stuart, *Hand. u Jahrbuch d. Chem. Phys.*, **B8**, 26 (1943).
14. E. I. Rjumtsev, M. A. Agafonov, T. A. Rotinian and V. N. Tsvetkov, *Dokl. Akad. Nauk SSSR* **279**, 1367 (1984).
15. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971).
16. V. N. Tsvetkov, E. I. Rjumtsev, A. P. Kovchik, G. I. Denis and Yu. Yu. Daugvila, *Dokl. Akad. Nauk. SSSR*, **216**, 1105 (1974).
17. H. Kresse, A. Weigeteben and D. Demus, *Krist und Tech.*, **15**, 341 (1980).
18. I. P. Juk and L. E. Golovitcher, *Isvest. Akad. Nauk SSSR, Ser. Phys. Energet.*, **2**, 90 (1978).
19. V. N. Tsvetkov, A. P. Kovshik, E. I. Rjumtsev, I. P. Kolomiets, M. A. Makarjev and Yu. Yu. Daugvila, *Dokl. Akad. Nauk SSSR*, **222**, 1399 (1975).