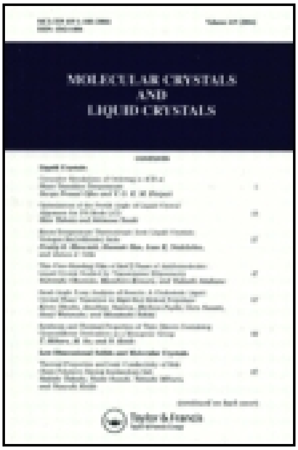

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Light-Induced Director Reorientation in Nematic Liquid Crystals Doped with Azobenzene-Containing Macromolecules of Different Architecture

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The results of the studies of the orientational optical nonlinearity of a nematic host doped with high-molar-mass compounds of different molecular architecture such as a comb-like polymer and a dendrimer containing azobenzene chromophores are presented. The nonlinearity induced by these compounds was found to be higher than that induced by the low-molar-mass dyes similar in structure to the light-absorbing constituents of the polymer and dendrimer. Possible reasons for the nonlinearity enhancement for macromolecular dopants are discussed.

Keywords: dendrimers; dyes; nematic liquid crystals; optical nonlinearity; polymers

INTRODUCTION

The electric field **E** of a light wave passing through transparent nematic liquid crystals (NLCs) rotates the director **n** toward the field direction and thus increases the refractive index of the extraordinary wave [1,2]. The corresponding ("positive") giant orientational optical

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nonlinearity is nine orders of magnitude as high as the Kerr nonlinearity of ordinary liquids [2]. The director reorientation is caused by the torque exerted by the light field **E** on the dipoles induced in rod-like molecules of an NLC by the same field. In the light interaction with a homeotropically aligned cells, the main characteristic features of the Freedericksz transition (the threshold at $\mathbf{n} \perp \mathbf{E}$ and the saturation of the director reorientation at high field) are observed [3,4].

If a nematic host is doped with dyes the orientational optical nonlinearity can greatly increase (by two orders of magnitude for the dye concentration of only $\sim$0.1 wt%) [5]. In dye-doped NLCs, the director can be rotated, depending on a dye, both toward and away from the field direction. In the latter case, the refractive index of the extraordinary wave decreases ("negative" nonlinearity) and the threshold reorientation can show up in a planar cell [6].

It was found later [7–11] that the nonlinearity sign (the sense of the light-induced director rotation) can be different for one and the same dye. Namely, the negative nonlinearity can transform into the positive one at decreasing the angle δ formed by **n** and the field **E** of the extraordinary wave (by changing the angle of light incidence on a cell or passing from the homeotropic to the planar cell) and at increasing the light intensity. If the angle δ is such that the nonlinearity is positive, the sign inversion can occur at passing from the extraordinary to the ordinary wave (by rotating the polarization plane of the light). The effect of the sign inversion was only observed for azodyes and explained [8] by the opposite signs of the nonlinearities induced in a nematic host by *trans*- and *cis*- isomers of an azomolecule (the negative nonlinearity for *trans*- isomers and the positive one for *cis*-isomers).

Initially, most molecules are in the *trans*- state. Under exposure to light, the isomers are excited and can undergo the conformational transition. For a given intensity, a certain steady-state ratio of the isomer concentrations is established. The probability of an isomer excitation (and with it the probability of the conformational transition) increases with decreasing the angle δ due to the orientational ordering of dye molecules in the nematic host. The order parameters of the isomers differ – the *trans*- isomers have a more pronounced rod-like shape and higher order parameter. Therefore, the ratio of the concentrations of *cis*- and *trans*- isomers in the light field also increases with a decrease in the angle δ which can lead to changing the nonlinearity sign. Similar phenomenon occurs due to the polarization plane rotation. An increase in intensity also changes the isomer concentrations and can affect the nonlinearity sign.

The mechanisms of the optical director reorientation itself in dye-doped NLCs still lack complete understanding, different models have been proposed [12–15]. It is however generally accepted that this phenomenon is due to an interaction of the ensemble of excited dye molecules having a nonsymmetrical (with respect to the director **n**) orientational distribution and the molecules of nematic host [16].

