

Effect of photoisomerization of azobenzene dopants on the flexoelectric properties of short-pitch cholesteric liquid crystals

Lachezar Komitov,^{1,*} Christian Ruslim,² and Kunihiro Ichimura²

¹*Department of Microelectronics and Nanoscience, Chalmers University of Technology and Göteborg University, S-41296 Göteborg, Sweden*

²*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

(Received 6 December 1999)

The flexoelectric properties of short-pitch cholesteric mixtures doped with three different azobenzenes, 4,4'-dihexyloxyazobenzene (4,4'-azo), 3,3'-dihexyloxy-2,2'-dimethylazobenzene (3,3'-azol), and 3,3'-dihexanoyloxy-2,2'-dimethylazobenzene (3,3'-azo2), respectively, were studied upon illumination with uv light. Their effective flexoelectric coefficients were derived from the flexoelectro-optic response of the mixtures aligned in uniform lying helix texture. Considering the fact that the pitch of the mixtures became shorter upon uv illumination, an increase of their effective flexoelectric coefficients was found to take place due to the photoisomerization of the dyes. The largest change was found for the coefficient of the guest-host mixture containing 4,4'-azo dye, most probably due to the bent shape of the dye *cis*-isomer. This observation is in good agreement with our previous studies on the influence of the molecular shape on the liquid-crystal flexoelectric properties and it suggests a possible way for enhancement of the amplitude of flexoelectro-optic response in cholesterics by using liquid-crystal materials with pronounced molecular shape dissymmetry.

PACS number(s): 61.30.-v

INTRODUCTION

During the past few years, the electro-optic effect exhibited by cholesterics [1–3], aligned in uniform lying helix (ULH) texture, has attracted a lot of interest due to its extraordinary performance. The effect, considered to be of flexoelectric origin, gives rise to a fast linear electro-optic response, that is, an in-plane field-induced deflection (tilt) of the sample optic axis, and, hence, demonstrating a gray scale capability [2,4,5]. Recently, a large field-induced tilt has been found in some cholesteric liquid-crystal materials. Values of the induced tilt of more than 30° have been reported [2,6]. Most remarkably, a temperature-independent flexoelectro-optic response has been observed in cholesterics with temperature-independent pitch. Moreover, the response time of the flexoelectro-optic effect is found to be very short, usually lying in the microsecond range (10–100 μs). Hence, with a proper design of single liquid-crystal substances and mixtures, a fast linear and a temperature-independent electro-optic response can be obtained in cholesterics which make them very attractive for different applications in the field of optoelectronics.

The flexoelectric properties of the liquid crystal and the magnitude of the cholesteric pitch and its temperature behavior are of major importance for the appearance of the flexoelectro-optic response. As it has been derived in [1], the field-induced tilt of the optic axis in a cholesteric, aligned in ULH texture, on applying an electric field normal to the helix axis, takes place in the plane of the sample and it is given by

$$\varphi(E) = \arctan \left[\frac{eEp}{2\pi K} \right], \quad (1)$$

where $e = e_s = e_b$ is the average flexoelectric coefficient with e_s and e_b being splay and bend flexoelectric coefficients, respectively. E is the applied electric field, p is the cholesteric pitch, and $K = \frac{1}{2}(K_1 + K_3)$ is the average elastic constant for splay (K_1) and bend (K_3) elastic deformations. At moderate applied electric field, i.e., $\varphi(E) \ll 1$, the field-induced tilt of the optic axis depends linearly on the field amplitude and can be simply expressed as

$$\varphi(E) \approx e^*Ep/2\pi, \quad (2)$$

where $e^* = e/K$ is an effective flexoelectric coefficient, a very important material parameter, which is temperature independent [5]. The linear dependence of $\varphi(E)$ with electric field gives rise to a linear electro-optic response [3]. In order to obtain a temperature-independent $\varphi(E)$, however, the cholesteric pitch has to be also a temperature-independent quantity. At present, there are some cholesteric liquid-crystal materials, commercially available, exhibiting such a feature. They are rather complex mixtures, some of them consisting of more than 20 single compounds [7]. Besides the temperature independence of the pitch, there is also another important requirement concerning the pitch magnitude. The cholesteric pitch should be smaller than the wavelength of the incident light in order to avoid losses of the transmitted light through the sample, due to the diffraction by the periodic texture of the cholesteric aligned in ULH texture. Hence, the magnitude of the cholesteric pitch is restricted from above. On the other hand, the pitch should be large enough, as seen from Eq. (2), in order to obtain a large $\varphi(E)$. This has to be taken into account when selecting liquid-crystal compounds for the flexoelectro-optic effect and optimizing their material parameters.

