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Comparison of photoinduced reorientation of *ortho, meta,* and *para* methyl red doped nematics on rubbed polyimide

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ABSTRACT

We compare the photoinduced reorientation of the easy axis on rubbed polyimide surfaces for the nematic E7 doped with three isomers of methyl red; *ortho*, *meta*, and *para*. Using optical techniques, the angle and the pitch of the director at the polymer surface were measured before, during, and after photoexcitation of the dye. Optical absorbances were also measured before and after photoexcitation. Extrapolation lengths, hence anchoring energies, were determined with the on/off application of a magnetic field for *meta* and *para*-methyl red doped nematics. Because of an elastic reorientation of the easy axis in the presence of the magnetic field, we could not determine the extrapolation length of the *ortho*-methyl red doped nematic. Our results confirm that photoinduced reorientation is facilitated by desorption of all dyes from the polymer surface. While there is little evidence of weak photoinduced adsorption of *meta*- and *para*-methyl red to the surface during photoexcitation, there is strong evidence of photoinduced adsorption of *ortho*methyl red, which is long lasting.

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1. Introduction.

Nematic liquid crystals doped with azobenzene (*azo*) dyes facilitate an enhancement of the optically induced reorientation of the liquid crystal director. This enhancement is achieved via photoexcitation of the dye, normally in the *trans* conformation, sometimes with subsequent isomerization to the *cis* conformation. Early work has demonstrated that this enhancement is, in part, the result of a bulk effect, where it has been suggested that an asymmetric distribution of *trans, cis,* and excited state dye molecules exert a torque both through a molecular field¹ and diffusion asymmetry^{2,3}. This torque is proportional to the intensity of light incident on the sample.

For some *azo* dye-doped samples the magnitude of the enhancement is such that reorientation of the liquid crystal director cannot be explained by the bulk effect alone. Evidence exists of photoinduced reorientation of the easy axis at the liquid crystal/polymer surface^{4,5}. For example, it has been observed that liquid crystal samples doped with the *azo* dye *ortho*-methyl red and with one surface coated with fluorinated polyvinyl cinnamate (PVCN-F) demonstrate a significant amount of reorientation of the easy axis on that surface^{6,7,8,9,10,11}. While Andrienko *et al.*¹² argue that this reorientation is the result of the transfer of angular momentum from the light to the dye, Lucchetti, Tifi, and Simoni¹¹ observed what they referred to as "sliding" on similar samples irradiated with circularly polarized light. The sliding was always in the same direction regardless of the handedness of the polarization of the light leading to the conclusion that transfer of angular momentum is not significant and that the reorientation is a surface effect. They describe this effect as a Surface Induced Nonlinear Effect (SINE)¹³ arising from photo-induced modifications of the anchoring conditions. It has been proposed that these modifications can be explained by the photoinduced desorption of the *trans* isomer from the polymer surface

and photoinduced adsorption of the dye back onto the surface¹⁴. Results of Fedorenko, *et al.*⁸ and Dubtsov, *et al.*¹⁵ support this argument. In addition, Lucchetti, Gentili, and Simoni¹⁶ have reported "colossal" optical nonlinearities when a low frequency electric field is applied to methyl red doped nematics. Considering the observation by Pagliusi, *et al.*¹⁷ that there is a buildup of electric charges near the electrodes reducing the effective voltage drop across the sample, they suggest that photo-induced desorption of dye molecules impacts the density of surface charges that screen an applied field. Most recently, Lucchetti and Simoni¹⁸ compared the effects of applied DC and AC fields, and of changing the polarity of the DC field. They argue that negative charge complexes, in fact, are involved in the light induced desorption and adsorption process, and that both the transient responses and the light-induced permanent anchoring have the same origin. In addition, their results indicate that the role of *trans* to *cis* isomerization is limited.

