

Quantification of photoinduced order increase in liquid crystals with naphthopyran guests

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Photoinduced order-increasing phase transitions can occur in dye-liquid crystal mixtures when the photoproduct of the excitation of the dye molecules is more compatible with the liquid crystalline medium than the initial dye species. A detailed investigation of the photoinduced changes of the phase behavior and optical properties of mixtures of liquid crystals with naphthopyran guests upon exposure to light at 365 nm is presented here. In these guest-host systems, the nematic-to-isotropic phase transition temperature is increased upon irradiation. We show that the nematic range can be extended up to 2.9 °C by illumination in 5CB (4-*n*-pentyl-4'-cyanobiphenyl) liquid crystal mixtures. The order parameter is significantly increased by illumination at all temperatures within the nematic range and the changes are larger at higher concentrations of the guests. In particular, the illuminated guest-host mixtures exhibit order parameters close to those of the neat liquid crystal host at the same temperature relative to the clearing point. An improved understanding of the photophysical processes taking place at the molecular level in these material systems can inform the design of photoresponsive materials and enhance their potential utility in optical or photonic devices.

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I. INTRODUCTION

The ability of nonmesogenic azobenzene dyes to affect the order and orientation of liquid crystal (LC) materials has been exploited in numerous electro-optic and photonic devices that can be remotely controlled by light [1–3]. Azobenzene compounds with liquid crystal phases have also been developed and can be used by themselves or in mixtures with nonphotosensitive LCs [4–8]. The photoinduced *trans*-to-*cis* or *cis*-to-*trans* isomerization of the azobenzene moiety drives these applications. In addition to a direct change in the optical properties of the azobenzene molecules with photoisomerization, the different shape of the *trans* and *cis* isomers can lead to different compatibility and solubility in ordered media like rod-shaped calamitic liquid crystals [9,10]. *Trans*-azobenzene has a rodlike shape, similar to that of the rigid portion of traditional calamitic LCs and when mixed in an ordered phase tends to align with the LC director, having relatively little effect on the order of the system. The *cis* isomer has a bent shape that is less compatible with the LC environment and reduces the stability of the system. In general, this is reflected in a change in the clearing point or phase transition temperature of the azobenzene-LC mixture upon irradiation (Fig. 1) [5,9]: If the transition temperature between an ordered and disordered phase of an LC containing a fraction of *trans*-azobenzene (composition *a*) is T_a , after the material has been exposed to light and part or all of the azobenzene is converted to the *cis* conformation (composition *b*), the transition temperature is depressed such that $T_b < T_a$. Similarly, for liquid crystalline azobenzene derivatives, the transition temperature is lowered when *trans* isomers are converted to *cis* isomers. If composition *a* is initially held

at temperature T' with $T_b < T' < T_a$, exposure of the sample to light at an appropriate wavelength converts composition *a* into composition *b* and the system undergoes a *phototropic* transition to the isotropic phase. Isothermal order-to-disorder transitions are well documented for LC mixtures prepared with azobenzene guests (as well as azobenzene derivatives that are inherently liquid crystalline [5,6,8,11]) and changes in transition temperature on the order of tens of degrees Celsius have been reported [4,12]. Decreases in transition temperatures with UV exposure have also been observed in stilbene-based LCs [13]. Various concepts of photoswitchable LC devices are based on this light-induced phase change effect [1]. Separate classes of photoresponsive devices containing azobenzenes utilize the change in intermolecular interactions as a way to tune the pitch of the chiral LC phase [10,14] or to modulate the orientation of the LC medium [15].

For some applications, access to materials that exhibit the opposite behavior, where light can induce a change from a disordered to an ordered phase, would be beneficial. With reference to the scheme in Fig. 1, in this class of materials, the thermodynamically stable system is composition *b* and this is photoconverted to composition *a*. At temperature T' with $T_b < T' < T_a$, the system is initially isotropic but an ordered nematic phase appears as *b* transforms into *a* under illumination.