The flexoelectric properties of the cholesteric materials are of major importance for the amplitude of the flexoelectro-optic response. In previous studies, we did some

*Author to whom correspondence should be addressed. FAX: 046-31-772-3436. Electronic address: komitov@fy.chalmers.se

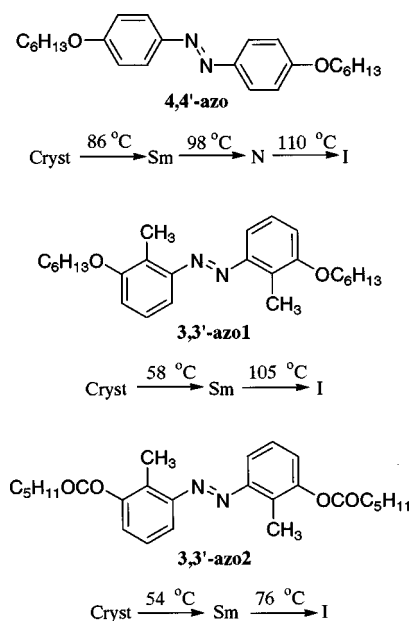


FIG. 1. Structures of azobenzene derivatives used as photochromic dopands.

evaluation of the influence of the molecular shape and of the net dipole moment on the flexoelectric properties of a nematic-liquid-crystal mixture [8]. We found that the bent shape of the molecules results in a substantial enhancement of the flexoelectric properties of the nematic [9].

In the present paper, we report on the influence of the molecular shape on the flexoelectric properties of cholesterics and, thus, on their flexoelectro-optic response. For this purpose, two different kind of photochromic dyes are used in this study. These dyes differ in the shape of their *cis*-isomers. The first kind of dye changes its molecular shape from linear, in the *trans*-form, to bent, in the *cis*-form, whereas the second one preserves its linear shape during the photoisomerization process [10]. The magnitude of their molecular net dipole moments, however, is quite similar before and after the photoisomerization. Thus, the influence of the molecular shape and of the molecular net dipole moment on the amplitude of the flexoelectro-optic response in short-pitch cholesterics has been estimated.

EXPERIMENT

The structure and phase sequences of the azobenzenes used as dopants are given in Fig. 1. Two short pitch cholesteric mixtures were used as host materials. The first one is the mixture TI-827 (Merck/BDH). The second one is a mixture of the short pitch cholesteric material CF1 (Hoffmann-LaRoche) with 8OCB (octyloxycyanobiphenyl) at a ratio of 89.5:10.5. Both host mixtures are with a right-handed pitch being practically constant over the whole temperature range of the cholesteric phase. The dyes were dissolved in the host mixtures in a concentration of 5 wt. %. The guest-host mixtures, each of them containing only one dye, were then injected in the isotropic phase into EHC cells with a 2- μm gap. (EHC cell is a conventional sandwich cell consisting of two parallel glass plates separated at constant distance. The substrates bear ITO electrodes precoated with a unidirectionally

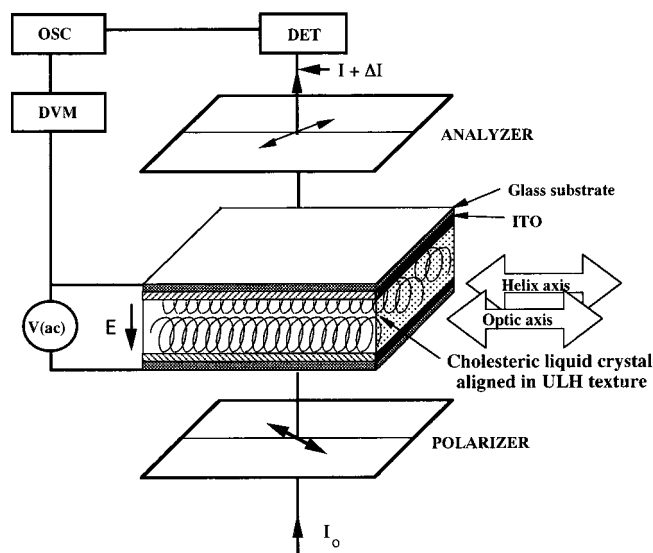


FIG. 2. Setup for measurements of field-induced tilt $\phi(E)$ of the sample optic axis. The voltage V (ac) (supplied by DVM) is applied across the cell, placed between crossed polarizers (AXP). The electro-optic response is detected and monitored by photodiode (DET) and oscilloscope (OSC), respectively.

rubbed polyimide alignment layer.) The cholesteric liquid crystal in the cells was aligned in ULH texture by slow-cooling from the isotropic phase under an applied electric field. The alignment of the liquid crystal was controlled using a Zeiss photomicroscope III Pol.