This photo-induced reorientation of the easy axis can be compared with the gliding of the easy axis observed when an external torque is applied via an electric or magnetic field to an undoped liquid crystal^{6,19,20,21}. In that case, both azimuthal (in-plane) and zenithal (out-of-plane) gliding for undoped nematics have been observed^{19,22}. While such gliding is most prominent on soft polymer surfaces, such as polymethyl methacrylate (PMMA), it has also been reported to occur on hard polymer surfaces such as polyimide (PI)^{20,22}. Various workers have suggested that for undoped nematics, this gliding of the easy axis might also be the result of adsorption and desorption of the liquid crystal on the polymer surface^{7,8}. Other explanations include a mutual reorienting of the liquid crystal and polymer network^{6,19,20}, or the existence of sub-layers with different physical properties near the polymer surface^{23,24}. One characteristic of this type of gliding is that it is not only slow, but appears to be plastic. Upon removal of the external torque,

the easy axis does not immediately return to its original orientation. That return can take hours or days, and is probably the result of the bulk liquid crystal molecules exerting a torque to bring the easy axis back to its original orientation.

While many of the reports of photoinduced reorientation of the easy axis involve the dye methyl red on PVCN-F, it has also been observed on other polymer surfaces. Lucchetti and Simoni recently reported photoinduced reorientation of the easy axis on cells without any special coating¹⁸. We have also measured photoinduced reorientation of the easy axis on both rubbed PI and unrubbed polymethyl methacrylate⁵, confirming that photoexcitation of *azo* dyes in nematics induces easy axis reorientation on rubbed PI as well as other polymers. We have found that this also involves a *memory* effect, consistent with the results of Ouchi, *et al.*²⁵. In particular, for a series of measurements, the amount of reorientation increased with each subsequent measurement. In addition, we found that illumination of the sample with circularly polarized light increased the amount of subsequent reorientation by several times. This appears to support the photoinduced desorption/adsorption hypothesis.

In this paper, we continue this study of the photoinduced reorientation of the easy axis for methyl red doped nematics on polyimide surfaces. In particular, we are interested in comparing the behaviors of three methyl red isomers, *ortho, meta*, and *para*, where the designation corresponds to the position of the carboxyl group on the phenyl ring, as shown in Fig. 1. Quantum mechanical calculations²⁶ indicate that all three isomers are planar as neutral species, meaning the dihedral angle between the phenyl rings is zero. However, the planarity of the *ortho* dye is stabilized by *intra*molecular hydrogen bonding, which does not occur in the other two dyes. In the absence of hydrogen bonding, such as when *ortho* methyl red is in the anionic form, the dihedral angle is calculated to be 30°. However, the *meta* and *para* dyes remain planar when

in the anionic form, as indicated by quantum chemical calculations. As opposed to the *ortho* dye, these dyes are only capable of *inte*rmolecular hydrogen bonding. In other words, the molecular orbitals describing the *meta* and *para* dyes are symmetrically different from those of the *ortho* dye, indicating different chemistries. The question we ask is how photoinduced reorientation of the easy axis differs for the three dyes.

Although many studies involved cells consisting of a reference surface coated with the rubbed polyimide (PI), which is known to strongly anchor, and a test surface coated with fluorinated polyvinyl cinnamate (PVCN-F) or just polyvinyl cinnamate (PVCN)⁶⁻¹⁷, in this study we coated both surfaces with rubbed polyimide. As mentioned, Lucchetti and Simoni¹⁸ have shown that photoinduced reorientation of the easy axis does not need any special coating. In our case there is no need for specially prepared reference or test surfaces, as we are interested in photoinduced reorientation on rubbed PI. As we will discuss, a reference surface is, nevertheless, maintained. In section 2 we describe our experiment. In section 3 we present results and discussion, with conclusions in section 4.

2. Experiment.

Dyed thermotropic liquid crystal samples (E7) were prepared at concentrations of 0.2% (dye/liquid crystal) by weight. Cleaned glass microscope slides were spin coated with polyamic acid and cured to PI in an oven. Uniformity of coating was determined from optical interference. Cured PI slides were rubbed with velvet. Cells were constructed using 20 µm spacers. In constructing the cells, the rubbing directions of the slides were slightly misaligned, thereby allowing a small initial twist in the director. This was done for calibration purposes, as will be described later. Epoxy was used to cement slides together and they were held together with

clamps while curing. The cell path lengths were then determined interferometrically in the red/infrared end of the spectrum, as we could not get interference fringes with reasonable visibility at the blue/green end of the spectrum. Typically the cells were found to be between 15 and 18 μ m in length with a standard deviation on the order of 0.2 μ m. This standard deviation is consistent with an optical flatness on the order of $\lambda/4$ at the blue/green end of the spectrum. In this study, our cell thicknesses were slightly smaller than the spacers, probably because of our clamping procedure.

