

Influence of anthraquinone dyes on optical reorientation of nematic liquid crystals

I. Jánossy and T. Kósa

Central Research Institute for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

Received April 20, 1992

Optical reorientation measurements in dye-doped nematic liquid crystals are reported. The dye-induced optical torque exceeds significantly the normal optical torque for all anthraquinone dyes investigated. With one of the dyes, optical Freedericksz transition in a planar layer is demonstrated.

In previous publications we demonstrated the strong influence of certain anthraquinone dyes on the optical reorientation process in nematic liquid crystals.¹⁻³ As reported in these papers, when small amounts (typically 1%) of the dyes 1,8-dihydroxy, 4,5-diamino, 2,7-diisobutyl-anthraquinone (AQ1) and 1,8-dihydroxy, 4,5-diamino, 2,7-diisopentyl-anthraquinone (AQ2) are added to a nematic host, the orienting action of an optical field increases by a factor of several hundred. To account for this anomaly, we suggested that the interaction between the excited dye molecules and the nematic host generates a new kind of optical torque in the system. This dye-induced torque can be much stronger than the direct optical torque observed in transparent nematics. The ratio of the dye-induced torque to the normal optical torque, η , is a characteristic of the molecular structure of the dye and is proportional to its concentration.

For the dyes AQ1 and AQ2, quantitative investigations were carried out through the study of the optical Freedericksz transition. As is well known, the optical Freedericksz transition takes place in homeotropically aligned nematic films, illuminated by a laser beam at normal incidence.^{4,5} In this geometry, reorientation of the director develops only above a threshold input power. In guest-host systems containing AQ1 or AQ2, the threshold was reduced drastically compared with that in the pure host. With other anthraquinone dyes, however, the Freedericksz transition could not be produced by a light beam in the homeotropic geometry. When the input power was increased, laser heating led to the melting of the nematic layer, without any previous reorientation of the director.

The aim of this Letter is to compare the effect of AQ1 and AQ2 with that of other anthraquinone dyes, in a quantitative way. To this end, instead of investigating the Freedericksz transition, we carried out reorientation measurements with oblique incidence and extraordinary polarization of the irradiating beam. Under such circumstances, reorientation occurs without threshold; thus by applying sufficiently low input powers one can avoid melting of the nematic material. Using this method, one can study the influence of any dye on the reorienta-

tion process. In particular, we determined the η parameter for all the dyes considered previously. As it turned out, the dye-induced torque is of opposite sign for AQ1 and AQ2 than for the other dyes.

We detected the deformation of the director configuration in the illuminated area with the help of the so-called Z-scan technique.^{6,7} Following this method, one keeps the input power of a focused laser beam constant and translates the sample along the optical axis of the beam (the Z direction). The intensity of the central part of the laser beam is monitored in the far field. In the absence of nonlinear interaction between the electromagnetic field and the substance, the detected intensity remains constant during translation. On the other hand, when nonlinearity is present, a characteristic variation of the signal is found. In the case of self-focusing (i.e., light-induced increase of the optical path), a minimum is observed at a position between the focusing lens and the focal point; a maximum occurs at a position behind the focal point. In the case of self-defocusing (decrease of the optical path), the positions of the minimum and maximum are reversed. Nonlinear absorption can be studied by this method also by repeating the scan with an open aperture, i.e., collecting the total transmitted light into the detector.⁷

The change of the optical path in a nematic film originates from the light-induced director reorientation and from thermally induced refractive-index variation.⁸ The two contributions can be separated by superimposing a stabilizing low-frequency electric field onto the optical field. While the reorientation process is suppressed by the applied field, thermal effects are, in a first approximation, not affected.

In the experiments, in addition to AQ2, *N,N'*-(4-methylphenyl)-1,4-diamino-AQ (D4), *N*-(4-nonyloxyphenyl)-1-amino-4-hydroxy-AQ (D16), and *N*-(4-dimethylaminophenyl)-1-amino-4-hydroxy-AQ (D27) were studied (where AQ denotes anthraquinone). They were dissolved in a concentration of 0.5% in the host material E63. E63 is a mixture composed mainly of biphenyls but containing some PCH-3, i.e., 1-(4'-cyanophenyl)-4-propyl-cyclohexane; it was developed by British Drug House to provide