The electro-optic response was detected in a setup schematically presented in Fig. 2. The cell was inserted in a Mettler FP52 hot stage with temperature controlled within 0.1 $^\circ\text{C}$ accuracy. The hot stage was mounted on the microscope rotatory table and the cell was studied between crossed polarizers. Since the pitch of the mixtures is short, the helix axis of the sample aligned in the ULH texture takes on the role of the sample optic axis. Thus, the uniformly aligned sample behaves between crossed polarizers as a uniaxial optical plate. In this case, the intensity of the transmitted light through the cell reads as [3]

$$I = I_0 \sin^2\{2[\Psi_0 + \varphi(E)]\} \sin^2\left[\frac{\pi d}{\lambda} \Delta n\right], \quad (3)$$

where Ψ_0 is the angle between one of the polarizers and the sample optic axis at field-off state ($E=0$), d is the thickness of the liquid-crystal layer, Δn is the effective birefringence of the cell, and λ is the wavelength of the incident light in vacuum. If Δn is constant with the applied electric field, then the factor $\sin^2(\pi d \Delta n / \lambda)$ for our cells can be considered approximately equal to 1 (half-wave optical plate condition). However, Δn is constant with the field only if there is no helix unwinding induced by the field (this is the case when there is no dielectric coupling, i.e., dielectric anisotropy of the liquid crystal $\Delta\epsilon \approx 0$, or the applied electric field is well below the threshold for helix unwinding [$E_{\text{thr}} = \pi^2(4\pi K/p^2\Delta\epsilon)^{1/2}$]). In all experiments performed in this study, the applied electric field was kept below this threshold field. Setting the angle Ψ_0 at 22.5 $^\circ$, the in-plane field-induced tilt of the optic axis resulted in a linear modulation of the transmitted light inten-

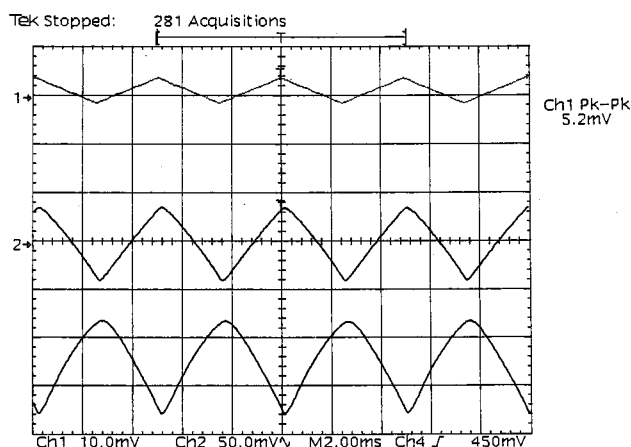


FIG. 3. Electro-optic response of the host mixtures TI-827 (curve 2) and CF1/8OCB (curve 3), respectively. Each sample is oriented with its optic axis at 22.5° with respect to the polarizer, and the applied voltage (curve 1) has the same direction of field polarity for both kinds of samples.

sity (linear electro-optic response) since, as mentioned above, the tilt angle is linearly proportional to the applied field. At fixed field polarity in the cell, the sign of the field-induced tilt depends on both helix handedness and sign of the effective flexoelectric coefficient e^* of the liquid crystal [3]. The electro-optic response of the host mixtures TI-827 and CF1/8OCB, detected at the same polarity of the applied electric field, is given in Fig. 3. As seen, there is a phase shift of 180° between the flexoelectro-optic response of the mixtures. Since they have the same pitch handedness, their e^* are with different sign, as it follows from [3]. Here, it should be mentioned also that e^* of the liquid crystal CF1 is almost zero. Therefore, the flexoelectric response of the mixture CF1 with 8OCB is basically originating from 8COB. Notice, the sign of e^* of the host mixtures does not change when mixing them with the azo dyes.

