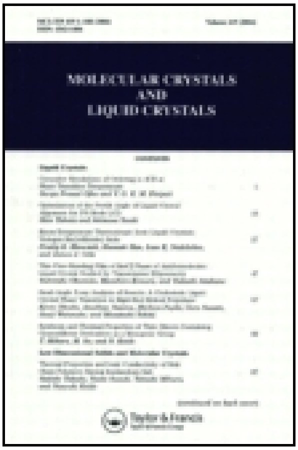

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Electro Optical Properties of Twisted Liquid Crystalline Structures Doped with Dichroic Dyes†

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When a voltage is applied to a twisted nematic cell ($\Delta\epsilon > 0$) containing a positive dichroic dye, and the cell is illuminated by light with its polarisation plane perpendicular to the director of the front electrode, a decrease in light transmission is observed (i.e. positive contrast).

In this paper we investigate the influence of different liquid crystal twist cell parameters such as the twist angle ϕ_t, the azimuthal angle γ between the polarization plane of the incident light and the director at the front substrate, the $\Delta nd/\lambda$ value, the dye order parameter S and the temperature τ on the transmission—voltage characteristics and the value of the positive contrast. The maximum positive contrast is found to correspond to γ and ϕ_t values close to $\pi/2$, maximum dye order parameter, minimum temperature, and finally, $\Delta nd/\lambda = 2.1 \pm 0.1$.

INTRODUCTION

Several different positive contrast colour liquid crystal "guest-host" displays making are known[1] using both positive and negative dichroic dyes. In the first case the positive image is obtained when using cells with an initial homeotropic LC orientation and a negative dielectric anisotropy (i.e. $\Delta\epsilon < 0$). In the field on state the LC configuration is then nematic or cholesteric.[1,2] Use of negative dichroic dyes give a positive image in the "guest-host" effect, only if the initial director orientation is either planar or twisted and $\Delta\epsilon > 0$.[1,3]

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We have recently reported a further possibility of achieving positive contrast in a "twist-cell" (T-cell), using both a positive dichroic dye and a positive LC (i.e. $\Delta\epsilon > 0$) if the incident light is polarized perpendicularly to the director at the front electrode.[4,5] After applying the voltage to the electrode the light transmission of such a cell firstly goes to a minimum value, then increases with increasing voltage achieving a maximum value for homeotropic LC director orientation, Figure 1. The effect takes place due to the violation of the Mauguin conditions in the process of the reorientation of the director induced by an electric field. One may therefore expect, for such a cell, that its electro optical characteristics will depend on those of a twisted cell without dyes,[4,5] as well as the degree of orientation of the dyes in the liquid crystal host.

This paper investigates the influence of different liquid crystal twist cell and dye parameters (the value of $M = \Delta nd/\lambda$, where $\Delta n = n_{\|} - n_{\perp}$ is the LC birefringence in zero field, d-cell thickness, λ-light wavelength; the cell twist angle ϕ_t; azimuthal angle γ between the polarization plane of the incident light and the director on the front substrate; the dye order parameter and the temperature τ) on the value of the positive contrast and the transmission-voltage characteristics of the "guest-host" effect in a "T-cell" using one polariser.

EXPERIMENTAL

We used in our experiment the liquid crystal ZLI-1646, produced by Merck Corp. Its optical, dielectric and elastic constants are well known at 27°C i.e. $n_{\|}$ (589 nm) = 1.55, $n_{\perp}$ = 1.478, $\epsilon_{\|}$ = 10.6, $\epsilon_{\perp}$ = 4.5, $K_{\|} = 0.77 \cdot 10^{-6}$ $K_{33} = 1.22 \cdot 10^{-6}$, $K_{22} = 0.4 \cdot 10^{-6}$ CGSE units.[6]

To avoid the areas of reverse twist in the T-cell the LC was doped with 0.1 % wt/wt of cholesteryl nonanoate. We also used as a dichroic dye KD-4, the anthraquinone derivative, having $S = 0.68$ at λ_{max} = 600 nm in ZLI-1646. The surface orientation was obtained using polyvinyl alcohol films, coated on the electrodes and rubbed in one direction.