Cells were filled with the dyed nematics and examined under a cross-polarized microscope to determine both quality of alignment and the twist angle. The pitch was calculated as the cell thickness divided by the twist angle. Using an Ocean Optics spectrometer, the absorption spectra of the samples were taken both before and after the photoinduced reorientation experiment.

The anchoring energy was measured, using a technique adapted from that developed by Jánossy²⁷, in an experimental set-up shown in Fig. 2 and described elsewhere⁵. The sample was placed between poles of an electromagnet, oriented so that the magnetic field, when applied, was approximately perpendicular to the initial orientation of the director and parallel to the plane of the sample. The magnetic field strength was set at 0.2T. A probe beam, from a white light source and filtered to exclude any light that might induce photoexcitation of the dye, was polarized parallel to the rubbing direction on the entrance face of the sample and passed through the sample. As explained by Jánossy²⁷, the probe must be from an incoherent source and the length of the sample must be long enough to avoid interference effects between the ordinary and extraordinary polarizations. The polarization state of the exiting probe, as described by the Stokes parameters, was measured by passing the signal through the photoelastic modulator (PEM – 100, Hinds Instruments) and then through an analyzer whose polarization was oriented 45° to

the initial polarization of the probe. The second harmonic signal from the PEM gave the second Stokes parameter, which, as shown by Jánossy²⁷, is proportional to the polarization angle, θ , of the exiting beam. This, in the Mauguin limit, is the orientation of the director, φ , at the exit surface. The sample was rotated so that the initial second harmonic signal was zero. The signal was then calibrated by measuring the second harmonic signal as the PEM was rotated through $\pm 2^{\circ}$. While ideally it would have been better to rotate the analyzer along with the PEM, this was logistically not possible, as the PEM and the analyzer could not be placed on the same mount. However, we were able to determine that for such a small rotation, any impact was negligible. The initial twist angle of the director was included in this calibration. To account for the initial twist to the director, it was added to the angle determined from the second harmonic signal during data analysis. The first harmonic signal from the PEM gave the third Stokes parameter, which, as shown by Jánossy²⁷, is inversely proportional to the pitch of the liquid crystal at the exit surface. For simplicity, we will refer to the inverse of the pitch as the twist, so the first harmonic signal is proportional to this *twist*. The first harmonic signal was calibrated to the initial twist. In general, we found that this calibration was consistent between samples with different initial twists, indicating that any offset in the signal from possible impact of other optical components was negligible. This method of determining both the orientation and twist of the director at the exit face is very sensitive to small changes in angle and in twist. It also includes whether the angle and twist are negative or positive in our experimental reference frame. The director angle and twist at the exit face were measured during a sequence in which the magnetic field was turned on and off. As will be explained in the results section, the extrapolation length, which is inversely proportional to the anchoring strength, was calculated by taking the ratio of the change in the director angle to the change in the twist, $\Delta \varphi / \Delta \varphi'$, as the

magnet is turned on and off. As shown by Jánossy²⁷, this ratio and its relationship to the extrapolation length at the probe exit is independent of whether the easy axis at the probe entrance also undergoes some photoinduced reorientation.

Photoinduced azimuthal reorientation of the easy axis was achieved using an Ar^+ laser tuned to the 488-nm line and polarized at an angle of $+45^\circ$ with respect to the initial polarization of the probe beam. The pump/probe configuration with the pump and probe beams entering the sample from opposite faces, the pump polarization at 45° to the initial polarization of the probe beam, and the probe beam parallel to the director at the probe entrance is the same as that described in our previous work, as well as in the most recent work of Lucchetti and Simoni¹⁸. The laser was set to a power of 15 mW and was collimated to have an irradiance of 16 mW/cm² at the sample. Before, during, and after irradiation, the director angle and the twist at the probe exit was measured while the magnetic field was repeatedly turned on and off. Typical results are shown in Figs. 3 – 5.

