Temperature dependence of the optical Fréedericksz transition in dyed nematic liquid crystals

I. Jánossy and L. Csillag
Central Research Institute for Physics, H-1525 Budapest P.O. Box 49, Budapest, Hungary

A. D. Lloyd
Department of Physics, Heriot-Watt University, Edinburgh EH14 4AS, Scotland

We investigated the temperature dependence of the optical Fréedericksz threshold in nematic liquid crystals doped with anthraquinone dyes. In the presence of these dyes, the Fréedericksz threshold is anomalously low and exhibits an unusual temperature dependence. A microscopic model is proposed, according to which the anisotropic orientational distribution and the rotational dynamics of the excited dye molecules play an important role in the observed phenomena.

PACS number(s): 61.30.−v, 42.65.−k

The reorientation of nematic liquid crystal layers in optical fields has been studied extensively in the past decade [1]. The reorientation process in transparent films is well understood by now. In stationary cases, the deformation of the nematic director pattern is governed by the balance between the "optical" and elastic torques, originating from the interaction of the electromagnetic field with the anisotropic nematic molecules and from the spatial variations of the director, respectively. A proper consideration of light propagation in the distorted nematic liquid crystal together with the balance of torques allows a full account of the rich variety of phenomena occurring in nematic liquid crystals in optical fields.

On the other hand, in nematic liquid crystal doped with certain anthraquinone dyes, anomalous behavior was found which has not yet been explained [2,3]. As reported earlier, by adding a few percent of the dyes 1,8-dihydroxy, 4,5-diamino, and 2,7-diisobutyl(pentyl)-anthraquinone (AQ1 and AQ2, respectively) to a nematic liquid crystal host, dramatic changes in the action of the optical field can be observed. Although the light-induced reorientation processes are qualitatively very similar in the dyed nematic liquid crystals and in the transparent host, the optical Fréedericksz threshold for homeotropic layers is smaller by more than two orders of magnitude in the former systems than in the latter one. As shown experimentally, the dye-induced changes of the elastic constants and the refractive indices are not more than a few percent, hence these cannot be responsible for the order-of-magnitude reduction of the threshold power. It was demonstrated, furthermore, that the anomaly is dye specific and it is not related in a direct way to the strength of the absorption of the dye. This fact excludes any interpretations based on laser heating.

In Ref. [3] the reorientation process in the dyed materials was interpreted in a phenomenological way. It was suggested that in addition to the usual optical torque, there is a further torque generated by the excited dye molecules. In order to account for the detailed qualitative agreement between the observations in the transparent and absorbing layers, it was assumed that the time average of the dye-induced torque, Γ_{dye}, is proportional to the optical torque, Γ_{opt}:

$$\langle \Gamma_{dye} \rangle = \eta \langle \Gamma_{opt} \rangle . \tag{1}$$

The parameter η is a characteristic of the dye; its value can be deduced from the optical Fréedericksz threshold.

In this Brief Report we present the temperature dependence of the optical Fréedericksz transition in nematic liquid crystals, doped with the above-mentioned anthraquinone dyes. It was found that in the presence of these dyes, the threshold power is not only drastically reduced, but the character of its temperature dependence is also modified compared to the case of transparent nematic liquid crystals. While in nonabsorbing layers the optical Fréedericksz threshold decreases monotonically as the temperature is raised [4,5], in the dyed samples a non-monotonic behavior was seen. Far from the nematic-isotropic phase transition the threshold power increased; in the vicinity of this phase transition, however, a steep decrease of the threshold was detected.

In Fig. 1, we present experimental results, obtained with 1% of AQ1 and AQ2 dissolved in the nematic biphenyl mixture E63 (BDH product). Homeotropic films were investigated, using a moderately focused He-Ne laser beam. The optical Fréedericksz threshold P_{th} was determined by monitoring the intensity at the center of the transmitted beam as a function of the input power. At the threshold, the measured intensity began to decrease due to the increase of the beam divergence. During the measurements the samples were thermostated with an accuracy of 0.2 °C or better. Heat-conductivity calculations showed that, at the threshold, the temperature rise due to the absorption of the laser radiation was less than 1 °C.