The transmission-voltage characteristics were investigated in a wedge-shaped T-cell for various LC layer thicknesses d. The cell possessed a spacing, slightly different from the wedge-shape due to nonuniform deformations of the glass substrates. To find the real distribution of the d values, we filled the T-cell with a pure LC and placed it between two parallel polaroids. When scanning by the laser beam with λ = 0.63 μm over the wedge thickness, the transmission intensity oscil-

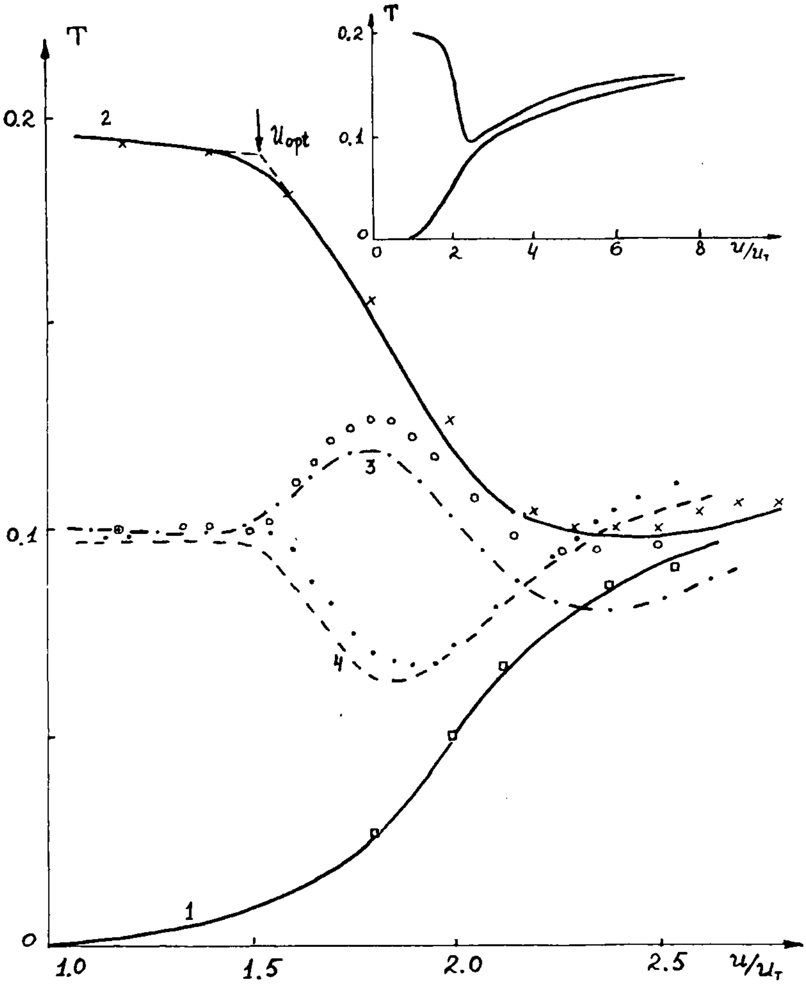

FIGURE 1 Normalised transmission-voltage characteristics of the T-cell with a dichroic dye (solid lines-theoretical calculations, symbols x, □, ○, ●—experimental data, and $d = 32.2\ \mu m$); curves 1 and 2 correspond to the light polarized parallel ($\alpha = 0°$) and perpendicular ($\alpha = 90°$) to the front surface cell director and 3, 4 to $\alpha = \mp 45°$ respectively. The insertion shows the same transmission-voltage characteristics on an expanded voltage scale, U_T—is the twist deformation threshold.

lations were recorded and the intensity minima are related to the thicknesses as follows:[7]

$$\sqrt{1 + u^2} = 2, 4, 6, \ldots 2k, \qquad \text{where } u = \frac{2\Delta nd}{\lambda}$$