Even though attenuation of the pump beam as it propagates through the sample is not large, we do not observe significant reorientation of the easy axis at the probe entrance. With the pump entering the sample at the probe exit with a polarization 45° to the director, the birefringent nematic sample initially behaves as a phase retarder. Because the cell thicknesses have a standard deviation on the order of $\lambda/2$ and the pump beam diameter is relatively large, at the surface of the probe entrance the pump is randomly polarized and cannot induce significant reorientation. Subsequent reorientation of the director at the probe exit results in the nematic being twisted. If that reorientation were large enough, the polarization of the pump would no longer be randomized. Rather it would be elliptical, and, in the Mauguin limit, its major axis would follow the director as it propagates through the sample. Therefore, even though we have

observed photoinduced reorientation on strongly anchoring surfaces such as rubbed polyimide, there is still very little reorientation of the easy axis at the probe entrance. That cell surface still acts as a reference surface, similar to that in previous studies.

3. Results and Discussion.

We observe photo-induced reorientation of the director at the *rubbed* polyimide surfaces for all three dyed samples. However, as can be seen in Figs. 3 - 5, the ortho dye-doped nematic behaves differently than meta and para dye-doped nematics. Most obvious is that while the director of *ortho* dye-doped nematic rotates *toward* the pump polarization by as much as 30° or more, the directors of the *meta* and *para* dye-doped nematics rotate away from the pump polarization and only by about 4° and less than 1°, respectively. Although what is significant is that the qualitative observation that the rotation of the director for the ortho isomer is much greater than that of the *meta* and *para* isomers, we were able to confirm that the rotation angles measured for the ortho were reasonably accurate by subsequently measuring them using a polarizing microscope. While not shown in these figures, often the ortho dye-doped nematic exhibits an initial transient rotation away from the pump polarization before rotating towards the pump polarization. This behavior of the ortho dye-doped nematic is consistent with the results and interpretation of Fedorenko, et al.¹⁰, Ouskova, et al.¹⁴, and Lucchetti and Simoni¹⁸. Lack of evidence of rotation reversal toward the pump polarization for the meta and para dye-doped nematics would suggest that if photoinduced adsorption occurs in these samples, it is not significant. Although the 488-nm absorption cross-sections of the *meta* and *para* dye-doped nematics are smaller than that of the ortho dye-doped nematic by a factor of two to three (c.f. Figs. 9-11), since the *meta* and *para* isomers show considerable relaxation of the photo-induced

director rotation once the pump is turned off and since relaxing species enter the rate equations, we do not believe that the smaller cross-sections can explain why, in these samples, the director continues to rotate away from the polarization, does not change rotation direction, and does not exhibit such a large reorientation. Therefore, consistent with the arguments of Lucchetti and Simoni, smaller cross-sections should only result in a change in the rate of reorientation and not the rotation direction¹⁸. We also see that while none of the directors of the three dye-doped nematics return to their original orientation, this quasi-permanent reorientation is much more significant and longer lived for the *ortho* dye-doped nematics.

For all three dye-doped nematics the photoinduced change in director angle, φ , is associated with a change in the orientation of the easy axis at the polymer surface. It can be shown that the relationship between the director angle and twist at the surface is determined by the balance of torques and given by

$$\varphi' = -\frac{1}{2\xi} \sin\left[2\left(\varphi - \varphi_{E}\right)\right] = -\frac{1}{\xi}\left(\varphi - \varphi_{E}\right)$$
(1)

where $\varphi' = d\varphi/dz$ is the twist, $\xi = K_{22}/W$ is the extrapolation length with *W* the anchoring strength and K_{22} the Frank constant, and φ_E is the azimuthal angle of the easy axis. Since the anchoring strength and the Frank constant are both positive, the extrapolation length must also be positive. Eq. 1 therefore predicts that if the easy axis is not rotating, the director angle at the surface and the twist must change in opposite directions, $d\varphi = -\xi d\varphi'$. The director angle and the twist both changing in the same direction is evidence that the easy axis itself must be rotating. Figs. 3 – 5 confirm the photoinduced change in easy axis for all three samples, as the director angle and the twist both change in the same direction when the pump beam is turned on. Comparisons of the director angle and the twist at the probe exit for all three samples show that there is some photoinduced reorientation of the director at the probe entrance, but that it is quite small and significantly less than that at the probe exit. This is indicated by plots of the director angle versus the twist for all three samples when the pump is subsequently turned off and there is no applied magnetic field, an example of which is shown in Fig. 6 for the *ortho* dye-doped sample. All plots give negative intercepts, and, within an experimental uncertainty that varies between 10% and 50% depending on the sample, slopes that are on the order of the cell thickness. For the *meta* and *para* dye-doped samples, the final twist after photoinduced reorientation of the easy axis was too small to measure under a polarizing microscope. Measurement of the final twist of the *ortho* dye-doped sample under a polarizing microscope was consistent with our plots of the director angle and twist such as that shown in Fig. 6.

