PHYSICAL REVIEW E VOLUME 55, NUMBER 3 MARCH 1997

Flexoelectric polarization changes induced by light in a nematic liquid crystal

D. S. Hermann,[1] P. Rudquist,[1] K. Ichimura,[2] K. Kudo,[2] L. Komitov,[1]
and S. T. Lagerwall[1]
[1]*Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden*
[2]*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan*

(Received 15 August 1996)

In a nematic liquid crystal where the director field has a splay-bend deformation mediated by the boundary conditions there is a certain intrinsic polarization density distribution characteristic of the flexoelectric properties of the medium. By application of an electric field perpendicular to the director, a twist is induced which is a measure of the flexoelectric anisotropy [I. Dozov, Ph. Martinot-Lagarde, and G. Durand, J. Phys. (Paris) Lett. **43**, L-365 (1982)]. We show that in molecules susceptible to a photoinduced configurational change we may change the volume polarization by UV illumination and relate the change in flexoelectric coefficients to the configurational change in the molecule. In the experiment we use the British Drug House (Merck) nematic mixture E7 doped with 5 wt % of the dye 4-hexyloxy-(4′-hexyl)azobenzene. The photoinduced *trans-cis* configurational change leads to an increase by 40% in the flexoelectric anisotropy $(e_s - e_b)/K$. [S1063-651X(97)01302-0]

PACS number(s): 61.30−v

INTRODUCTION

In certain solids, the application of mechanical stress results in a strain, which in some cases, e.g., quartz, can induce a polarization. The phenomenon is known as piezoelectricity. A similar or analogous effect but of different nature may be observed in liquid crystals and is called flexoelectricity [1]. Elastic splay and bend deformations are here connected with the appearance of a local polarization density in the liquid crystal material. Whereas the piezoelectric effect requires a certain dissymmetry in the crystal structure (existence of polar axes), the flexoelectric effect requires a certain dissymmetry in the shape of the molecules constituting the liquid crystal phase. In practice this dissymmetry is always present. Any tendency to droplike or bananalike shape will lead to a tendency to dissymmetric short-range ordering of splay and bend character, respectively. The size of the connected charge separation will depend on the distribution and size of the dipoles in the molecule, where longitudinal dipoles are important in splay, transversal dipoles in bend deformations. If we impose such deformations on the liquid crystal by external means, they make favorable such a molecular ordering which fits to the molecular shape, thus inducing a polarization.

Like the piezoelectric effect, the flexoelectric effect is linear, hence it also works in the opposite direction: An applied electric field may induce splay or bend deformations by orienting the permanent dipoles. Then, drop-shaped and bananalike molecules induce splay and bend deformations, respectively. The most general form of the flexoelectric polarization density in a nematic liquid crystal is given by [1]

$$\mathbf{P} = e_S\,\mathbf{n}(\nabla\cdot\mathbf{n}) + e_b(\nabla\cdot\mathbf{n})\times\mathbf{n}, \tag{1}$$

where **n** is the director and e_s and e_b are the flexoelectric coefficients for splay and bend. In liquid crystals with more internal degrees of freedom, like smectic *C*, many more kinds of deformation may cause charge separation, with an increasing number of flexoelectric coefficients as a result.

Although flexoelectricity has been known since 1969, little is known about the flexoelectric coefficients and the influence of the molecular properties on them. Recently, the interest in flexoelectricity in cholesterics has increased considerably because of progress in a very interesting linear electro-optic effect [2]. More knowledge about the flexoelectric coefficients, however, is needed for optimization of materials to exploit this effect.

In certain organic molecules, which might also exhibit liquid crystal phases, reversible transformations between different isomers can be induced by absorption of light or changes in temperature. A *trans-cis* photoisomerization leads to a drastic molecular shape alteration and hence the flexoelectric coefficients of the material are also expected to change.

In this work we report a light-induced change in the flexoelectric response due to the *trans-cis* isomerization of a nematic dye, 4-hexyloxy-(4′-hexyl)azobenzene, dissolved in a nematic liquid crystal. Knowledge about the molecular structure for the two isomers together with the values of the flexoelectric coefficients of the nematic mixture may give useful information about flexoelectricity in liquid crystals.

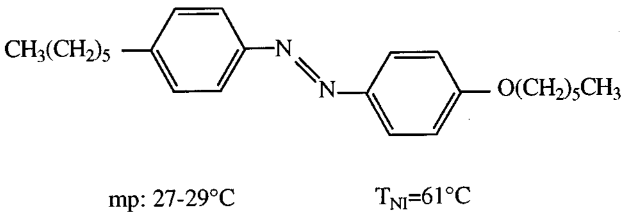

FIG. 1. The chemical formula and transition temperatures of the dye liquid crystal 4-hexyloxy-(4′-hexyl)azobenzene.