For AQ2, we measured the critical magnetic field of the static Fréedericksz transition and the absorption coefficient, α, as a function of the temperature (Fig. 2). As we show below, with these data it is possible to evaluate the temperature dependence of the coefficient η, characterizing the strength of the dye-induced torque.
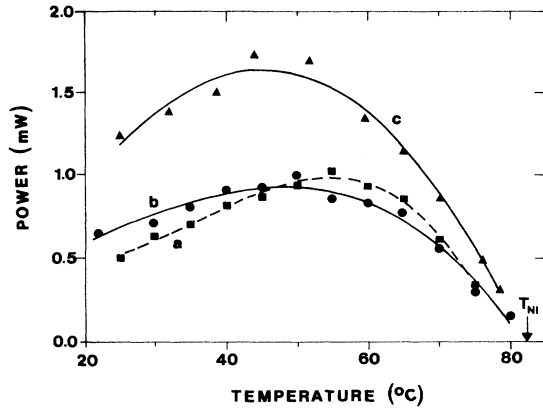
BRIEF REPORTS

FIG. 1. Optical threshold power as a function of the temperature. *a*, 1%AQ1 in E63. $L=50$ μm, $r_0=28$ μm. *b*, 1%AQ2 in E63. $L=50$ μm, $r_0=28$ μm. *c*, 1%AQ2 in E63. $L=60$ μm, $r_0=50$ μm.

As outlined above, in order to derive the threshold, the balance of torques has to be investigated. As is well known, in the plane-wave limit the threshold intensity for transparent layers is [6]

$$I_{th}^{trans} = \frac{n_e^2}{n_o} \frac{c\pi^2 K_3}{L^2(n_e^2 - n_o^2)} , \qquad (2)$$

where n_e and n_o are the extraordinary and ordinary refractive indices, respectively, K_3 is the bend elastic constant and L is the sample thickness. With the help of the well-known relation for the Fréedericksz threshold in magnetic fields [7], $H_{th} = (\pi/L)\sqrt{K_3/\chi_a}$ (χ_a anisotropy of the magnetic susceptibility), Eq. (2) can be rewritten as

$$I_{th}^{trans} = \frac{n_e^2}{n_o} \frac{c\chi_a}{n_e^2 - n_o^2} H_{th}^2 = \mu H_{th}^2 . \qquad (3)$$

For the dyed layers, the above relation has to be modified in two respects. First, the attenuation of the optical field within the film has to be taken into account. This problem was treated theoretically by Tabiryan [8]. He showed that in the plane-wave approximation and for not too high attenuations ($\alpha L < 2$) the optical Fréedericksz threshold can be obtained by replacing the input intensity with the average light intensity in the layer. Second, the dye-induced torque that is, according to our hypothesis, proportional to the optical torque should be considered. Hence its presence can be taken into account simply by multiplying the optical torque with the factor $1+\eta$. With these modifications the threshold becomes

$$I_{th}^{dye}(\alpha L) = \frac{I_{th}^{trans}}{\eta + 1} \frac{\alpha L}{1 - \exp(-\alpha L)} . \qquad (4)$$

The threshold power for a Gaussian beam with spot radius r_0 is related to the plane-wave threshold intensity as

$$P_{th} = I_{th} r_0^2 \pi g(r_0/L) , \qquad (5)$$

where the factor g gives the correction for transverse effects, neglected in the plane-wave approximation. Khoo, Liu, and Yan [9] calculated this factor, assuming that the bend and splay elastic constants are equal. For $r_0/L = 0.8$ (which corresponds to the geometry of curve *c* of Fig. 1), $g = 1.95$. Combining Eqs. (3), (4), and (5), one obtains

$$\eta = k \frac{H_{th}^2}{P_{th}} - 1 \quad \text{with} \quad k = \mu r_0^2 \pi g(R_0/L) \frac{\alpha L}{1 - \exp(-\alpha L)} . \qquad (6)$$