Few examples of materials exhibiting this order-increasing phototropic behavior have been reported [16]. Kurihara *et al.* have achieved a nematic-to-isotropic phase transition in 5CB doped with a spiropyran derivative at the reduced temperature of 1.005 (relative to the transition temperature of the stable isomer) [17]. In spiropyrans, photoexcitation with UV light leads to a ring-opening intramolecular reaction and a photoisomer with a merocyanine form, which is more planar and compatible with the LC medium than the initial form. Allison and Gleeson have studied a series of thiophene and furan fulgides [18]. These compounds undergo a ring-closure reaction under UV

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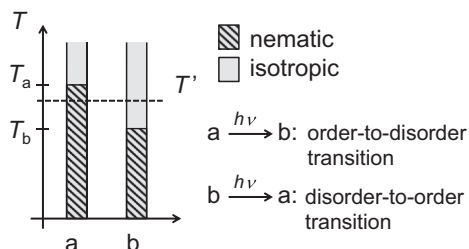


FIG. 1. Illustration of phototropic order-decreasing and order-increasing phase transitions. Two compositions, a and b , are shown, exhibiting a nematic phase below temperatures T_a and T_b , respectively. At temperature T' with $T_b < T' < T_a$, a phototropic phase transition can be induced if composition a is photoconverted to b or vice versa.

irradiation and when dispersed in the liquid crystal E7 were shown to increase the nematic-to-isotropic phase transition temperature by 0.1 to 1.2 °C. An order-increasing transition has also been observed for a unique azobenzene-based system where the pristine material exhibited a reentrant nematic phase below a smectic- A phase. Exposure to UV light from the reentrant phase led to the appearance of the smectic phase (due to a change in transition temperature in the same direction as discussed above for all azobenzenes), and thus an increase in order [19].

More recently diaryl- $2H$ -naphtho[1,2- b]pyrans were shown to be efficient guests for achieving photoinduced order-increasing transitions in LCs [20]. Naphthopyrans (or benzochromenes) are photochromic dyes that are used in ophthalmic lenses [21,22]. The $2H$ -naphtho[1,2- b]pyrans have the generic molecular structure shown on the left side of Fig. 2 (other classes of naphthopyrans exist, depending on the relative arrangement of the fused rings) and they are typically colorless in this form (pyran form or *closed form*). When irradiated with UV light, the molecules undergo a ring-opening reaction and one or more colored photoisomers are produced having a merocyanine form differing in the conformation of the single and double bonds in the conjugated bridge [23–25]. Two possible merocyanine forms (or *open forms*) of $2H$ -naphtho[1,2- b]pyrans are shown on the right side of Fig. 2. The process is generally reversible in the dark, with relaxation times and rates of interconversion between the various isomers that depend on the type and position of the substituents [24,26].

Recent work has shown light-induced transitions from the isotropic to the nematic state, from the nematic to the smectic- A state, and from the isotropic to the chiral nematic state with certain diaryl- $2H$ -naphtho[1,2- b]pyran guests in LC hosts [20]. In the study reported here, the temperature range for

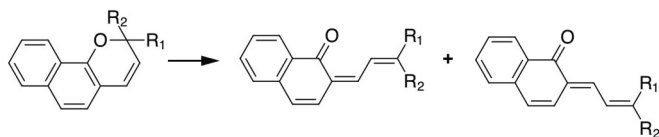


FIG. 2. General structure of (left) the ground state of a diaryl- $2H$ -naphtho[1,2- b]pyran (closed form) and (right) two photogenerated colored isomers (open forms).

phototropic disorder-to-order phase transitions is examined in greater detail. The photoinduced isotropic-to-nematic phase transition was found to shift to higher temperatures by increasing amounts when the guest content was increased, up to about 2.9 °C. In order to better understand the phenomenon, we also investigated the effect of the photoisomerization of the guests on the order of the LC system away from the transition temperature. A significant isothermal increase in order was observed in the nematic phase of the guest-host systems as a result of UV illumination, partly compensating for the impurity effect of the naphthopyrans on the LC medium.