Photoisomerization of the azobenzene dopant in the cells was promoted by illumination with 365-nm light from mercury lamp (Zeiss) after passing through glass filters UV35 and UVD36 (Toshiba). The pitch of the cholesteric mixtures before and after the illumination was estimated from the wavelength of maximum reflection in the corresponding light transmittance curves recorded by means of an uv spectrophotometer (Shimadzu UV3100) using 10- μm -thick cells. The pitch can be calculated using the relation $\lambda = np$, where λ is the wavelength of the reflected light and n is the effective refractive index of the liquid crystal which is not being affected substantially by the photoisomerization [11].

The field-induced tilt of the optic axis was estimated from the electro-optic response of the cells using the method described in [12]. The measurements were carried out at room temperature for each sample before and after uv illumination.

RESULTS AND DISCUSSION

Study on light-induced changes of $\phi(E)$ as the effect of *trans*- to *cis*-photoisomerization of azobenzene dopants, with different positional and type of terminal substituents dissolved in chiral nematic liquid crystals, was carried out. The results are discussed in term of modification of e^* and p upon photoisomerization.

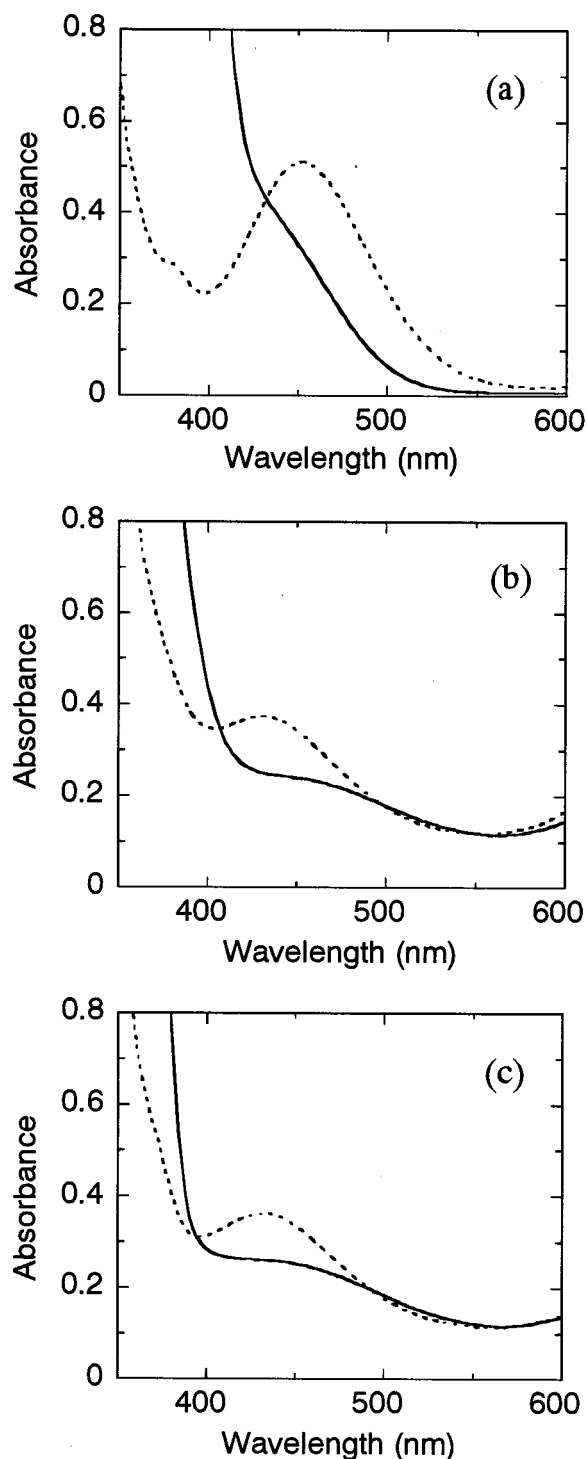


FIG. 4. Absorption spectra of (a) 4,4'-azo, (b) 3,3'-azo1, and (c) 3,3'-azo2 in CF1/8OCB mixture before (solid line) and after (dashed line) illumination with uv light.