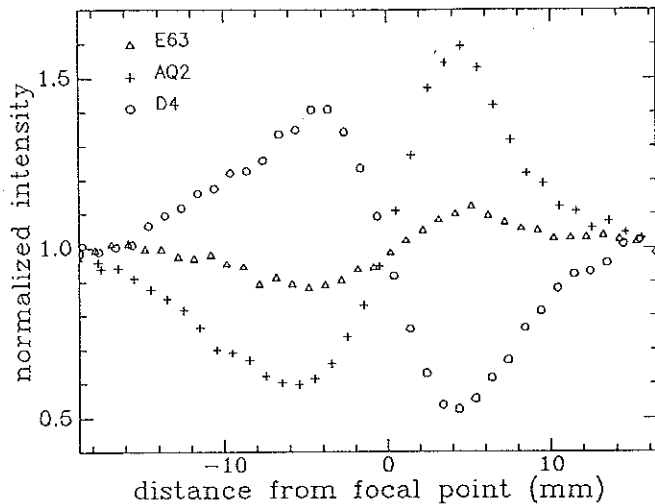


Fig. 1. Z-scan curve of the host nematic ($P = 8$ mW), the AQ2-doped sample ($P = 0.19$ mW), and the D4-doped sample ($P = 0.46$ mW). The curves are normalized to the intensities, measured at large distances from the focal point.

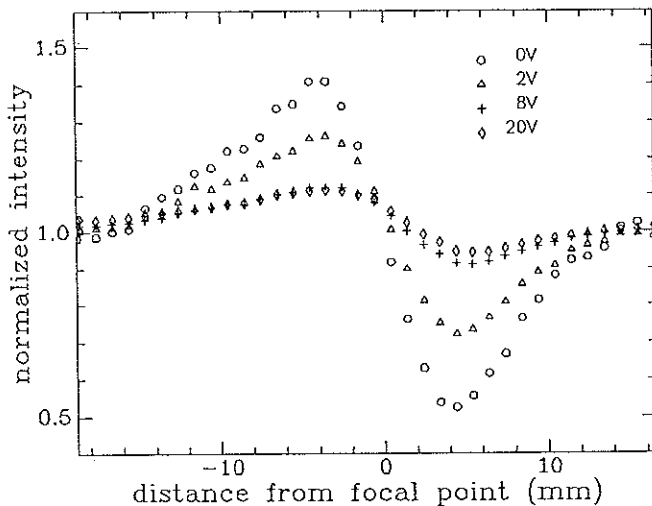


Fig. 2. Effect of a low-frequency (1-kHz) electric field on the Z-scan curve for D4 at various voltages.

adequate solubility for all the dyes. Homeotropic films of 35- μm thickness were prepared. The cells were illuminated by a He-Ne laser under an angle of incidence of 42°. The focal length of the lens was 95 mm, producing a spot radius of 21 μm at the focal point. The measurements were carried out at room temperature.

In Fig. 1, Z-scan curves are shown for the pure host, for E63 doped with AQ2, and for E63 doped with D4. In Fig. 2 the effect of an applied voltage is shown for the D4-doped sample. This figure shows that above a few volts, the signal becomes independent from the applied voltage. As explained above, the limiting curve represents the thermo-optical contribution to the nonlinearity. We carried out scans with open aperture also and found that nonlinear absorption is negligible in the present case.

As seen from Fig. 1, for E63 self-focusing is observed, in accordance with the fact that in transparent nematics the electromagnetic field rotates the director toward the electric-field vector, and thus

the optical path increases. In the case of AQ2, self-focusing takes place again, but it is much stronger than for the host itself. (Note the factor of ≈ 40 between the input powers applied for the host and for the AQ2-doped film.) This observation corresponds to the detected decrease in the optical Freedericksz threshold. For D4, self-defocusing is observed, indicating a light-induced decrease in the optical path. A plausible interpretation of this fact is to assume that in the D4-doped material the electromagnetic field turns the director toward the wave vector of the beam rather than toward the electric-field vector. In terms of dye-induced torques, for AQ2 this torque has the same sign as the normal optical torque, while for D4 the sign is opposite.

In the following, we determine the η coefficient quantitatively by comparing the Z-scan curves for the host and the dye-doped materials. Following the arguments given in previous publications, we take the dye-induced torque, Γ_{dye} proportional to the optical torque, Γ_{opt} :

$$\Gamma_{\text{dye}} = \eta \Gamma_{\text{opt}}, \quad \Gamma_{\text{opt}} = \epsilon_0 \epsilon_n (\mathbf{n} \cdot \mathbf{E})(\mathbf{n} \times \mathbf{E}). \quad (1)$$

Here \mathbf{E} is the electric field of the light beam, \mathbf{n} is the director, and $\epsilon_n = n_e^2 - n_o^2$. The total light-induced torque is

$$\Gamma_{\text{light}} = (1 + \eta) \Gamma_{\text{opt}}, \quad (2)$$

which is, in the steady state, balanced by the elastic torque.