II. EXPERIMENTAL METHODS

Two guests in the $2H$ -naphtho[1,2- b]pyran class, G-1 and G-2 (Fig. 3) [27–29], were investigated. These molecules have the same core and biphenyl pendant group and differ in the aryl substituents at the 2 position of the pyran ring. The structural differences in these molecules shift the position of the absorption band of the open-form conformer. Compound G-2 was the primary focus of the previous investigation [20]. In all of the experiments reported here, the liquid crystal host was 4'-pentyl-4-biphenylcarbonitrile (5CB), which exhibits a nematic-to-isotropic phase transition around 35 °C [30]. The guests are soluble in 5CB up to approximately 5%, enabled primarily by the presence of the alkyl-biphenyl substituent.

Solution measurements in isopropanol were conducted in 1-mm quartz cuvettes. LC cells with homogeneous alignment were used for all other experiments. These were fabricated from two ITO-coated glass substrates, subsequently coated with polyimide layers that were rubbed in antiparallel directions, and sealed with optical adhesive that included 9–10- μ m spacers. The LC mixtures were vigorously stirred while in the isotropic phase before filling the cells. The guest content, f , is reported throughout as percentage by weight (wt %).

Room temperature spectroscopic measurements were conducted on an Agilent Cary 5000 spectrophotometer. Measurements as a function of temperature or in the presence of irradiation at 365 nm were undertaken within a custom-built spectrometer system consisting of a white light source (halogen lamp), optical fibers, lenses, and a linear charge-coupled device (CCD) sensor (Ocean Optics USB2000 or USB2000+). Two Glan-Laser calcite polarizers were placed before and after the sample to control the polarization state of the probing light. The sample temperature was controlled using a heating stage (HCS402, Intec) and all temperature-dependent measurements were recorded on heating at the rate of 1.0 °C/min.

The source of UV light was a Novacure 2100 lamp (Exfo) with a 365-nm band-pass filter. The UV beam formed an angle of ca. 20° with the white probe beam and had a diameter of approximately 25 mm at the sample. The diameter of the white light probe upon the sample was 7 mm. The irradiance for the UV light incident on the front substrate of the LC cells was 9 mW/cm² (due to reflection losses, the irradiance at the front face of the LC mixture was slightly less).

Birefringence at room temperature was measured following the method of Wu *et al.* [31], wherein the transmittance of an LC cell with its rubbing direction, R , at 45° with respect to the polarizer was measured with crossed and parallel polarizers. In addition, the voltage-transmittance curve for

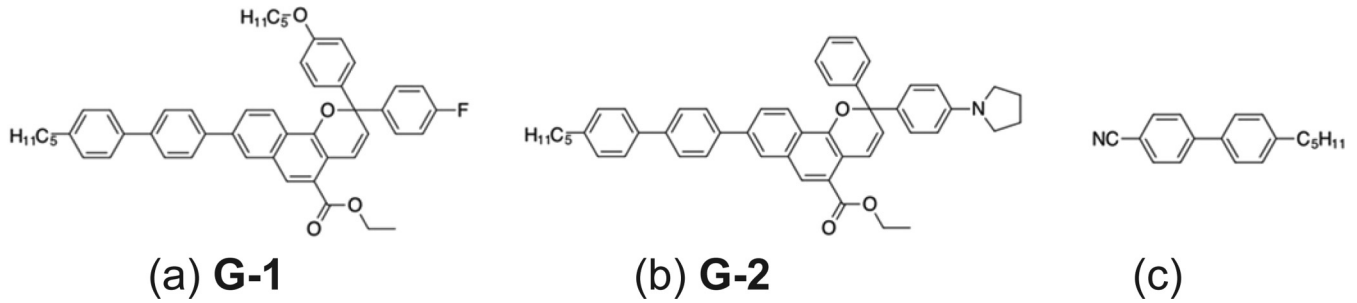


FIG. 3. Molecular structure of (a,b) the two guests considered in this study and (c) the liquid crystal host, 4'-pentyl-4-biphenylcarbonitrile (5CB).

the homogeneous-to-homeotropic transition was measured when applying a potential difference across the cell [32]. We fitted the experimental results in the visible range to a three-parameter Cauchy expression for the birefringence dispersion:

$$\Delta n(\lambda) = A_1 + \frac{A_2}{\lambda^2} + \frac{A_3}{\lambda^4} \quad (1)$$

where $\Delta n(\lambda)$ is the birefringence at wavelength λ and A_i are constants.