The photoisomerization of azobenzenes in the chiral nematic mixtures proceeded to a large extent, i.e., approximately 90% and 80% for 4,4'-azo and 3,3'-azo1 or 3,3'-azo2, respectively, as monitored at the $n-\pi^*$ band of the azobenzenes. These values are in agreement with the photoisomerization of the dyes in nematic liquid crystals, as has been reported previously [10]. The spectra of the azobenzenes in CF1/8OCB mixtures before and after photostationary uv light illumination are shown in Fig. 4. In the spectra of the

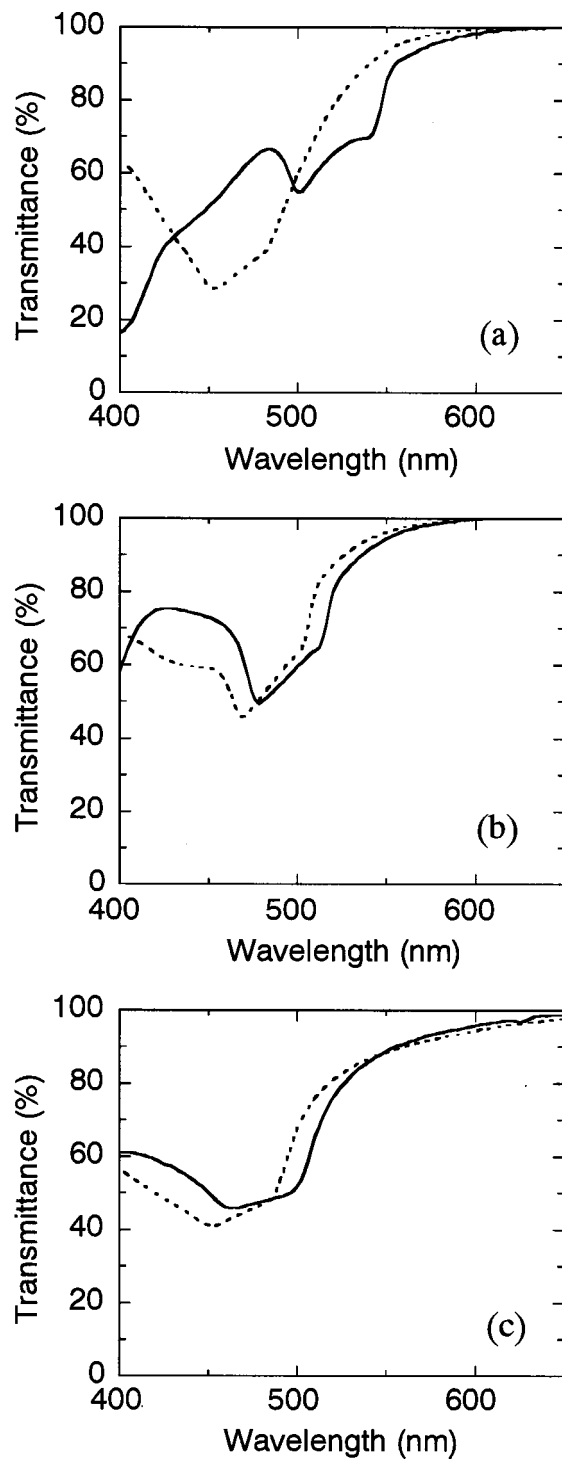


FIG. 5. Wavelength of light selective reflection λ of TI-827 doped with (a) 4,4'-azo, (b) 3,3'-azo1, and (c) 3,3'-azo2 before (solid line) and after (dashed line) uv light illumination.

azobenzenes in TI-827 mixtures, due to the shorter pitch of these mixtures, the dye absorption peaks are overlapping with the peak of the selective light reflection and these spectral dependences are, therefore, not shown here.

The pitch of the cholesteric mixtures under study was found to be in the interval 0.3–0.5 μm . Figures 5 and 6 show the change of the wavelength of selective reflection (proportional to the helical pitch) of the azo-dyes in TI-827 and CF1/8OCB, respectively, upon illumination of uv light and