In Fig. 3 we present η as a function of the temperature, calculated on the basis of Eq. (6). The anisotropy of the magnetic susceptibility and the refractive indices, which are necessary for the calculation of the factor μ, are taken from Jákli *et al.* [10] and Jákli [11], respectively. (It should be noted that Jákli's measurements refer to pure E63, for which the clearing point is about 2 °C higher
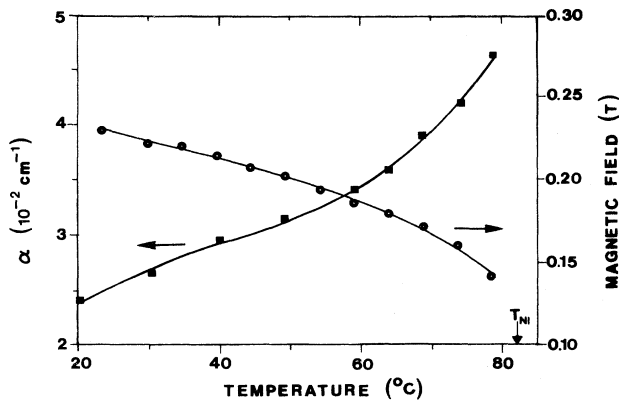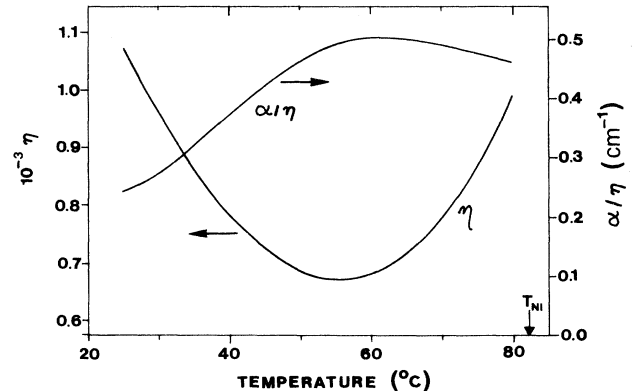
FIG. 2. The perpendicular component of the absorption coefficient, α, and the magnetic threshold for the Fréedericksz transition as a function of the temperature. The measurements were carried out on sample *c* of Fig. 1.

FIG. 3. The parameters η and α/η as a function of the temperature, evaluated from the data presented in Fig. 1 (curve *c*) and Fig. 2.

than for the doped material. To correct for this deviation, we shifted the temperature scale for μ by 2 °C, thus data with the same $T_{NI} - T$ values were used in the evaluation of η. This gave, however, only a small correction, as μ is only weakly temperature dependent.)

On a microscopic level, the observations can be interpreted in the following way. After excitation, the dye molecules are transformed into a metastable state, in which the interaction with the surrounding nematic liquid crystal is different from that in the ground state. Hence the excited dye molecules can be regarded as a certain kind of "impurity." Such an effect was noted already by Odulov et al. [12], who observed in methoxy-benzylidene-butyl-aniline (MBBA) a decrease of the nematic liquid crystal order parameter, due to light-induced conformational changes of the MBBA molecules. In order to understand the orientating action of the metastable dye molecules, one should consider their orientational distribution. While without excitation the orientational distribution of the dye molecules is cylindrically symmetric around the nematic liquid crystal director, for the excited molecules the director is *not* a symmetry axis in general. The transition dipole moments of AQ1 and AQ2 are essentially along the long axes of the molecules. Therefore, those dye molecules which are aligned along the polarization direction of the light beam have the highest probability for excitation, while the ones with a long axis perpendicular to the polarization are not excited at all. This selective excitation leads to an orientational distribution, which is not symmetric around the director. We suggest that the interaction between the asymmetrically distributed metastable dye "impurities" and the nematic liquid crystal host is responsible for the dye-induced torque and thus for the low-power reorientation of the nematic.

Although the detailed mathematical description of the above model is beyond the scope of the present report, we point out that it is consistent with the phenomenological relation, Eq. (1). No torque is expected, when the electric field of the light beam is parallel or perpendicular to the director, because in these special cases the orientational distribution of the excited molecules is symmetric around the director. In the general case, the plane determined by the director and the polarization is a symmetry plane of the distribution; hence the torque must be perpendicular to this plane. The same symmetry properties hold for the

optical torque also.