Here we had to fix an approximate thickness at least at one wedge point, for instance, in the vicinity of the spacer. We also changed the value of M, taking various LC birefringence differences Δn. Since we could vary Δn only by temperature changes or by taking another LC we were unable to provide fixed values of the elastic and dielectric LC parameters in our experiment. In view of this, we carried out a computer simulation of the problem, using the method of Montgomery,[8] extended to the case of the complex refractive LC indices $n_{\parallel,\perp} = n'_{\parallel,\perp} + in''_{\parallel,\perp}$, thus taking into account the dye absorption of the light. The values of $n'_{\parallel,\perp}$ were calculated in the following way:[4]

$$n''_{\parallel,\perp} = \frac{\lambda\, D_{\parallel,\perp}\, ln\ 10}{4\pi d} \cong 2.3\,\frac{\lambda_m c e_{\parallel,\perp}}{4\pi}$$

where $D_{\parallel,\perp} = -lg\, I_{\parallel,\perp}/T_o$ is the optical density of the homogeneously oriented LC with the dye for the light polarization parallel (||) and perpendicular ($\perp$) to the director, λ_m—wavelength of the maximum dye absorption, $e_{\parallel,\perp}$— the corresponding extinction coefficients of the dye, c—molar concentration of the dye in the LC. In this way, we can see, that $n''_{\parallel,\perp}$ depends on λ_m, c and the order parameter of the dye in the LC. In our calculations we use $n''_{\parallel} = 0.0107$, $n''_{\perp} = 0.0014$, ref 5.

The computer method also allowed us to calculate the director distribution within the layer and, therefore, the dye-doped T-cell transmission—applied voltage characteristics. To verify the program we carried out a comparison between the calculated and experimental curves. Figure 1 shows the transmission-voltage characteristics using one polariser of the twist cell plus dye. One can see, that the calculated and experimental curves are in good agreement over the whole range of the reduced voltages U/U_T(U_T—is the threshold voltage of the LC twist-cell deformation).

The influence of the twist angle on the transmission-voltage characteristic was studied in the 15 μm cell by means of one glass cell substrate rotating with respect to the other.

RESULTS AND DISCUSSION

Figure 1 shows the transmission-voltage characteristics of the "guest-host" effect for different azimuthal angles α between the polarization vector of the incident light and front substrate. The angle α is considered to be positive, if it coincides with the rotation direction of the helix. Figure 1 illustrates the characteristic changes in the transmission-voltage curves with the variation of α between 0° and 90°. The angle α = 0°, as expected, corresponds to increasing negative contrast of the T-cell with increasing applied voltage. If α = +45° or 90°, then the transmission decreases, passes through a minimum (positive contrast) and then increases to a clear state again. The voltage, corresponding to the sharp decreasing of the transmission in this curve we regard as an "optical threshold" voltage (U_{opt}). When applying this voltage, the Mauguin light propagation condition is critically violated. We have found that the positive contrast achieves its maximum for α = +90°. For instance, if α = 45°, the contrast $K_T = T_0/T_{min} = 1.53$, while for α = +90°, $K_T = 2.01$ (T_o is the zero field cell transmission, T_{min} is the minimum cell transmission). If α = −45° the positive contrast is not observed, Figure 1.

Figure 2 shows the T-cell transmission—characteristics voltage for different LC-layer thicknesses *d*. As it can be seen, the larger values of *d* shift the transmission minimum and "the optical threshold" to higher voltages. It is noteworthy that positive contrast can not be observed in thin T-cells (for instance, if *d* ~ 4μm). A possible explanation of this phenomenon will be given below.

We should point out, that the increase of the parameter M, on account of the thickness *d*, is accompanied by the simultaneous in-

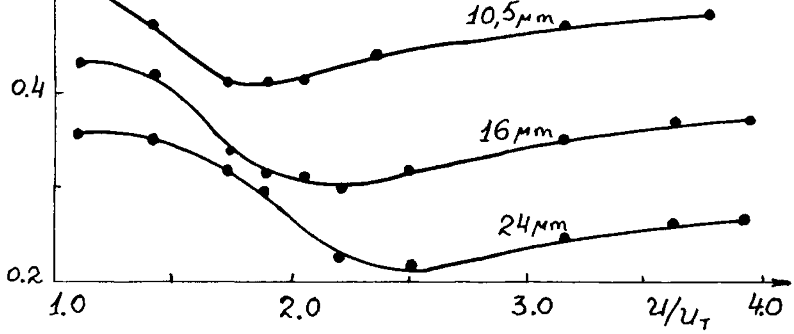

FIGURE 2 Normalised transmission-voltage characteristics of the T-cell with a dichroic dye, measured for different LC layer thicknesses *d*.