Another significant difference between the *ortho* dye-doped nematic and the *meta* and *para* dye-doped nematics is shown in Figs. 7 – 9. These figures give a close-up view of the director angle and twist at the probe exit as the magnetic field is turned on and off before the pump is applied. To interpret these figures, it is important to note that the initial director angle at the probe entrance is 0° . The magnetic field is approximately perpendicular, however, to the initial director angle at the probe exit. Therefore, with respect to the director at the probe entrance, the magnetic field is oriented at angles of about 85° , 97° and 93° for the *ortho*, *meta*, and *para* dye-doped nematic samples, respectively. In other words, in the bulk, we would expect the magnetic field to rotate the director in the positive direction for the *ortho* dye-doped nematic, and in the negative direction for the *meta* and *para* dye-doped nematic. All things being equal, these

differences, which are only a consequence of cell construction, should not have any impact on our results or their interpretation.

These figures show that the angle and twist of the *meta* and *para* dye-doped nematics change in opposite directions with the application of the magnetic field. On the other hand, the angle and the twist of the ortho dye-doped nematic change in the same direction. At the probe exit, both the director angle and the twist for the *ortho* dye-doped nematic become more negative in the presence of the magnetic field. According to Eq. 1 and the previous discussion, the magnetic field must therefore be responsible for a torque not just on the director, but also on the easy axis of the ortho dye-doped nematic resulting in its rotation even before any photoinduced reorientation. This cannot be the result of any photoinduced effects on the entrance surface, as the measurement only corresponds to changes with the application of the magnetic field. This rotation is not the same as the gliding observed when a magnetic field is applied to an undoped nematic on a soft polymer^{6,19,20,21,22,23,24}. It is *elastic*. The easy axis returns to its original orientation when the magnetic field is removed. The ratio of the change in director angle to the change in twist, $\Delta \phi / \Delta \phi'$, is calculated to be 0.14 ± 0.04 µm, which is much smaller than the cell length. Therefore, the torque applied by the magnetic field on the easy axis at the probe exit must be in the opposite direction to the torque applied by the magnetic field on the director in the bulk nematic. There is little evidence that the magnetic field facilitates a similar elastic rotation on the *meta* and *para* dye-doped nematics.

Elastic rotation for the *ortho* dye-doped nematic in the presence of the magnetic field continues during photoexcitation of the dye. When the pump is applied, as shown in Fig. 3, both the director angle and the twist at the probe exit become positive and quite large with a ratio slightly less than the cell length. When the magnetic field is applied, both the director angle and

the twist at the probe exit decrease. Just as before the application of the pump, the ratio $\Delta \varphi / \Delta \varphi'$ is significantly less than the length of the cell, changing from $0.25 \pm 0.08 \ \mu\text{m}$ to $0.08 \pm 0.04 \ \mu\text{m}$. Therefore, the torque on the easy axis at the probe exit continues to be in the opposite direction of the torque on the director in the bulk nematic. The decrease in the director angle at the probe exit indicates that the torque, hence the elastic rotation of the easy axis at the probe exit, is away from the magnetic field. When the pump is turned off, the director angle at the probe surface decreases slightly, *c.f.* Fig. 3. With the application of the magnetic field, the ratio $\Delta \varphi / \Delta \varphi'$ remains positive and increases to $0.4 \pm 0.1 \ \mu\text{m}$. Again, the elastic rotation is away from the magnetic field.

For both the *meta* and *para* dye-doped nematics, the director angle and the twist at the probe exit change in opposite directions, as seen in Figs. 8 and 9. If there is any elastic rotation of the easy axis in the presence of the magnetic field, it is very weak. Therefore Eq. 1 can be used to estimate the extrapolation length for the *meta* and *para* dye-doped nematics, by considering that if the easy axis angle, φ_E , does not change significantly during the application of the magnetic field, then the extrapolation length is given by