In the limit of small attenuations, the ratio of the total light-induced torques in a dyed sample and in the host is $(1 + \eta)P_{\text{dye}}/P_{\text{host}}$ in the whole irradiated area. Here the P 's denote the input powers. Furthermore, for the small input powers applied in the present experiments, the amplitude of a normalized Z-scan curve (i.e., the difference between the maximum and minimum, Δv) is proportional to the input power.⁷ With these two conditions, the amplitudes belonging to the dyed film and the host are related as

$$\Delta v_{\text{dye}}/P_{\text{dye}} = (1 + \eta)\Delta v_{\text{host}}/P_{\text{host}}.$$

In order to correct for the attenuation of the laser beam within the dyed layers, we use the same procedure as for the optical Freedericksz transition,³ namely, we replace the input power P with the average power P^{av} :

$$P^{\text{av}} = P \frac{1 - \exp(-\alpha d)}{\alpha d}.$$

Here α denotes the absorption coefficient for the actual polarization and the angle of incidence and d is the length of the path of the laser beam through the film. Thus we evaluate η from the relation

$$\eta = \frac{\Delta v_{\text{dye}}}{P_{\text{dye}}^{\text{av}}} \frac{P_{\text{host}}}{\Delta v_{\text{host}}} - 1. \quad (3)$$

The results are summarized in Table 1. The Z-scan curves were corrected for thermal effects by taking the difference between the curves measured at 0 and 20 V of applied voltage. The α values were

Table 1. Values of η and η/α for the Different Dyes

Material	α (cm ⁻¹)	η	η/α (cm)
AQ2	142	238	1.7
D4	275	-95	-0.35
D16	142	-19	-0.14
D27	105	-5	-0.048

deduced from transmission measurements. In Table 1 we also present the η/α values, which are independent of the concentration and thus depend only on the molecular structure of the dye.

From the optical Freedericksz threshold, we obtain for AQ2 a value of $\eta/\alpha = 3.5$ cm,³ which is significantly higher than the value deduced from the present method. The deviation might come from the approximations used in the evaluation of the experimental data and from the uncertainties in the measurement of the optical threshold in the dyed films.² We think that the present method provides more reliable values of η than the previous one, because the experimental data are more precise and fewer approximations were used in the evaluation procedure. This point will be investigated further in our future research.

With materials for which η is negative and $|\eta| > 1$ the Freedericksz transition cannot occur in the homeotropic geometry, because the total light-induced torque stabilizes the director configuration. This conclusion is in agreement with experimental facts described above. On the other hand, one expects the Freedericksz transition to take place for such materials in the planar configuration. We proved this supposition experimentally, using a planar layer of the D4-doped material. At normal incidence and extraordinary polarization of the laser beam, the optical Freedericksz transition was observed with a threshold of 1.2-mW input power (spot radius 21 μ m). This observation gives strong support to our idea of the negative dye-induced torque. As a first estimation showed, the detected threshold

value is more or less compatible with the η value deduced from the Z-scan method. This point will also be considered in more detail in our future research.

In conclusion, we showed that significant dye-induced torque is generated by a series of anthraquinone dyes. Even in the case of D27, which produced the weakest effect among the dyes studied here, a concentration of 0.5% gave rise to a torque five times larger than the normal optical torque. We demonstrated that the η coefficient can be both of positive and negative sign. The magnitude and the sign of the effect obviously depend on the molecular structure of the dye. We note that the dyes D4, D16, and D27 are composed of rather elongated molecules, whereas AQ1 and AQ2 have more compact structures; maybe the different sign of η is connected with this circumstance. Apart from the molecular origin of the effect, the observation of negative light-induced torque opens up the possibility of studying reorientation effects that could not be investigated experimentally in the past; the optical Freedericksz transition in planar cells is one example.

References

1. I. Jánossy, A. D. Lloyd, and B. S. Wherrett, *Mol. Cryst. Liquid Cryst.* **179**, 1 (1990).
2. I. Jánossy and A. D. Lloyd, *Mol. Cryst. Liq. Cryst.* **203**, 77 (1991).
3. I. Jánossy, L. Csillag, and A. D. Lloyd, *Phys. Rev. A* **44**, 8410 (1991).
4. A. S. Zolotko, V. F. Kitaeva, N. Kroó, N. N. Sobolev, and L. Chillag, *JETP Lett.* **33**, 162 (1980).
5. S. D. Durbin, S. M. Arakelian, and Y. R. Shen, *Phys. Rev. Lett.* **47**, 1411 (1981).
6. S. G. Odulov, Yu. A. Reznikov, M. S. Soskin, and A. I. Khizhnyak, *Izv. Akad. Nauk SSSR Ser. Fiz.* **48**, 596 (1984).
7. M. Sheik-Bahae, A. A. Said, and E. W. Van Stryland, *Opt. Lett.* **14**, 955 (1989).
8. I. C. Khoo, in *Progress in Optics XXIV*, E. Wolf, ed. (North-Holland, New York, 1988).