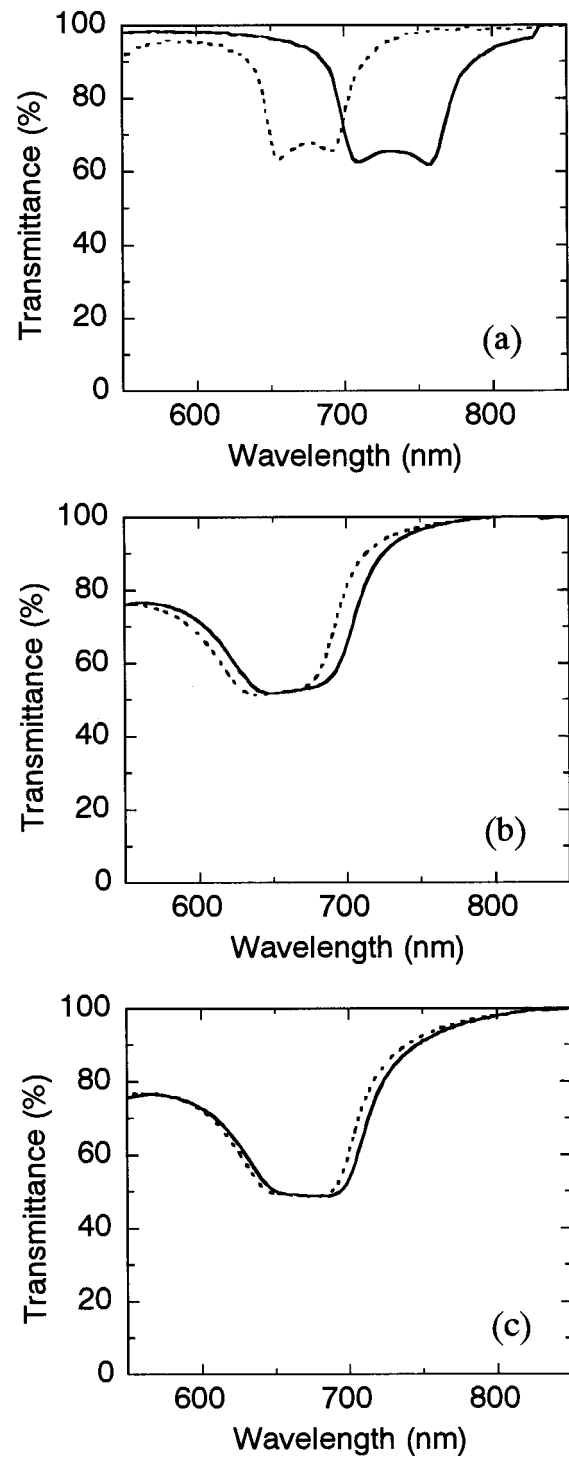


FIG. 6. Wavelength of light selective reflection λ of CF1/8OCB doped with (a) 4,4'-azo, (b) 3,3'-azo1, and (c) 3,3'-azo2 before (solid line) and after (dashed line) uv light illumination.

the results are summarized in Table I. As seen, the pitch of all mixtures shrinks under uv illumination. The largest shortening of the pitch takes place in the case of 4,4'-azo dye.

The field-induced tilt of the optic axes before $\phi_0(E)$ and after $\phi_{uv}(E)$ illumination with uv light is summarized in Table II. From the table, it seems that there are only slight changes of $\phi(E)$ for the 4,4'-azo containing mixtures after the illumination and no changes at all in the case of

TABLE I. Wavelength of light selective reflection λ of guest-host mixtures doped with azobenzenes before (λ_0) and after (λ_{uv}) illumination with uv light. The helical pitch can be estimated through the relation $\lambda = np$ with $n \approx 1.5$.

Host \ Dopant	TI-827		CF1/8OCB	
	λ_0	λ_{uv}	λ_0	λ_{uv}
4,4'-azo	520	467	732	673
3,3'-azo1	495	485	664	652
3,3'-azo2	481	467	668	664

3,3'-azo1 and 3,3'-azo2. However, when the changes in the helical pitch after uv light illumination are taken into consideration, then, according to Eq. (1), an increase of $\phi(E)$ for all mixtures, but in different degree, has been found. This can be seen from Table II, where the renormalized value of $\phi(E)$,

$$\phi_{\text{ren}}(E) = \phi_{uv}(E)\lambda_0/\lambda_{uv}, \quad (4)$$

is given for all mixtures. λ_0 and λ_{uv} are the wavelength of selective reflection before and after uv illumination, respectively. $\phi_{\text{ren}}(E)$ is the field-induced tilt after uv illumination rescaled to a pitch corresponding to the one before the illumination. As seen, the largest changes in $\phi(E)$ are detected in the case of 4,4'-azo dye. In order to evaluate the origin of the changes of e^* in the guest-host mixtures, we have to consider first the changes of the other important material parameters of the mixtures which take place under uv illumination.

The shift of transition temperatures of the cholesteric mixtures during *trans*- to *cis*-photoisomerization, which is very small indeed, is thought to have almost no influence on the measured values of $\phi(E)$. The short pitch cholesteric hosts TI-827 and CF1 are designed to have practically temperature-independent pitch over the whole cholesteric phase. Even after mixing CF1 with 8OCB, the pitch of the mixture remains a constant with the temperature. Moreover, all guest-host mixtures showed no temperature dependence of induced $\phi(E)$ in a broad temperature interval. Therefore, since the pitch is temperature independent, the e^* of the mixtures also does not depend on the temperature, even though the scalar order S decreases due to the photoisomerization process. This is due to the fact that e^* , the average flexoelectric coefficient, and K , the average elastic constant, have the same dependence on S , i.e., $e^* \approx S^2$ as well as $K \approx S^2$, and therefore their ratio e^* is independent of S and, hence, on temperature [5].