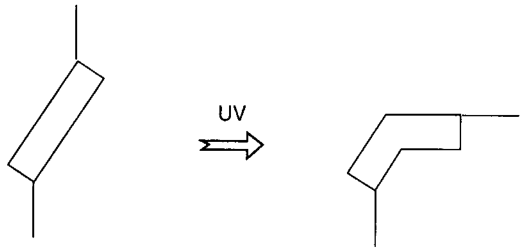

FIG. 2. Photoinduced transition from *trans* to *cis* isomer in the azobenzene moiety.

EXPERIMENT

The liquid crystal shown in Fig. 1 has an azobenzene moiety with —*N*═*N*— as photosensitive chromophore and shows a transformation from *trans* to *cis* isomer upon irradiation with UV light [3] (cf. Fig. 2) and the process is reversible with time. The *trans* configuration gives a nematic phase whereas the *cis* configuration gives an isotropic liquid, thus making the study of the flexoelectric properties after the UV illumination impossible in the pure compound. Therefore we used a mixture of a small amount of the dye dissolved in an appropriate nematic host (E7) to keep the nematic phase also after the UV irradiation.

We used the method of Dozov, Martinot-Lagarde, and Durand [4] to determine the quantity ($\Delta e/K$, where K is the average elastic constant and $\Delta e = e_s - e_b$ is the flexoelectric anisotropy. In a hybrid aligned nematic (HAN) cell, the molecular alignment is homeotropic at one surface and planar (parallel) at the other surface. Thus the boundary conditions cause a two-dimensional bend-splay deformation in the nematic layer resulting in a permanent flexoelectric polarization density in the volume of the medium. An applied electric field, in the plane of the nematic layer and normal to the deformation plane, couples to the polarization and induces a twist deformation (cf. Fig. 3). From the magnitude of the induced twist ϕ at the homeotropic surface, the flexoelectric anisotropy is obtained [4] according to

$$\phi = -\frac{\Delta e E d}{\pi K}, \tag{2}$$

where ϕ is the guided angle of rotation (equal to the director twist) of the polarization plane of transmitted light, E is the electric field, and d is the cell thickness. The meaning of the sign of the electrically induced director twist is illustrated in Fig. 4.

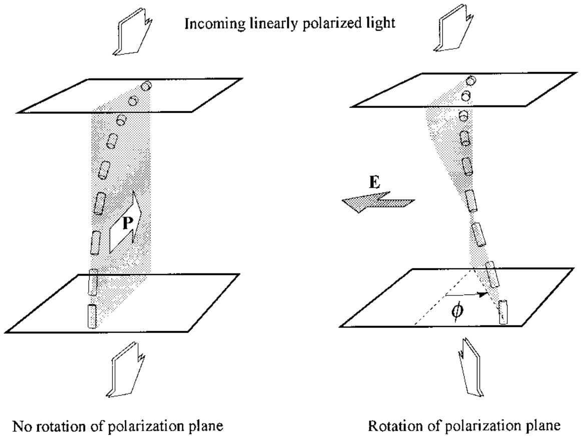

FIG. 3. Field-induced twist in a HAN cell.

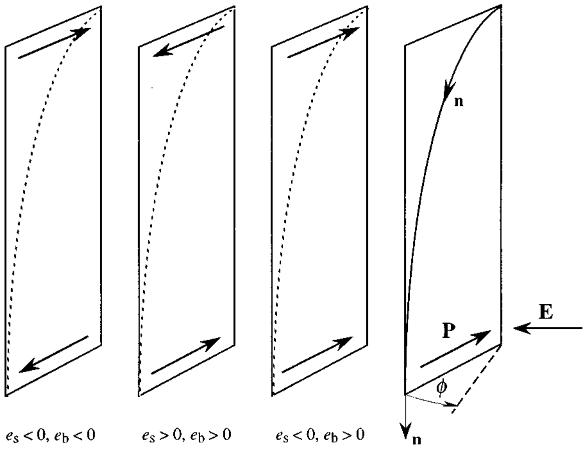

FIG. 4. Polarity conditions in the flexoelectric effect. The direction of flexoelectric polarization is shown at top (pure splay) and bottom (pure bend) for different signs of the coefficients e_s and e_b. If $e_s \approx 0$ or numerically smaller than e_b, then the sign of the flexoelectric anisotropy $\Delta e = (e_s - e_b)$ is always opposite to the sign of e_b. Hence if $e_b > 0$ then $\Delta e < 0$, and the torque from **E** on **P** is antiparallel to **n**. The negative sign in the formula for ϕ then corresponds to the actually observed deflection (Fig. 3).