$$\xi = -\frac{\Delta\varphi}{\Delta\varphi'} \tag{2}$$

The extrapolation lengths for the *meta* and *para* doped-dye nematics before, during, and after irradiation are given in Table 1. Unfortunately we cannot determine the extrapolation length for the *ortho* dye-doped nematic because of the elastic rotation of the easy axis in the presence of a magnetic field. Table 1 also lists estimated anchoring strengths of the *meta* and *para* doped-dye nematics based on a value of 7.35 pN for K_{22}^{28} . These values can be compared with azimuthal

anchoring strength of 160 μ J/m² for E7 on rubbed polyimide, as reported by Yu, *et al.*²⁸ From Table 1, it can be seen that before irradiation, the anchoring strengths are less than that reported in the literature. During irradiation by the pump, the extrapolation length decreases and the anchoring strengths start to approach that of E7 on polyimide in the absence of adsorbed dye. When the pump is turned off, the extrapolation length increases and the anchoring strengths decrease, although they do not appear to return to their original values for the *meta* dye-doped nematic.

Before and after optical absorbance spectra of the dye-doped nematics, shown in Figs. 10 - 12, indicate that the dyes exist in equilibrium mixtures of the anionic and the neutral forms. For all three dyes, the optical absorbance of the anionic form occurs between 425 and 450 nm and has a smaller cross-section than the optical absorbance of the neutral form, which occurs between 525 and 550 nm^{29,30}. These spectra indicate that the anionic form of the dye is dominant in the *meta* and *para* dye doped nematics. The *ortho* dye-doped nematic, however, shows a more equal mix of the anionic and neutral forms of the dye. This is probably because intramolecular hydrogen bonding stabilizes the neutral form. The shoulder at 440 nm, however, confirms the presence of the anionic form.

After photoinduced reorientation, the absorbance of the *ortho* dye-doped nematic is significantly decreased and slightly shifted to the blue, as seen in Fig. 10. This indicates an increase in the amount of dye present in the anionic form. The decrease in absorbance can be seen visually as a bleached "hole" in the sample, which has a diameter of about 1.1 cm (same as that of the pump beam). In fact, it typically takes several months to a year or so for this "hole" to

disappear, and for the *ortho* dye-doped nematic sample to return to its original absorbance spectrum as well as its original director orientation. Back of the envelope calculations show that there are about 30 "layers" of dye molecules per micrometer of optical path length. For the observed 35 - 40% change in absorbance in the *ortho* dye-doped sample, about 10 - 11 layers of dye within a micrometer length, or 180 – 200 layers within a typical sample, would need to be affected. This does seem to be rather large as a surface effect, suggesting that most of the decrease and shift in optical absorbance observed only in the "hole," occurs in the bulk. Yet under the microscope we observe neither spreading nor change of shape of the "hole" over the course of several months. The "hole" appears to be semi-permanent. Therefore, we are inclined to believe that there is very little, if any, translational diffusion, as otherwise the diffusion coefficient would be incredibly small. We suggest that the change in the absorbance of the *ortho* dye-doped nematic is the result of a photophysical/photochemical surface effect during the photoexcitation process, which may well extend into the bulk dye in the vicinity of the affected surface.

The optical absorbance band corresponds to the $n \rightarrow \pi^*$ transition. This involves moving the lone pair electrons on the nitrogen atoms into the π^* antibonding orbital, making them no longer available for hydrogen bonding. It is likely that such a transition weakens the intramolecular hydrogen bonding, allowing for the ionization of dye molecule. Apparently the anionic dye molecule in the excited state strongly adsorbs to the polymer surface. In other words, during photoexcitation *ortho* dye molecules are ionized and, if near the polymer surface, strongly adsorbed to that surface.

Contrast the behavior of the *ortho* dye-doped nematics with the *meta* and *para* dye-doped nematics where we observe a spectral shift to the blue with an increase in the absorbance, *c.f.*

Figs. 11 and 12. This spectral shift is localized to the region where photoexcitation occurs, with little evidence of diffusion. It is comparatively short lived. This suggests that during photoexcitation, the anionic form of the dye desorbs from the surface, leaving room neutral forms. Re-adsorption of the anionic form to the surface does not appear to occur to any significant extent until after the pump is removed.

4. Conclusion.

It is well known that azobenzene dyes are responsible for photoinduced reorientation of the director for nematic liquid crystals. While some of the reorientation occurs in the bulk, it has been clear that surface effects play an important role in this effect. Previous work has shown that when the azobenzene dye is *ortho* methyl red, these surface effects involve negatively charged species^{16,17,18}. We have extended this work to include *meta* and *para* methyl red. For all three isomers of methyl red, we have identified the negative species as the anionic, or basic form of the dyes.