The orientational optical effects induced in a nematic host by high-molar-mass compounds were not studied until recently. However, such a study can be of great interest because the high-molar-mass compounds are in some respects, important for the light-induced molecular orientation, different from the low-molar-mass substances. For example, large molecules must have lower rotational diffusivity and larger moments of inertia. The spatial distribution of chromophores attached to a polymer chain can be highly inhomogeneous, unlike the low-molar-mass dyes dissolved in a nematic host.

The orientational nonlinearity due to high-molar-mass dopants was first observed for the MEH-PPV polymer [17]. In [18,19] the optical director reorientation in NLCs doped with comb-like polymers containing azobenzene chromophores in side chains were studied in detail. It was found that the nonlinearity induced by the comb-like polymers is much higher than the nonlinearity induced by the low-molar-mass dye analogous to the light-absorbing side fragment of the polymers.

Below we present the main features of the nonlinearities induced by the comb-like polymer and a dendrimer, the high-molar-mass compound of another molecular architecture.

EXPERIMENTAL

Figure 1 shows molecular structure of azobenzene-containing dopants. The macromolecular compounds were comb-like polymer **1** and the dendrimer **2** of the fifth generation. The molecular mass of the polymer **1** was $\sim 5 \cdot 10^4$. The polymer contains cyanobiphenyl and light-absorbing azobenzene side groups attached to the main polymeric chain. The dendrimer **2** contains azobenzene chromophores as terminal fragments. The absorption peaks of these substances are in the UV range; in the visible their absorption decreases with increasing light wavelength. For comparison, experiments were also performed with the low-molar-mass azobenzene dye **1′** analogous to the side fragment of the polymer **1** and the azobenzene dye **2′** similar in structure to the azobenzene chromophore of the dendrimer **2**.

The nematic host used was the liquid-crystalline material ZhKM-1277 (NIOPIK, Russia) consisting of biphenyls and esters. This material exhibits the nematic phase in the temperature range from -20° to 60°C and has a positive dielectric anisotropy. The

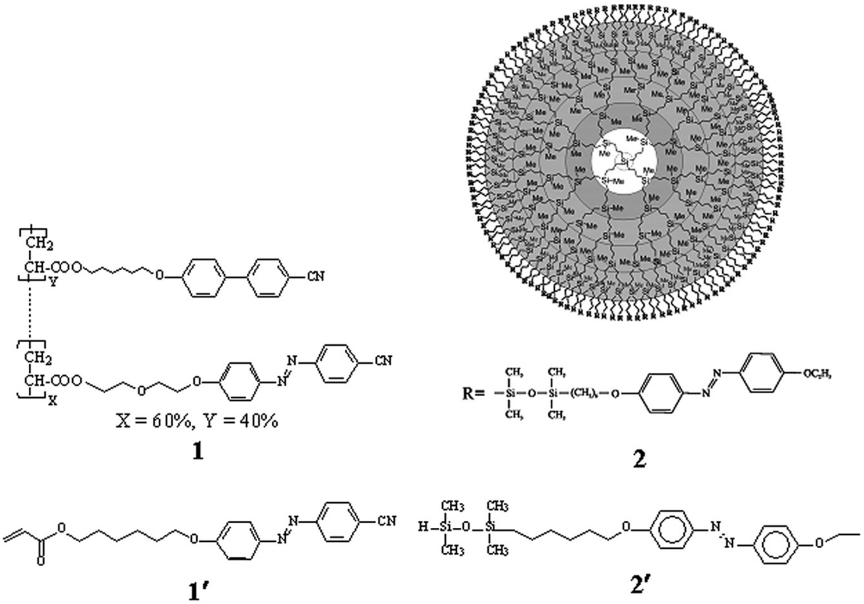


FIGURE 1 Chemical formulas of the comb-like polymer **1**, dendrimer **2,** and azobenzene dyes **1**′ and **2**′.

refractive indices of the extraordinary and ordinary waves are, respectively, 1.71 and 1.52 ($\lambda = 589\,\text{nm}$).