The cells used in the experiment each consisted of two parallel glass plates separated by aluminum spacers that are also the electrodes of the cell. The upper plate was coated with a polyimide layer, rubbed unidirectionally along the electrodes in order to obtain a planar alignment with preferred direction parallel to the electrode edges. The lower plate was covered with lecithin for homeotropic anchoring and the assembled cell was filled with the liquid crystal material in the isotropic phase

Two cells were prepared: One with the nematic liquid crystal E7 [5] only, and the other with a mixture of 95 wt % E7 and 5 wt % dye. This E7-dye mixture corresponds to 96% E7 and 4% dye in terms of *molar* percent, and was found to exhibit the nematic phase before and after the UV illumination.

RESULTS AND DISCUSSION

The measurements of the maximum induced twist are shown in Fig. 5 for pure E7 and in Fig. 6 for the E7-dye mixture before and after UV illumination, respectively. The slopes $d\phi/dU$ were measured in each case as indicated by the straight lines. These lines are least-squares fits to the linear parts of the measured data points.

First the data points before UV illumination were taken in sequence and then the same measurement was performed after UV illumination. The sample was illuminated for 60 s for each data point and during the illumination the electric field was switched off. After the illumination the field was switched on and the data point was taken immediately, as it was found that the induced twist started decreasing towards

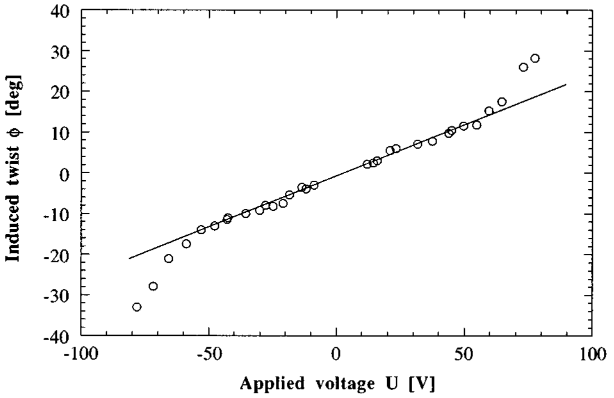

FIG. 5. The field-induced twist for 100% E7.

the value measured before the illumination. The complete relaxation took about 30 s.

In order to extract the values of $(e_s-e_b)/K$ the distance between the electrodes as well as the cell thickness must be known. These parameters were measured for both cells to be (2.5±0.1) mm and (20±2) μm, respectively.

For pure E7 $(e_s-e_b)/K\approx-1.7$ C m^{-1}N^{-1} was obtained. For the E7-dye mixture before the illumination with UV light $(e_s-e_b)/K\approx-1.9$ C m^{-1}N^{-1}. After the illumination for 60 s, $(e_s-e_b)/K\approx-2.6$ C m^{-1}N^{-1} was measured. The magnitude of $(e_s-e_b)/K$ thus increased by a factor of about 1.4 upon the UV irradiation. An additional UV illumination gave no further increase of the magnitude of $(e_s-e_b)/K$. The photoisomerization of the dye can thus be regarded to have saturated after the first illumination.

In order to account for the order of magnitude of the observed effect we may argue as follows. The 5 wt % dye mesogen corresponds to 4 mol %. For this 4% dye–E7 mixture, the measured slope $d\phi/dU$ of the field-induced twist with respect to the applied voltage increases by a factor of 1.4 upon UV illumination. This is an increase of 40%. In the following it will be shown that the configuration change of the dye molecules accounts for this increase.

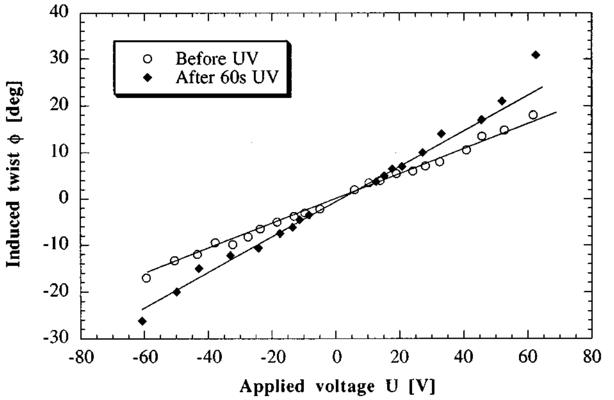

FIG. 6. The field-induced twist for the E7-dye mixture. Hollow circles: Before UV illumination. Solid diamonds: After UV illumination for 60 s.