Our results show that for all three isomers, during photoexcitation of the dye, anionic dye molecules previously adsorbed to the surface are desorbed. For the *meta* and *para* isomers, desorption of anionic dye molecules is confirmed by a red shift in the absorbance spectra, and is accompanied by an increase in the anchoring strength. Shortly after desorption begins, the anionic form of *ortho* methyl red experiences photoinduced adsorption back onto the surface, consistent with the results of other researchers. This is also confirmed by changes in the absorption spectra. Re-adsorbed anionic dye molecules are bound to the surface stronger than before and our results show that they are not as easily desorbed when photoexcited. Anchoring strengths for the nematics doped with *ortho* methyl red could not be determined, as a magnetic

field not only applied a torque to the director, but also to the easy axis resulting in an elastic rotation of the easy axis.

These results lead us to propose the following mechanism for photoinduced reorientation of *azo* dye-doped nematics: Both neutral and anionic forms of the dye are initially adsorbed to the surface aligned with the easy axis as determined by the rubbing direction. The anionic form provides a negative surface charge responsible for a stable orientation of the nematic throughout the sample. When a pump beam is applied, dyes with transition dipoles more in alignment with the polarization of the light are preferentially photoexcited. Anionic forms of these dyes desorb, resulting in a depletion of anionic dye molecules aligned with the polarization of the pump beam and a non-symmetric distribution of anionic dyes around the original easy axis. The result is a new easy axis rotated away from the polarization of the pump beam, but by no more than a few degrees. While this is the end of the story for *meta* and *para* methyl red, apparently, *ortho* methyl red in the bulk can ionize and adsorb back to the surface upon photoexcitation. These negatively charged dye molecules are adsorbed with an orientation more in line with the polarization of the pump beam. The result is rotation of the easy axis towards the polarization of the pump beam. This rotation can be quite large, as has been observed.

The elastic rotation of the easy axis observed when a magnetic field is applied only to *ortho* methyl red, we believe is the result of structural differences in the anionic form of the dyes. While the neutral forms off all three dyes are planar, the anionic forms only of *meta* and *para* methyl red are planar. The anionic form of *ortho* methyl red has the carboxylated phenyl ring rotated out of the plane of the molecule by about 30°. We propose that this phenyl ring is rotated out of the polymer surface. The magnetic field applies a torque to this negatively charged phenyl ring, resulting in a rotation of the easy axis away from the magnetic field. When the magnetic

field is removed, the phenyl ring returns to its original position, hence the elastic rotation of the easy axis. This does not occur with planar anionic *meta* and *para* methyl red dyes adsorbed to the surface. Within the bulk nematic, the torque applied by the magnetic field on the liquid crystal molecules rotates the director toward the magnetic field regardless of the *azo* dye.

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Table 1. Extrapolation length and anchoring energy (assuming $K_{22} = 7.35$ pN) for dyedoped nematics.

dye	$\zeta (\mu m) / W(\mu J/m^2)$		
	before	during	after
meta-methyl red	$0.40 \pm 0.02 \ / \ 18 \pm 1$	$0.06 \pm 0.03 \ / \ 120 \pm 60$	$0.24 \pm 0.03 \ / \ 31 \pm 4$
para-methyl red	$0.22 \pm 0.04 / 33 \pm 6$	0.11 ± 0.03 / 67 ± 18	$0.20 \pm 0.03 / 37 \pm 5$

Figure captions:

- Fig. 1. Structure of *ortho*-methyl red. *o*, *m*, and *p* refer to the *ortho*, *meta*, and *para* sites on phenyl ring.
- Fig. 2. Experimental design: P polarizer, BS beam splitter, D1– pump input detector, D2 signal detector, L lens, EM electromagnet, PEM photoelastic modulator, M mirror, S shutter, A analyzer. The applied magnetic field is parallel to the plane of the sample and perpendicular to the probe beam.
- Fig. 3. *Ortho*-methyl red doped sample: Director angle and twist (1/pitch) in degrees and degrees/µm. The twist becomes more negative (or decreases when the twist is positive) when the magnetic field is applied, and it becomes more positive when the magnetic field is removed.
- Fig. 4. *Meta*-methyl red doped sample: Director angle and twist (1/pitch) in degrees and degrees/µm. The twist becomes more positive when the magnetic field is applied, and it becomes more negative when the magnetic field is removed.
- Fig. 5. *Para*-methyl red doped sample: Director angle and twist (1/pitch) in degrees and degrees/µm. The twist becomes more positive when the magnetic field is applied, and it becomes more negative when the magnetic field is removed.
- Fig. 6. Ortho methyl red doped sample immediately after irradiation. Director angle versus twist. Data is fit to $\phi = a + b\phi'$; $a = -5.560^{\circ}$, and $b = 18.54 \,\mu\text{m}$. $R^2 = 0.91945$.
- Fig. 7. Ortho methyl red doped sample before irradiation. Director angle and twist (1/pitch) in degrees and degrees/μm. The twist and the angle become more negative when the magnetic field is applied, and they become more positive when the magnetic field is removed.
- Fig. 8. *Meta* methyl red doped sample before irradiation. Director angle and twist (1/pitch) in degrees and degrees/µm. The twist increases and the angle decreases when the magnetic field is applied. The twist decreases and the angle increases when the magnetic field is removed.
- Fig. 9. Para methyl red doped sample before irradiation. Director angle and twist (1/pitch) in degrees and degrees/μm. The twist increases and the angle decreases when the magnetic field is applied. The twist decreases and the angle increases when the magnetic field is removed.
- Fig. 10. Absorbance spectra of ortho-methyl red before (red) and after (blue) photoexcitation.
- Fig. 11. Absorbance spectra of meta-methyl red before (red) and after (blue) photoexcitation.
- Fig. 12. Absorbance spectra of para-methyl red before (red) and after (blue) photoexcitation.



Fig. 1: Structure of *ortho*-methyl red. *o*, *m*, and *p* refer to the *ortho*, *meta*, and *para* sites on phenyl ring.



Fig. 2. Experimental design: P – polarizer, BS – beam splitter, D1– pump input detector, D2 – signal detector, L – lens, EM – electromagnet, PEM – photoelastic modulator, M – mirror, S – shutter, A - analyzer. The applied magnetic field is parallel to the plane of the sample and perpendicular to the probe beam.



Fig. 3. *Ortho*-methyl red doped sample: Director angle and twist (1/pitch) in degrees and degrees/µm. The twist becomes more negative (or decreases when the twist is positive) when the magnetic field is applied, and it becomes more positive when the magnetic field is removed.



Fig. 4. *Meta*-methyl red doped sample: Director angle and twist (1/pitch) in degrees and degrees/µm. The twist becomes more positive when the magnetic field is applied, and it becomes more negative when the magnetic field is removed.



Fig. 5. *Para*-methyl red doped sample: Director angle and twist (1/pitch) in degrees and degrees/µm. The twist becomes more positive when the magnetic field is applied, and it becomes more negative when the magnetic field is removed.



Fig. 6. Ortho methyl red doped sample immediately after irradiation. Director angle versus twist. Data is fit to $\phi = a + b\phi'$; $a = -5.560^{\circ}$, and $b = 18.54 \,\mu\text{m}$. $R^2 = 0.91945$.



Fig. 7. Ortho methyl red doped sample before irradiation. Director angle and twist (1/pitch) in degrees and degrees/µm. The twist and the angle become more negative when the magnetic field is applied, and they become more positive when the magnetic field is removed.



Fig. 8. *Meta* methyl red doped sample before irradiation. Director angle and twist (1/pitch) in degrees and degrees/µm. The twist increases and the angle decreases when the magnetic field is applied. The twist decreases and the angle increases when the magnetic field is removed.



Fig. 9. *Para* methyl red doped sample before irradiation. Director angle and twist (1/pitch) in degrees and degrees/µm. The twist increases and the angle decreases when the magnetic field is applied. The twist decreases and the angle increases when the magnetic field is removed.



Fig. 10. Absorbance spectra of *ortho*-methyl red before (dashed) and after (solid) photoexcitation.



Fig. 11. Absorbance spectra of *meta*-methyl red before (dashed) and after (solid) photoexcitation.



Fig. 12. Absorbance spectra of para-methyl red before (dashed) and after (solid) photoexcitation.

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