TABLE III. uv light-induced changes in the magnitude of the effective flexoelectric coefficient e^* for ~ 5.0 wt. % azobenzenes doped guest-host mixtures at room temperature and applied field $V_{pp} = 10$ V, $f = 100$ Hz. The ratio $m = e_{uv}^*/e^*$ is representing the relative change of e^* .

Host \ Dopant	m	
	TI-827	CF1/8OCB
4,4'-azo	1.06	1.20
3,3'-azo1	1.02	1.04
3,3'-azo2	1.03	1.06

Substantially, if we consider that the observed changes in the flexoelectric response of the mixtures, i.e., in the field-induced tilt of the optic axis $\phi(E)$, are due to the modification of the helical pitch and the effective flexoelectric coefficient, we can estimate the changes of the flexoelectric properties of the mixtures due to the photoisomerization by using the ratio $m = e_{uv}^*/e^*$ representing the relative change of e^* as an estimate of these changes. The ratio m is calculated using Eq. (2) and the data are given in Table III. In all mixtures, as seen, an increase of e^* after illumination was observed. The photoisomerization of the dyes resulted in an increase of about 2–6 % of e^* in the mixtures with 3,3'-azo1 or 3,3'-azo2, and an increase of 6% and 20% for mixtures with 4,4'-azo in TI827 and CF1/8OCB, respectively, which means that the changes of e^* for the guest-host mixtures with TI-827 are almost the same for the three dyes. Moreover, there is no significant difference between the behavior of e^* in these mixtures and the one obtained in the mixtures of CF1/8OCB with 3,3'-azo1 or 3,3'-azo2 dyes. In the mixture of CF1/8OCB with 4,4'-azo dye, however, this difference is substantial. Obviously, the character of the photoinduced changes of the dyes is of importance for the flexoelectric properties of the guest-host mixtures. The observed differences in the behavior of the mixtures, however, depend also strongly on the flexoelectric properties of the host mixtures.

The flexoelectric properties of the guest-host mixtures with CF1/8OCB are due to the presence of 8OCB. For the last one it is known that the compound possesses $e_s - e_b < 0$ and $e_s + e_b > 0$, indicating that e_s and e_b , and thus e^* , are with a positive sign and that $e_s < e_b$ [13,14], i.e., e_b is the one of importance for the flexoelectric properties of this compound. On the other hand, the guest-host mixtures with TI-827 possess $e^* < 0$, as found from the flexoelectro-optic response. If we consider only dipolar flexoelectricity, and ignore the quadrupolar one, we may conclude that in the case

TABLE II. Field-induced tilt of optic axes φ (degree) for ~ 5.0 wt. % azobenzenes doped in TI-827 and CF1/8OCB mixtures at room temperature and applied field $V_{pp} = 10$ V, $f = 100$ Hz. $\varphi_0(E)$, before uv irradiation; $\varphi_{uv}(E)$, after uv irradiation; $\varphi_{\text{ren}}(E) = \varphi_{uv}(E)\lambda_0/\lambda_{uv}$.

Host \ Dopant	TI-827			CF1/8OCB		
	$\varphi_0(E)$	$\varphi_{uv}(E)$	$\varphi_{\text{ren}}(E)$	$\varphi_0(E)$	$\varphi_{uv}(E)$	$\varphi_{\text{ren}}(E)$
4,4'-azo	2.53	2.41	2.67	1.22	1.34	1.46
3,3'-azo1	2.38	2.38	2.43	1.18	1.21	1.23
3,3'-azo2	2.36	2.36	2.43	1.46	1.53	1.55