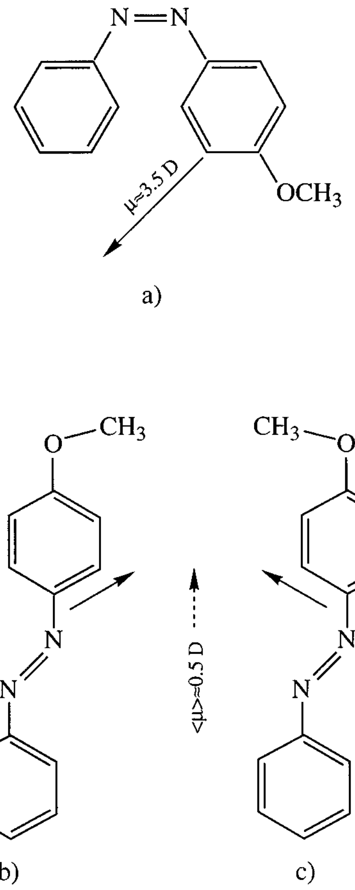

FIG. 7. The results of the quantum chemical calculation for the direction and magnitude of the permanent dipole moments for the *cis-trans* configurations of the model compound 4-methoxyazobenzene. All arrows are drawn according to the physicist's sign convention, i.e., from negative to positive. (a) The dipole moment of the *cis* configuration. (b) The dipole moment of the *trans* conformer of the *trans* configuration. (c) The dipole moment of the *cis* conformer of the *trans* configuration. The average dipole moment resulting from the two conformers in (a) and (b) is shown as a dashed arrow.

To have an estimation of the expected effect at the *trans-cis* transformation we have made a semiempirical quantum chemical calculation (using the program MOPAC PM3) on the simpler model compound 4-methoxyazobenzene. The dipole moment for the *cis* configuration is about 3.5 D, in the direction indicated in Fig. 7(c). Therefore the effective dipole moment acting in the bend flexoelectric effect should be of the order of 2–3 D.

The dipole moment for the *trans* configuration is about 0.5 D, along the molecular long axis. This number is obtained as the average value of the dipole moments of the two conformers (*s-trans* and *s-cis*) of the *trans* configuration [Figs. 7(a) and 7(b)]. The effective dipole moment active in this case (transverse to the long axis and to a high degree averaged out by the rotation around that axis) can only be a fraction of this, i.e., of the order of some tenths of a debye. The dipole moment of the dye molecule thus increases by an order of magnitude. Considering the low concentration (4%) of dye molecules in the E7-dye mixture, a 40% increase of $(e_s-e_b)/K$ then lies within the expected range. Thus the configurational change of the dye molecule reasonably well accounts for the experimentally observed behavior.

According to Eq. (2) the increase in ϕ after illumination could also, in principle, be explained by a decrease in the average elastic constant K. Two factors make us believe that this would be a small effect. First, the decrease in K_{33} would at least be partly compensated by an increase in K_{11}. Second, it is well known that variations in K_{22} even between molecules of rather different shape are not particularly large

We thus conclude that the photoisomerization of the dye, albeit its low concentration, changes the flexoelectric properties through the change of molecular shape and hence of the distribution of dipole moments in the HAN cell.

A similar effect of light-induced change of the flexoelectric response, but due to a mechanism different from the one that we have studied, has previously been observed in lyotropic lipid membrane systems [6,7]. In these cases the term ‘‘photoflexoelectric’’ was used to describe the effect. We find this to be an inappropriate term, however, since flexoelectricity is present also without the light. Such a term would rather imply that light were the cause of flexoelectricity, consistently with, e.g., the term ‘‘photoconductive’’ where light is the cause of an electric current.

ACKNOWLEDGMENTS

Financial support from the Swedish National Science Foundation as well as the Swedish National Board for Technical Development is gratefully acknowledged.

---

[1] R. B. Meyer, Phys. Rev. Lett. **22**, 319 (1969).
[2] J. S. Patel and R. B. Meyer, Phys. Rev. Lett. **58**, 15 (1987); P. Rudquist, M. Buivydas, L. Komitov, and S. T. Lagerwall, J. Appl. Phys. **76**, 12 (1994); P. Rudquist, L. Komitov, and S. T. Lagerwall, Phys. Rev. E **50**, 6 (1994).
[3] K. Ichimura, T. Seki, Y. Kawanishi, Y. Suzuki, M. Sakuragi, and T. Tamaki, in *Photo-reactive Materials for Ultrahigh Density Optical Memory*, edited by M. Irie (Elsevier, Amsterdam, 1994).
[4] I. Dozov, Ph. Martinot-Lagarde, and G. Durand, J. Phys. (Paris) Lett. **43**, L-365 (1982).
[5] Z. Z. Zhong, D. E. Schuele, W. L. Gordon, K. J. Adamic, and R. B. Akins, J. Polym. Sci. Polym. Phys. Ed. **B30**, 1443 (1992). E7 manufactured by BDH Ltd., Poole, England.
[6] M. Spassova, A. G. Petrov, and J. H. Fendler, J. Phys. Chem. **99**, 9485 (1995), and references therein.
[7] A. G. Petrov, Europhys. News **27**, 92 (1996).