crease of the layer optical density, thus complicating the voltage-transmission characteristic analysis. This complication is avoided, if one defines the contrast, as the ratio of the optical densities $K_D = D_{max}/D_o$, where D_o is the optical density in zero field, D_{max} is the maximum optical density in the field on state. Figure 3 shows the dependence of the contrast K_D upon the layer thickness d. K_D is seen to have its maximum value for $d = 17 \pm 1 \mu m$, thus leading to the value of $M = 2.1 \pm 0.1$.

The influence of the LC zero field birefringence Δn on the shape of the transmission-voltage curves is illustrated in Figure 4. The larger Δn values correspond to the larger "optical thresholds" U_{opt}, and the transmission minimum is achieved for higher voltages. The contrast K_D dependence on Δn takes the form of a curve with a maximum near $\Delta n \sim 0.042$, so that M is equal to 2.14, i.e. practically the same as for the previous case, Figure 3. In view of this, applying both M variation methods we come to the conclusion, that there is an optimum value of $M = 2.1 \pm 0.1$, giving the maximum positive contrast. This feature distinguishes the given effect from the twist-effect in the cells without dyes, when the contrast has local maxima for the discrete set of M values $M = \sqrt{3}/2, \sqrt{15}/2, \sqrt{35}/2$ etc.[7]

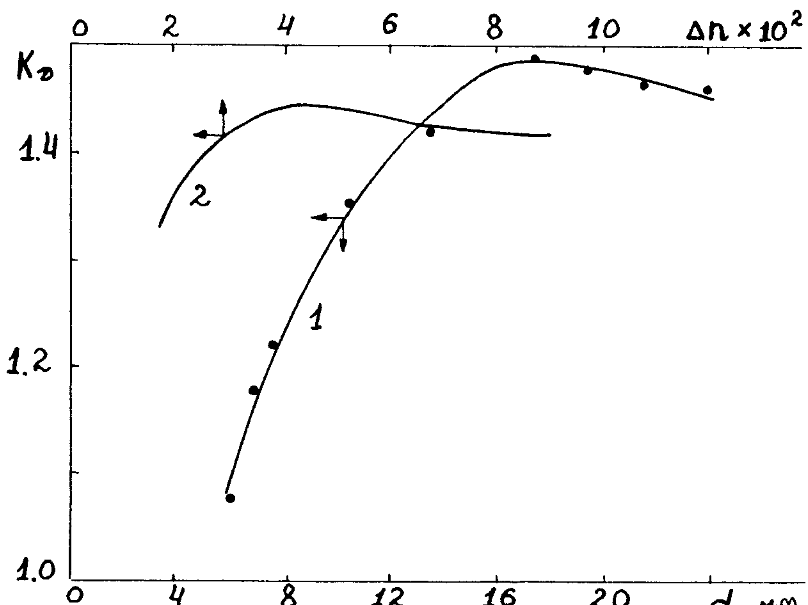

FIGURE 3 T-cell contrast characteristic K_D vs. thickness d (curve 1) and Δn (curve 2).