The presence of cyanobiphenyl fragments provides a good solubility (up to about 5 wt%) of the polymer **1** in the nematic host. The solubility of the dendrimer **2** was somewhat less, but no worse than 0.1 wt%. For the 0.5% solution of **1** in ZhKM-1277, the absorption coefficients were $\alpha_{\|} = 43,\ 33,\ 14\,\text{cm}^{-1}$ and $\alpha_{\perp} = 11,\ 8,\ 3\,\text{cm}^{-1}$ at $\lambda = 473,\ 488,\ 515\,\text{nm}$, respectively. The absorption coefficients of the **1**′—ZhKM-1277 mixture were the same as for the **1**—ZhKM-1277, provided that the chromophore concentrations coincide.

The thickness of the homeotropic and planar cells was $L = 100\,\mu\text{m}$. The planar alignment was produced by rubbing polyimide layers; homeotropic alignment, by using chromium stearyl chloride. The textures of the samples were checked with a polarizing microscope POLAM L-213 and found to be of good quality; no domain formation was observed independent of the dopant concentration.

To study the light interaction with NLCs we used the phenomena of aberration self-action of a light beam [3–4,9,20–21]. From the ring number N, it is possible to find the modulus of the nonlinear phase shift $|\Delta S|$ directly related to the change in the refractive index of the extraordinary wave. The character of the intensity transformation in the pattern upon transverse shift of the cell with respect to the beam allows one to determine easily the sign of the self-action (self-focusing or self-defocusing) and thus the sense of the director rotation [9].

Let us discuss this in more detail for the case of the self-focusing. Let us consider a light beam with the bell-shaped intensity profile (Fig. 2a). The wave front of the beam (initially plane) after passing through the NLC cell with distorted director field has the shape shown in Figure 2b. This shape is owing to a decrease in the light velocity due to the refractive-index increase, which is maximal at the beam axis. The wave front distortion implies a deflection of the rays comprising the beam and the corresponding increase in the beam divergence in

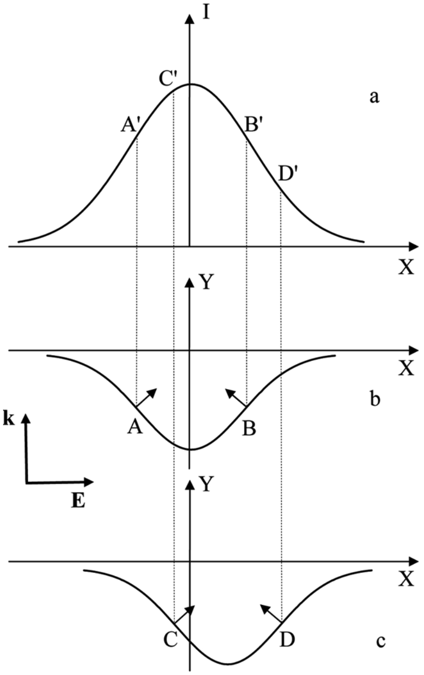


FIGURE 2 (a) Intensity profile of a light beam propagating along the Y axis; (b) the shape of the wave front of the beam passed through an NLC cell for the case of self-focusing; (c) the shape of the wave front upon fast shift of the NLC cell to the right. The pairs of rays (A, B) and (C, D) exhibit maximum nonlinear refraction. Points A′, B′, C′, and D′ in Figure 2a corresponds to the ray intensities.

the far field. The rays with maximum deflection angles (forming the outer ring of the aberration pattern) are shown by arrows at points A and B. The wave front surface is obviously axially symmetric and has the common symmetry axis with the intensity profile. The intensities of the rays A and B are equal. If we quickly shift now the NLC cell, e.g., to the right, the director field will be conserved (for a period smaller than the characteristic time (about several seconds) of the director relaxation) and the wave front surface will also be displaced in the same direction. Then (see Fig. 2c) the intensities of the rays C and D with maximum deflection becomes unequal: the intensity of ray C deflecting in the direction of the NLC cell shift appears to be higher than the intensity of ray D deflecting in the opposite direction. It is thus evident that shifting the cell results in the intensity redistribution in the aberration pattern. For the self-focusing (considered above), the intensity increases in that part of the pattern (the right in Fig. 2) to which the NLC cell is moved. For the self-defocusing, the opposite is the case.