Using the Vuks approximation, the relationship between the refractive indices of an LC and the order parameter S can be written as [33,34]

$$\frac{n_e^2 - n_o^2}{\langle n^2 \rangle + 2} = \frac{N(\alpha_{\parallel} - \alpha_{\perp})}{3\epsilon_0} S, \quad (2)$$

where n_o and n_e are the ordinary and extraordinary refractive indices, respectively, $\langle n^2 \rangle = (n_e^2 + 2n_o^2)/3$, N is the number of molecules per unit volume, ϵ_0 is the vacuum permittivity, and α_{\parallel} and α_{\perp} are the molecular polarizabilities parallel and perpendicular, respectively, to the long axis of the LC molecules (assuming cylindrical symmetry; their value is independent of the order). Using $\Delta n = n_e - n_o$ and introducing $\langle n \rangle = n_e + n_o$, Eq. (2) can be rewritten as

$$\Delta n = \frac{\langle n^2 \rangle + 2}{\langle n \rangle} \frac{N(\alpha_{\parallel} - \alpha_{\perp})}{3\epsilon_0} S. \quad (3)$$

The two forms of the average refractive index in Eq. (3), $\langle n^2 \rangle$ and $\langle n \rangle$, generally have a weak temperature dependence (each has been shown to decrease linearly with temperature with a small slope [35]) and, to a first approximation, the first fraction in the above equation is constant over the temperature range of our experiment ($<20^\circ\text{C}$). Similarly, the change in number density can be neglected over this temperature range. We can further assume that $\alpha_{\parallel} - \alpha_{\perp}$ is approximately the same for all samples away from guest resonances, because the guest is present at low concentration. Equation Eq. (3) then becomes

$$S = K(\lambda_0)\Delta n(\lambda_0), \quad (4)$$

where $K(\lambda_0)$ is constant over the temperature range and sample compositions for any given wavelength. Using the value reported in the literature for 5CB at 25°C of $S = 0.55$ [36] and the birefringence value measured at $\lambda_0 = 700\text{ nm}$ at the same temperature results in $K(700\text{ nm}) = 0.55/0.1688 = 3.258$ [37].

III. RESULTS AND DISCUSSION

A. Optical properties of G-i-5CB mixtures at room temperature

The lowest-energy electronic transition for G-1 and G-2 in 2-propanol is observed around 340 nm (Fig. 4, solute concentration $<5 \times 10^{-4}\text{ M}$). For 2,2-diaryl-2H-naphtho[1,2-b]pyrans, the position of this band and its shape depend on the core substituents and the solvating environment [24]. In the same solvent, 5CB exhibits an absorption maximum at 280 nm and has negligible absorption above 330 nm (Fig. 4).

The lowest-energy absorption band of G-1 and G-2 remains approximately in the same position when either guest is mixed with 5CB and measured in LC cells, as shown in Fig. 5. These spectra are not corrected for reflection losses, which are responsible for the nonzero baseline at long wavelengths. For the cell thickness and compositions used in these experiments, only very weak absorption due to 5CB at 365 nm is present, confirming this is an effective excitation wavelength for the guest molecules. All samples were in the nematic phase at room temperature.

The birefringence of the G-i-5CB mixtures in homogeneous cells was measured in the visible range at room temperature (Fig. 6). The result for neat 5CB at 589 nm, $\Delta n(589\text{ nm}) = 0.178$, is in acceptable agreement with literature values, 0.184 [36], 0.1786 [38], and 0.1779 [35]. This suggests that our experimental setup should provide birefringence estimates

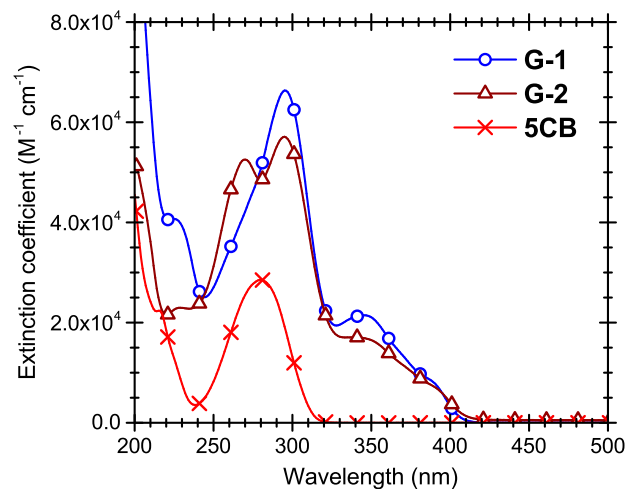


FIG. 4. Absorption spectra of the LC host and of the naphthopyran compounds G-i in dilute solutions. Solvent: isopropanol, concentration $<5 \times 10^{-4}\text{ M}$.