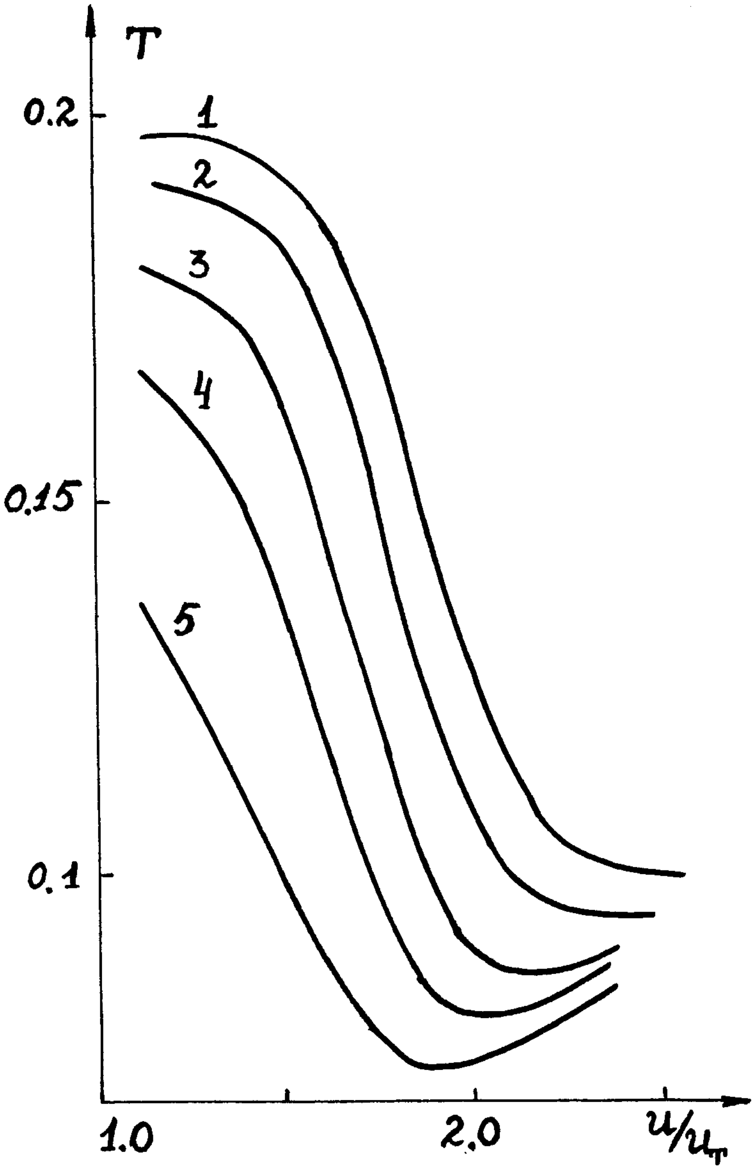

FIGURE 4 Normalised transmission-voltage characteristics of the T-cell (d = 32.2μm calculated for the different $\Delta n (= n_{\parallel} - n_{\perp})$ values, corresponding to various numbers of ellipticity maxima and minima (see Figure 7) Δn = 0.092 (curve 1), 0.06 (2), 0.038 (3), 0.0268 (4), 0.017 (5).

Figure 5 shows the T-cell transmission-voltage characteristics for different cell twist angles ϕ_t of the LC director. The depth of the transmission minimum is seen to become greater with increasing ϕ_t, so that the positive contrast is improving up to the maximum at $\phi_t \sim 90°$. The large ϕ_t angles lead to a shift of the transmission minimum