In experiment, we used the radiation of argon or solid-state lasers in the range 458–532 nm. The light beam was focused into NLC samples by a lens with the focal length $f = 18\,\mathrm{cm}$. The NLC cell could be rotated about the vertical axis, changing the angle α of the light incidence. The planar cell was positioned in such a way that the director was in a horizontal plane. The linear polarization of the laser beam could be rotated by a double Fresnel rhomb to change the angle φ between the polarization direction and the horizontal plane (in the indicated geometry the values $\varphi = 0^\circ$ and 90° correspond, respectively, to the extraordinary and the ordinary waves inside NLC cells).

RESULTS

A typical ring-shaped aberration pattern appeared in the cross-section of the beam with extraordinary polarization passed through planar and homeotropic cells with the nematic host doped with the polymer **1**, dendrimer **2**, and the dyes **1′** and **2′** (see Fig. 3 for the case of the polymer).

The characteristic time of the pattern formation is $10\,\mathrm{s} - 1\,\mathrm{min}$ depending on the beam power P and the angle of incidence α; the relaxation time is about 10 s. These times imply that the pattern cannot be due to thermal effects, in which case the characteristic times are $\sim 10^{-2}\,\mathrm{s}$ [22].

When the polarization plane of the incident light beam (initially extraordinary) was rotated by an angle φ, we observed the appearance of a vertically polarized bright spot in the center of the aberration

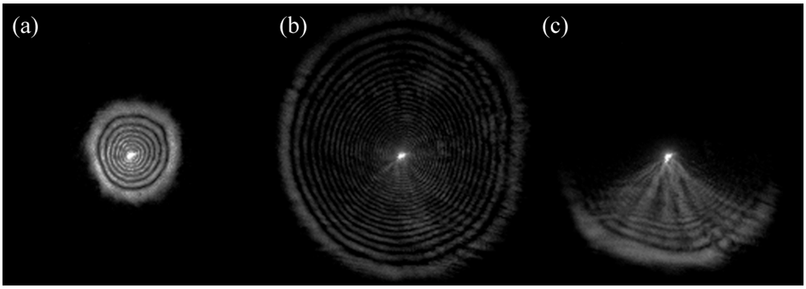


FIGURE 3 Aberration pattern in the cross-section of the light beam ($\lambda = 473\,\text{nm}$, $\alpha = 50^\circ$, $P = 2.2\,\text{mW}$) passed through the cells with ZhKM-1277 + 0.5% **1**: (a) the homeotropic cell; (b) the planar cell; and (c) direct determination of the self-action sign for the planar cell (transformation of the pattern upon rapidly shifting the cell upwards). Higher intensity in the lower part of the pattern suggests the self-defocusing (director is rotated away from the light field).

pattern. This indicates that the nonlinearity connected with molecular photo-transformations [23] cannot be responsible for the pattern formation. Indeed, the molecular photo-transformations change the order parameter and the refractive indices of both the extraordinary and ordinary waves. The change in the ordinary-wave refractive index would lead to the appearance of the vertically polarized rings and not the spot.

We can thus conclude that the aberration self-action in our experiment is due to the director reorientation. Besides of the bulk torques described in Introduction, this reorientation can be related to changes in the director alignment at the NLC cell substrates or the photorefractive effect. Surface effects however are usually accompanied by memorizing the distorted director field. No such memory was manifested in our experiments. In addition, the gliding effect in planar cells (the drift of the easy orientation axis) should be accompanied by polarization effects (generation of the ordinary wave for the extraordinary polarized incident light or the rotation of the aberration-pattern polarization) which were not observed in the experiment. The photorefractive effect (director reorientation due to an electric field generated by the charges produced at light absorption), if present, should show up for both the extraordinary and ordinary waves. In experiment, no substantial increase in the beam divergence was found for the polarization close to the ordinary one. Therefore, neither surface nor photorefractive effects can be responsible for the director reorientation.