According to our considerations, the dye-induced torque should be proportional to the number of excited molecules per unit volume, which is, in turn, proportional to $\alpha \tau_f$, where τ_f is the lifetime of the excited state. However, the thermal rotational diffusion of the dye molecules has to be taken into account also. At a given moment, only those metastable dye molecules which have not yet diffused away significantly from the orientation at which they were excited contribute to the orienting action. As a result of this effect, the torque is reduced by a factor of $\tau_0/(\tau_0+\tau_f)$, where τ_0 is a characteristic time for rotational diffusion of the dye molecules. Actually, time-resolved polarization fluorescence studies [13,14] indicate that in low-viscosity nematic liquid crystals τ_0 is much shorter than τ_f. In this limit, we expect

$$\eta \sim \alpha\tau_0 \sim \alpha/D_r ,$$

where D_r is the rotational diffusion constant.

The quantity α/η is presented in Fig. 3. Far from the transition temperature it increases with an activation energy of 0.1 eV, which may be consistent with a corresponding increase of D_r. In connection with the decrease of α/η near the clearing point, we note that a similar behavior was found by Dozov, Temkin, and Kirov [14] for the rotational diffusion coefficient of dimethylamino-4'-nitrostilbene in 4-*n*-octyloxy-4'-cyanobiphenyl (8OCB). They interpreted the non-Arrhenius-type temperature dependence by the collective nature of the orientational movements of molecules in the nematic phase. A similar effect may take place in the present system as well. Polarized fluorescence studies may help to clarify this question in the future.

In conclusion, we showed that anthraquinone dyes can modify the interaction of nematic liquid crystals with optical fields dramatically. In the studied materials, the optical Fréedericksz threshold has an anomalously low value and shows an unusual temperature dependence also. We outlined a microscopic model, according to which the rotational dynamics of the dye molecules plays an important role in the observed phenomenon. The temperature dependence of the rotational diffusion coefficient is thought to be responsible for the nonmonotonic behavior of the threshold.

[1] For review papers see, e.g., N. V. Tabiryan, A. V. Sukhov, and B. Ya. Zel'dovich, Mol. Cryst. Liq. Cryst. Special Topics XIX **136**, 1 (1986); I. C. Khoo, in *Progress in Optics*, edited by E. Wolf (North-Holland, New York, 1988), Vol. XXIV.
[2] I. Jánossy, A. D. Lloyd, and B. S. Wherrett, Mol. Cryst. Liq. Cryst. **179**, 1 (1990).
[3] I. Jánossy and A. D. Lloyd, Mol. Cryst. Liq. Cryst. **203**, 77 (1991).
[4] S. D. Durbin, S. M. Arakelian, and Y. R. Shen, Phys. Rev.

Lett. **47**, 1411 (1981).
[5] F. Bloisi, L. Vicari, and F. Simoni, Opt. Commun. **76**, 261 (1990).
[6] H. L. Ong, Phys. Rev. A **28**, 2393 (1983).
[7] L. M. Blinov, *Electro-optical and Magneto-optical Properties of Liquid Crystals* (Wiley, New York, 1983), Chap. 4.
[8] N. V. Tabiryan, Opt. Spectrosc. (USSR) **58**, 697 (1985).
[9] I. C. Khoo, T. H. Liu, and P. Y. Yan, J. Opt. Soc. Am. B **4**, 115 (1987).
[10] A. Jákli, D. R. Kim, M. R. Kuzma, and A. Saupe, Mol.

Cryst. Liq. Cryst. **198**, 331 (1991).

[11] A. Jákli (private communication).

[12] S. G. Odulov, Yu. A. Reznikov, M. S. Soskin, and A. I. Khizhnyak, Zh. Eksp. Teor. Fiz. **85**, 1988 (1983) [Sov. Phys. JETP **58**, 1154 (1983)].

[13] A. Arcioni, F. Bertinelli, R. Tarroni, and C. Zannoni, Mol. Phys. **61**, 1161 (1987).

[14] I. Dozov, S. Temkin, and N. Kirov, Liq. Cryst. **8**, 727 (1990).