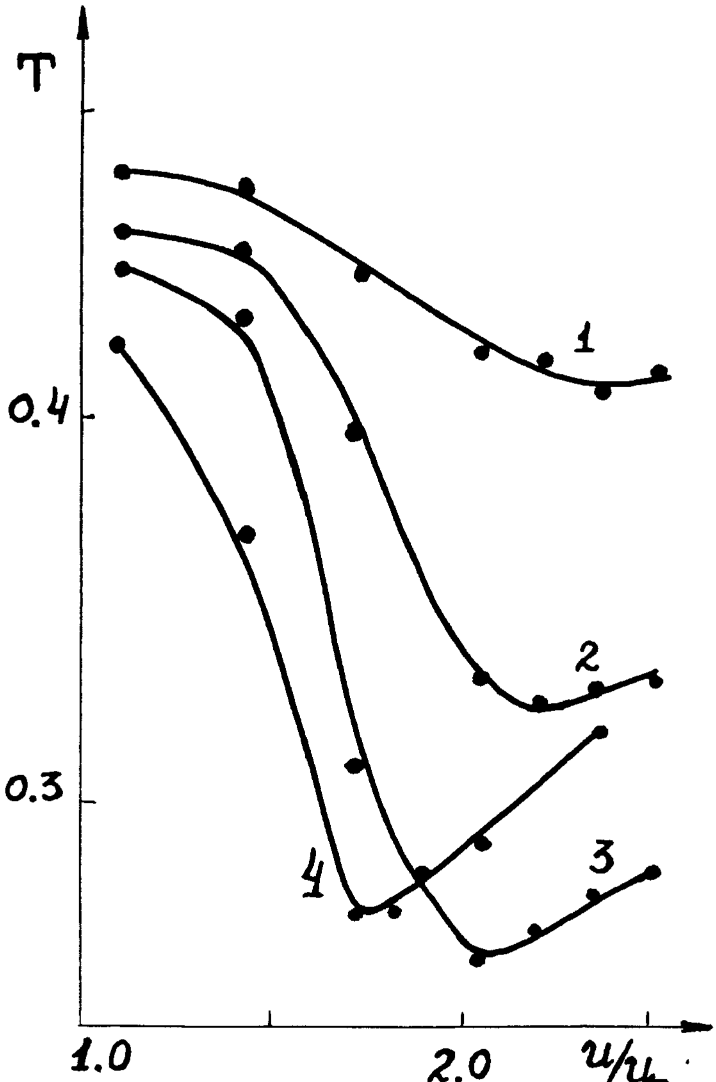

FIGURE 5 T-cell normalised transmission-voltage characteristics for the different twist angles ϕ_t, d = 15μm, ϕ_t = 30° (curve 1), 60° (2), 90° (3), 120° (4).

to lower voltages, increasing sharpness of the transmission-voltage curve and reducing the value of U_{opt}.

To clarify the influence of the dye order parameter on the positive contrast value, we have compared its value for two dark blue dyes from the anthraquinones derivatives, having different order parameters in ZLI-1646: i.e. $S_1 = 0.33$; $S_2 = 0.68$. The contrast ratio K for the first dye proves to be equal to $K_T^{(1)} = T_o/T_{min} = 1.26$, while for the second $K_T^{(2)} = 2.01$, i.e. the positive contrast, as expected, improves with increasing dye order parameter (the initial transmission of the solution in zero field is fixed).

Figure 6 illustrates the action of temperature τ on the transmission-voltage characteristics. We should note, that increasing the temperature results in simultaneous alterations of the optical, dielectric and elastic LC properties as well as a reduction of the dye order parameter. These alterations lead to a decrease of both the initial (zero field) light transmission and U_{opt} and a shifting of the transmission minimum to a lower voltage. Figure 6 shows the contrast improving with reducing temperature.

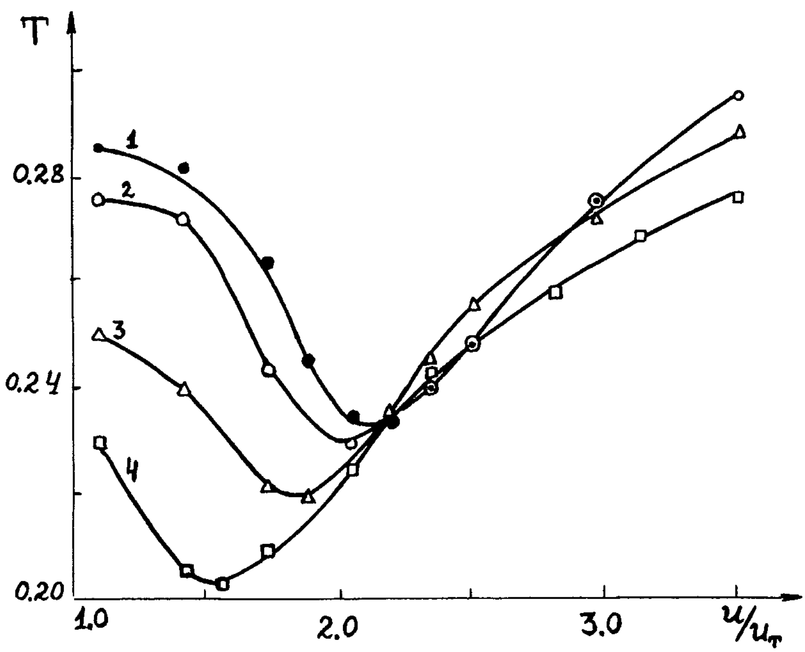

FIGURE 6 Dependence of the T-cell normalised transmission-voltage characteristics on temperature τ : τ = 20.4°C (curve 1), 32.5°C (2), 44°C (3), 54°C (4).