The dependences of the ring number N on the beam power P are shown in Figure 4 (for dopants **1** and **1′**) and Figure 5 (for **2** and **2′**).

The results obtained for the cells doped with the polymer **1** and the dendrimer **2** proved to be qualitatively similar. It can be seen from Figures 4 and 5 (curves 1–3) that the main features of the Freedericksz transition (threshold at $\alpha = 0^\circ$ and the director rotation saturation at high power P) are manifested in the light interaction with planar samples. The corresponding optical nonlinearity is negative, as is obvious from the experimental geometry and can be directly confirmed by the self-action sign determination (Fig. 2c). Negative nonlinearity was also found for homeotropic cells (curves 4 in Figs. 4 and 5).

It should be noted that the negative sign of the nonlinearity and the manifestation of the main features of the Freedericksz transition prove conclusively that the observed self-action of light beam is caused by the director reorientation due to the excitation of dopants.

No change in the nonlinearity sign was observed at rotating the direction of incident polarization (i.e., at passing from the extraordinary to the ordinary wave), independently of the director alignment (planar or

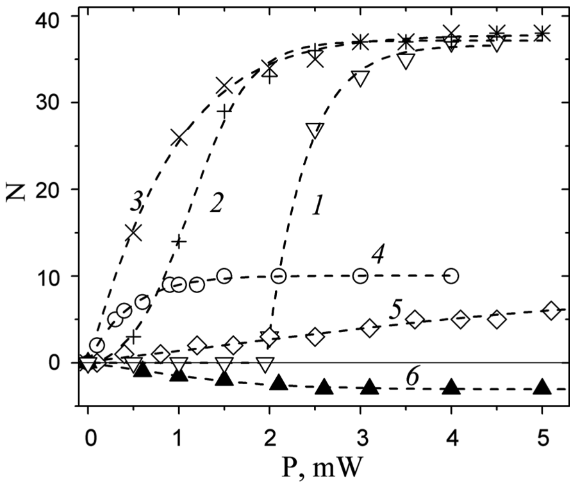


FIGURE 4 Dependences of the aberration ring number N on the light beam ($\lambda = 473\,\text{nm}$) power P for planar cell ZhKM-1277 + 0.5% **1** (α = (1) 0°, (2) 20°, (3) 40°)), homeotropic cell ZhKM-1277 + 0.5% **1**((4), $\alpha = 50^\circ$), homeotropic cell ZhKM-1277 + 0.3% **1′**((5), $\alpha = 50^\circ$), and planar cell ZhKM-1277 + 0.3% **1′**((6), $\alpha = 50^\circ$). The positive N values correspond to self-defocusing; the negative ones, to self-focusing.

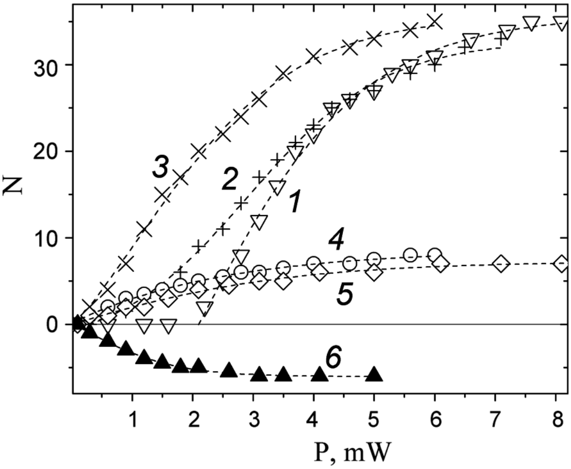


FIGURE 5 Dependences of the aberration ring number N on the light beam ($\lambda = 473\,\text{nm}$) power P for planar cell ZhKM-1277 + 0.1% **2** (α = (1) 0°, (2) 20°, (3) 40°)), homeotropic cell ZhKM-1277 + 0.1% **2** ((4), $\alpha = 50°$), homeotropic cell ZhKM-1277 + 0.5% **2′** ((5), $\alpha = 50°$), and planar cell ZhKM-1277 + 0.5% **2′** ((6), $\alpha = 50°$). The positive N values correspond to self-defocusing; the negative ones, to self-focusing.