of the mixtures with TI-827 as a host material, $e_s < 0$ and $e_s > e_b$. During the photoisomerization, the dyes changed substantially their molecular transverse net dipole moment, which should lead to an enhancement mostly of e_b and less of e_s . That is exactly what the experimental results indicate. The enhancement of e^* of the guest-host mixtures with TI827, even though very small, is almost the same for the three dyes since the flexoelectric response of these mixtures depends mainly on e_s , which slightly increases with the increase of the transverse molecular dipole moment of the dyes. On the other hand, since the flexoelectric response, i.e., e^* , of the guest-host mixtures with CF1/8OCB depend mainly on e_b , the increase of e^* of these mixtures due to the photoisomerization of the dyes will be more pronounced, as it has been indicated from the experiment as well. However, the largest increase of e^* has been found in the guest-host mixture with CF1/8OCB containing 4,4'-azo dye, which is about four times larger compared with the same guest-host mixtures containing the other two azo dyes, 3,3'-azo1 and 3,3'-azo2, respectively. Since the values of the net dipole moments of the three dyes before and after the uv illumination are almost the same, we may conclude that the change of the molecular shape in the case of 4,4'-azo dye, due to photoisomerization, appears to be the most important one for the observed enhancement of e^* . This result is a clear indication that the bent molecular shape of *cis*-4,4'-azo is more suitably fitted in the deformation pattern of the guest-host mixture, giving rise to the flexoelectric polarization, and, thus, resulting in an enhancement of e^* . This result is also in good agreement with the observed photoinduced enhancement of e^* of a nematic mixed with another kind 4,4'-azo dye reported in [8]. In this case, however, the value of e^* increased about 40% upon uv illumination, i.e., twice as much as the one found in the present study. This can be

related to the difference in the structures of both 4,4'-azo dyes. The 4,4'-azo dye of the present study has a symmetric molecular structure, whereas the one in the previous study contains oxygen only in one of its tails, i.e., being more asymmetric. Hence, the molecular dissymmetry seems also to contribute to the enhancement of e^* .

CONCLUSION

The effect of some molecular characteristics, such as net dipole moment and molecular shape, on the flexoelectric properties of short pitch cholesteric liquid crystals has been studied. For this purpose, two different kinds of azo-dyes have been dissolved in host materials with a different sign of their effective flexoelectric coefficients e^* . The azo dyes exhibited different photoisomerization behavior, which allowed us to estimate the influence of the molecular shape dissymmetry of the dyes on the flexoelectric properties of their mixtures. The largest increase of e^* , about 20%, has been observed in a guest-host mixture, with flexoelectric response substantially dependent on the bend flexoelectric constant e_b , containing an azo dye whose *cis*-isomer has a pronounced bent shape. This result is a direct indication of the importance of a certain type of molecular dissymmetry, in our case the bent shape, for obtaining an enhancement of the flexoelectric polarization, i.e., an increase of e^* . Increasing e^* , however, a substantial flexoelectro-optic response will be obtained at lower applied voltages. The results of the present study can be used as a guideline for choosing an appropriate strategy for syntheses of liquid-crystal materials with enhanced flexoelectric properties. However, further study on the influence of the molecular structure and its dissymmetry on the liquid-crystal flexoelectric properties, especially those of cholesterics, is required.

-
- [1] J. S. Patel and R. B. Meyer, Phys. Rev. Lett. **58**, 1538 (1987).
- [2] L. Komitov, S. T. Lagerwall, G. Scherowsky, and B. Stebler (unpublished).
- [3] L. Komitov, S. T. Lagerwall, B. Stebler, and A. Strigazzi, J. Appl. Phys. **76**, 3762 (1994).
- [4] P. Rudquist, T. Carlsson, L. Komitov, and S. T. Lagerwall, Liq. Cryst. **22**, 445 (1997).
- [5] P. Rudquist, L. Komitov, and S. T. Lagerwall, Ferroelectrics **213**, 53 (1998).
- [6] P. Rudquist, M. Buivydas, L. Komitov, and S. T. Lagerwall, J. Appl. Phys. **76**, 7778 (1994).
- [7] M. Schadt (private communication).
- [8] D. S. Hermann, P. Rudquist, K. Ichimura, K. Kudo, L. Komitov, and S. T. Lagerwall, Phys. Rev. E **55**, 2857 (1997).
- [9] L. Blixt, G. Scalia, L. Komitov, and W. Weissflog (unpublished).
- [10] C. Ruslim and K. Ichimura, J. Mater. Chem. **9**, 673 (1999).
- [11] S. Morino, S. Machida, T. Yamashita, and K. Horie, J. Phys. Chem. **99**, 10 281 (1995).
- [12] G. Andersson, I. Dahl, L. Komitov, S. T. Lagerwall, K. Skarp, and B. Stebler, J. Appl. Phys. **66**, 4983 (1989).
- [13] I. Dozov, Ph. Martinot-Lagarde, and G. Durand, J. Phys. (France) Lett. **44**, L-817 (1983).
- [14] I. Dozov, I. Pencev, Ph. Martinot-Lagarde, and G. Durand, Ferroelectr. Lett. Sect. **2**, 135 (1984).