As we have already mentioned, the positive contrast arises from the violation of the Mauguin regime and the appearance of elliptically polarized waves during the LC reorientation process. The ellipticity e_t of the light in the T-cell output for different $\Delta nd/\lambda$ values is shown in Figure 7. According to the ellipticity curve, large values of the parameter M correspond to the number of the ellipticity maxima within the T-cell layer. In view of this, when the T-cell thickness is sufficiently large, the dye absorption of the light is very high.

According to the above, we can give a qualitative explanation of the observed phenomena (Figures 1–6). For ease of description we consider Figure 4. In zero field and for $M \approx 1$ there exists only one large ellipticity maximum (N 1) within the whole T-cell thickness,

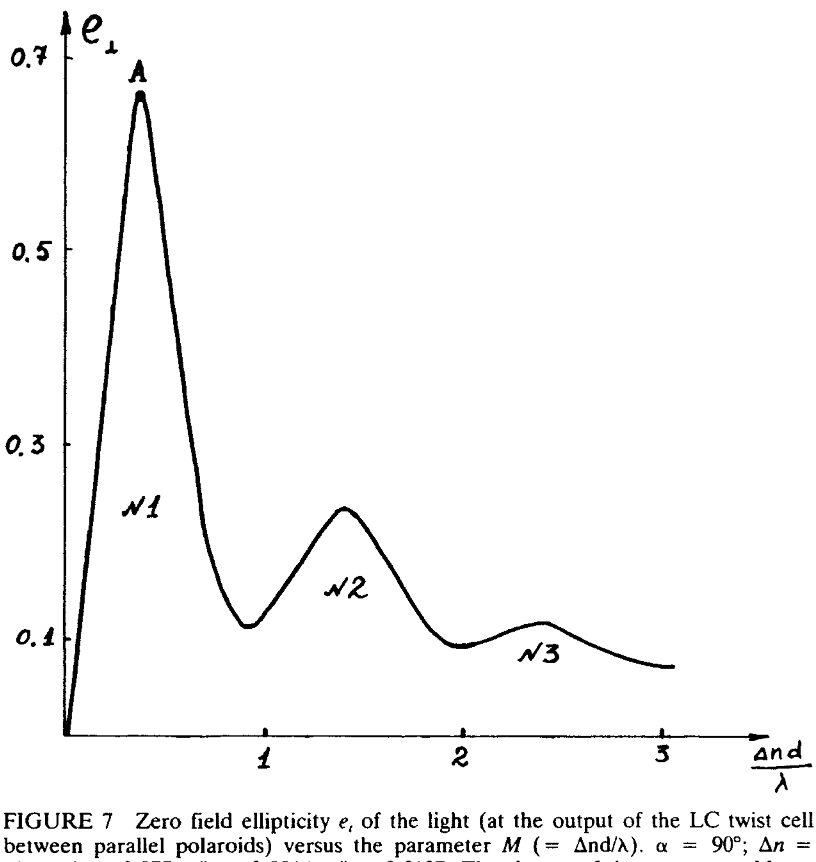

FIGURE 7 Zero field ellipticity e_t of the light (at the output of the LC twist cell between parallel polaroids) versus the parameter M (= $\Delta nd/\lambda$). α = 90°; Δn = $n'_\parallel - n'_\perp$ = 0.077, $n''_\perp$ = 0.0014, $n''_\parallel$ = 0.0107. The change of the parameter M was achieved by means of variation of d.

which is responsible for the strong dye absorption of the light. If $M \simeq 2$ two ellipticity maxima of different amplitudes are present at the cell (N 1, N 2) together with the ellipticity minimum, where no absorption takes place. Thus, for $M \simeq 2$ the light transmission increases, compared with $M \simeq 1$. For $M \simeq 5$, for instance, five ellipticity maxima and four minima lead to a higher light transmission, than in the two previous cases.