homeotropic). The value of the nonlinearity was found to increase with decreasing the light wavelength and increasing the dopant concentration.

Different results were observed for the nematic host doped with low-molar-mass dyes **1′** and **2′**. In this case the sign-inversion nonlinearity was observed—it was positive for planar cells (curves 6 in Figs. 4 and 5) and negative for the homeotropic ones (curves 5 in Figs. 4 and 5). The change in the nonlinearity sign was also observed at the polarization rotation: in the case of oblique light incidence on the planar samples the positive nonlinearity is substituted by the negative one with increasing the angle φ.

As can be seen from Figures 4 and 5, the nonlinearities induced by the high-molar-mass substances **1** and **2** are much higher than the nonlinearities induced by the respective low-molar-mass dyes **1′** and **2′**. Comparing the nonlinear-optical response of the cells with ZhKM-1277 doped with the polymer **1** and the cells with undoped nematic host we determined the enhancement factor η. For the polymer concentration 0.1%, we found $\eta = -30$ in the geometries of oblique light incidence on the planar and homeotropic cells ($\lambda = 473\,\text{nm}$). The corresponding parameter $\eta_\alpha = \eta/(\alpha_\parallel + 2\alpha_\perp)$ (independent of dopant concentration) equals $\eta_\alpha = -2.3\,\text{cm}$. The η_α value determined for the normal light incidence at $\lambda = 488\,\text{nm}$ (by comparison of the Freedericksz transition thresholds in polymer doped planar and undoped homeotropic cells) was 2.5 times less. The parameter $\eta_\alpha = -2.3\,\text{cm}$ is much higher in magnitude than the maximum value $\eta_\alpha = -0.05\,\text{cm}$ for the negative nonlinearity (calculated from data[6] for anthraquinone dye D4). This parameter also exceeds the maximum positive value $\eta_\alpha = 0.8\,\text{cm}$ (calculated from data [24] for oligothiophene dye TR5).

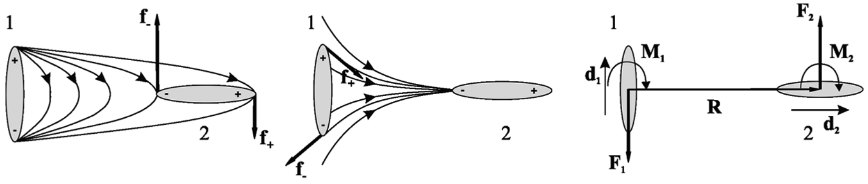
DISCUSSION

First of all, we notice that the phenomena observed for the low-molar-mass dyes **1′** and **2′** are quite similar to those observed previously for azobenzene dyes [7–11] and can be explained by the photoconformational transitions of dye molecules. In this context, it seems possible that increasing the nonlinearity at complication of the molecular structure (passing from **1′** to **1** and from **2′** to **2**) is due to suppression of the photoisomerization. In this case, the chromophores will mainly remain in the *trans*- state (inducing negative nonlinearity). However, the photoisomerization of the azobenzene compounds should be determined by the part of a molecule adjacent to the azobenzene group, which is identical for high-molar and low-molar-mass compounds. Therefore, the possibility of the photoisomerization suppression requires a separate investigation.

We shall discuss, following [19], another possible reason for the large nonlinearity associated with the high-molar-mass compounds using mainly the model [14].

An increase in the nonlinearity can be due to the difference in the symmetry of the spatial arrangement of the chromophore and nematic-host molecules: a low-molar-mass dye molecule is surrounded by nematic molecules all around, which is not true for the azobenzene fragment attached, e.g., to the polymeric chain.