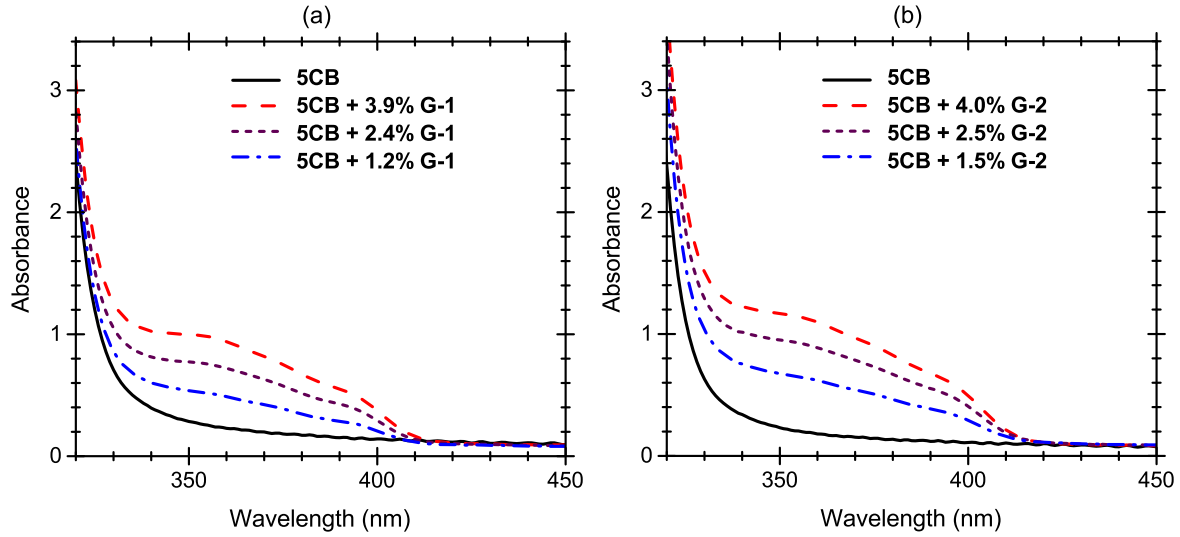


FIG. 5. Absorption spectra of mixtures of G-i in 5CB at three concentrations in LC cells of $\sim 10 \mu\text{m}$ thickness: (a) G-1; (b) G-2. The spectrum of a cell containing only 5CB is included for comparison (solid line). The samples were probed with unpolarized light at room temperature. The data are reported in absorbance units.

accurate enough for comparisons between samples of different compositions or for monitoring temperature dependences. Figure 6 indicates that the birefringence decreases monotonically with an increase in guest concentration. The changes are larger in magnitude for the G-1 system, with values at 700 nm being reduced from 0.169 for 5CB to 0.127 at $f = 3.9\%$. From these results, the order parameter for the mixed systems at room temperature can be obtained from Eq. (4) (Fig. 7, open symbols). S decreases with increasing guest content for each guest species albeit in differing magnitudes. The decrease in order parameter is an indication that the guests are acting as impurities in the LC mixtures, partially disrupting the order of the LC host.