When the voltage increases, the effective birefringence Δn_{eff} decreases, and, therefore, the number of ellipticity maxima within the layer becomes less, than in the initial state. If the value of M is large, then in this process the transmission at first slightly decreases. The more abrupt decrease of the transmission corresponds to the Δn_{eff} value at which only one maximum of the ellipticity (N 1) exists within the layer. The transmission minima on the curves 1, 2, 3 (Figure 4) correspond to the point A on the first ellipticity maximum (Figure 7), the larger Δn and invariable $\Delta\epsilon$ and K_{ii} values require higher voltages to achieve the point A, where Δn_{eff} is fixed for all the curves, (Figure 4).

The transmission at the minimum, i.e. at the point A, increases considerably with increasing Δn (Figure 4). This is due to the increase of the number of dye molecules with electrically induced homeotropic orientation. The further rise of the voltage lowers Δn_{eff} and e_t to zero, thus giving the maximum cell transmission. Now we give a possible explanation of the disappearance of the positive contrast for the thin cells (d = 4μm, Figure 2). In this case the zero field ellipticity ($M \simeq 0{,}5$) is close to the ellipticity at the point A (Figure 7), and, therefore, even in the initial zero field state T-cell is in the vicinity of the transmission minimum. According to this, under the application of the external voltage we can obtain only the higher transmission of the cell, shown in Figure 2.

The time response characteristics of the effect, described above, are slightly different from those of an ordinary "guest-host" effect with a negative contrast in the T-cell, although both the effects occur due to director reorientation. To make a comparison between them, we have measured the switching on and off times of the two effects in ZLI-1646 under a voltage of 3v. The rise time of our effect (taking into account the delay interval) proves to be equal to 1.68 sec, while the corresponding time of the negative contrast "guest-host" effect is equal to 1.22 sec under the same voltage. The decay times are 0.94 sec and 1.4 sec respectively. In view of this, the switching on times, obtained by the transmission vs. voltage measurements, are longer in our effect than in an ordinary "guest-host" effect while the switching off (relaxation) times are shorter. However, in our opinion, the definition of these times from the shape of the "guest-host" effect transmission-voltage curves needs further clarification.

Thus, the maximum positive contrast is obtained for α and ϕ angles close to 90°, the highest dye order parameter, the minimum LC layer temperature, and $M = \Delta nd/\lambda = 2.1 \pm 0.1$.

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References

1. T. Uchida and M. Wada, *Mol. Cryst. Liq. Cryst.*, **63**, 19 (1981).
2. F. Gharadjedaghi, *Mol. Cryst. Liq. Cryst.*, **68**, 127 (1981).
3. V. G. Rumyantsev, A. V. Ivashchenko, V. M. Muratov, V. T. Lazareva, E. K. Prudnikova and L. M. Blinov, *Mol. Cryst. Liq. Cryst.*, **94**, 205 (1983).
4. V. G. Chigrinov, Yu. B. Podyachev, N. V. Malimonenko, V. M. Muratov, V. G. Rumyantsev and V. A. Tsvetkov, *Liq. Cryst. Conf. of Soc. Countr.*, Odessa, 1983, Abstracts, G-54.
5. M. I. Barnik, A. V. Ivashchenko, V. M. Muratov, V. G. Rumyantsev, V. V. Titov and V. G. Chigrinov, *3rd Int. Display Research. Conf. Japan*, Kobe, 1983. Advance program, p. 34.
6. L. Pohl, G. Weber, R. Eidenschink, G. Baur and W. Fehrenbach, *Appl. Phys. Lett.*, **38**, 497 (1981).
7. G. H. Gooch and H. A. Tarry, *J. Phys. D*, **8**, 1575 (1975).
8. G. P. Montgomery, *J. Opt. Soc. Amer.*, **70**, 287 and 843 (1980).