Let us consider this in more detail. According to [14], the torque rotating the director is produced due to a change in the noncentral intermolecular (van der Waals) forces at orientationally selective excitation of the dye molecules. The specific feature of the noncentral interaction (i.e., the interaction at which the forces applied to the molecules are not parallel to the radius vector **R** connecting their centers) is the possibility of the occurrence of the nonzero torque rotating the molecules. This property of the noncentral interaction is illustrated in Figure 6 by a most simple example of two permanent dipoles $\mathbf{d}_1$ and $\mathbf{d}_2$ with the interaction potential



(a) (b) (c)

FIGURE 6 Interaction of two permanent dipoles. (a) The forces $\mathbf{f}_+$ and $\mathbf{f}_-$ acting on the positive and negative charges of the dipole (2) produce a clockwise torque $\mathbf{M}_2$. (b) The forces acting on the charges of dipole (1) also produce a clockwise torque $\mathbf{M}_1$. (c) The sum of the torques $\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2$ rotating the molecules is compensated by the torque of the forces $\mathbf{F}_1$ and $\mathbf{F}_2$, being the sums $\mathbf{f}_+ + \mathbf{f}_-$ for the dipoles (1) and (2), respectively.

$$\mathrm{U}^{(1,2)} = \frac{(\mathbf{d}_1\mathbf{d}_2) - 3(\mathbf{md}_1)(\mathbf{md}_2)}{\mathrm{R}^3}, \tag{1}$$

where $\mathbf{m} = \mathbf{R}/\mathrm{R}$.

Now let us consider the van der Waals interaction of the dye and nematic host molecules (Fig. 7) assuming that the host molecules are aligned exactly along the NLC director $\mathbf{n}$. In this case, the van der Waals potential has the form

$$\mathrm{U}^{(\mathrm{d,m})} = -\frac{\mathrm{B}}{\mathrm{R}^6}\left[(\mathbf{l}^{(\mathrm{d})}\mathbf{n})^2 - 6(\mathbf{l}^{(\mathrm{d})}\mathbf{n})(\mathbf{ml}^{(\mathrm{d})})(\mathbf{mn}) + 9(\mathbf{ml}^{(\mathrm{d})})^2(\mathbf{mn})^2\right], \tag{2}$$

where $\mathbf{l}^{(\mathrm{d})}$ is the unit vector parallel to the dye molecule axis and B is a coefficient depending on the electronic state of the dye molecule. The torque acting on this pair of molecules is

$$\mathbf{M}^{(\mathrm{d,m})} = \left[\mathbf{m} \times \frac{\partial \mathrm{U}^{(\mathrm{d,m})}}{\partial \mathbf{m}}\right]. \tag{3}$$

The change in this torque due to the dye excitation (changing the B coefficient) equals

$$\Delta\mathbf{M}^{(\mathrm{d,m})} = \frac{6\Delta\mathrm{B}}{\mathrm{R}^6}\Big((\mathbf{l}^{(\mathrm{d})}\mathbf{n}) - 3(\mathbf{ml}^{(\mathrm{d})})(\mathbf{mn})\Big)\Big((\mathbf{mn})[\mathbf{m}\times\mathbf{l}^{(\mathrm{d})}] + (\mathbf{ml}^{(\mathrm{d})})[\mathbf{m}\times\mathbf{n}]\Big). \tag{4}$$

This torque should be averaged over the spatial arrangement of the molecules. Assume first that the positions of the centers of

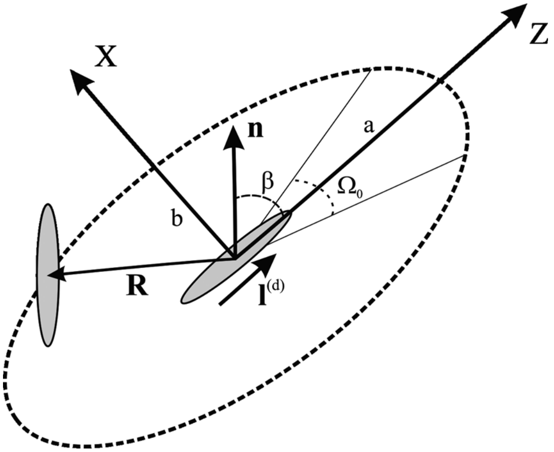


FIGURE 7 Geometry of the interaction between the dye molecule (or polymer side group, dendrimer terminal fragment) and the surrounding nematic molecules: $\mathbf{l}^{(d)}$ is the unit vector parallel to the dye molecule axis; **R** is the radius vector joining the centers of the molecules; **n** is the NLC director; β is the angle between $\mathbf{l}^{d}$ and **n**; a and b are the lengths of the major and minor semiaxes of the ellipsoid on which the nematic-molecule centers can be located; and Ω_0 is the polar angle within which (in the case of a high-molar-mass compound) the presence of the nematic-host molecules is excluded.

nematic-host molecules are uniformly distributed over the surface of uniaxial ellipsoid with the semiaxis lengths a and b (a>b) (the case of low-molar-mass dye). In this case the averaged torque is

$$\left\langle \Delta\mathbf{M}^{(\mathrm{d,m})} \right\rangle = \frac{\mathrm{N_n}}{\mathrm{S_{el}}} \int_{\mathrm{s}} \Delta\mathbf{M}^{(\mathrm{d,m})} \mathrm{dS}, \tag{5}$$

where $\mathrm{N_n}$ is the number of surrounding molecules and the integration is taken over the ellipsoid surface. Simple calculation [19] shows that

$$\left\langle \Delta\mathrm{M}^{(d,m)} \right\rangle = \frac{3\Delta\mathrm{B}}{b^6} g(\mu)(\mathbf{n}\mathbf{l}^{(d)})[\mathbf{n} \times \mathbf{l}^{(d)}], \tag{6}$$

where

$$g(\mu) = \frac{\int_0^{\pi} d\Omega \sin\Omega (1-\mu\cos^2\Omega)\sqrt{1-\mu(2-\mu)\cos^2\Omega}(15\cos^4\Omega - 12\cos^2\Omega + 1)}{\int_0^{\pi} d\Omega\ \sin\Omega \frac{\sqrt{1-\mu(2-\mu)\cos^2\Omega}}{(1-\mu\cos^2\Omega)^2}}, \tag{7}$$

$\mu = (a^2 - b^2)/a^2$, and Ω is the polar angle with respect to the Z axis (Fig. 7). If $a = b$, $g = 0$. That is, the presence of the dependence of the distance between the molecule centers on the radius vector **R** is required for the nonzero torque. In the case of the high-molar-mass compound, the nematic host molecules are not distributed within the full solid angle 4π, e.g., due to the presence of the polymeric backbone. To take this into account, the integration in (7) should be performed over a certain range $\Omega_0 < \Omega < \pi$. Then, the g value proves to be nonzero $g = (3\cos^5\Omega_0 - 4\cos^3\Omega_0 + \cos\Omega_0)/2$ even at $\mu = 0$.

This simple example illustrates the possible effect of the symmetry of the spatial molecular arrangement on the optical nonlinearity. It should be noted that consideration of the nonlinearity sign requires the account of the difference in the shapes of the isomer molecules.

CONCLUSION

We studied experimentally the light-induced director reorientation due to the light absorption by (1) two high-molar-mass compounds of different architecture (comb-like polymer and dendrimer) containing azobenzene chromophores and (2) two low-molar-mass azobenzene dyes analogous to the azobenzene chromophores of the polymer and dendrimer. The orientational nonlinearity induced by the polymer and dendrimer is always negative, while that induced by the dyes can be of any sign depending on the interaction geometry of the light field and NLC director. The induced nonlinearity is higher for high-molar-mass compounds, as compared to the low-molar-mass dyes. Possible reasons for increasing the nonlinearity with complication of molecular structure are discussed.

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