To test whether G-i molecules assume a preferential orientation in the LC host, absorption spectra were also measured with light polarized parallel and perpendicular to the rubbing direction, R . We found that the absorbance of all samples was larger for the parallel polarization case (for the

4% samples, see Fig. 8, solid lines; absorbance values as a function of guest content for various polarization conditions are reported in Fig. SM1 of the Supplemental Material [39]). The dichroic ratio, D , defined as $D = A_{P\parallel R}/A_{P\perp R}$ (where $A_{P\parallel R}$ and $A_{P\perp R}$ are the absorbances measured when the polarization of the light incident on the sample is parallel and perpendicular, respectively, to R), was not constant but also decreased with increasing guest concentration. For the lowest-energy absorption band of G-1 in the dark, we obtained values of $D = 2.95$ at 1.2% and $D = 2.31$ at 3.9%.

The value of the dichroic ratio can be used to determine the order parameter for the guest molecules in the mixtures from

$$S_g = \frac{D - 1}{D + 2} \tag{5}$$

[the subscript g on S is used to differentiate this guest-based estimate from that obtained from the birefringence through

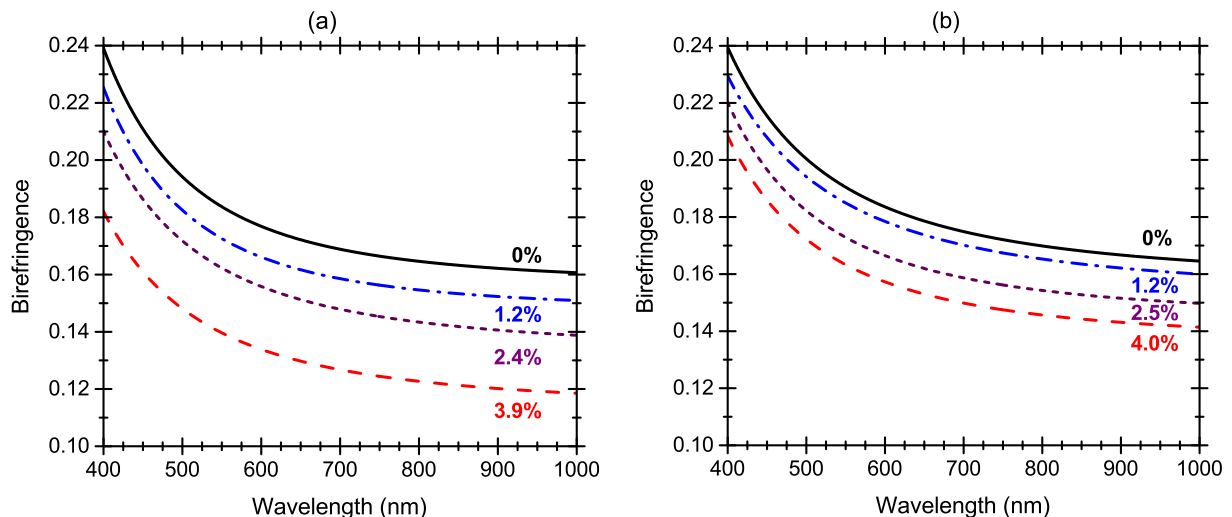


FIG. 6. Birefringence dispersion for the G-i-5CB mixtures in cells with planar alignment at room temperature. (a) G-1; (b) G-2.

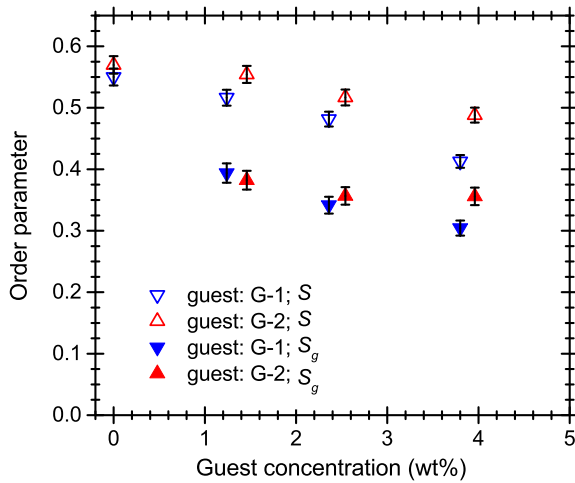


FIG. 7. Order parameter for G-i-5CB mixtures in the dark and at room temperature as a function of guest content, as measured in LC cells with homogeneous alignment. Open symbols: S values obtained from the mixture's birefringence at 700 nm; filled symbols: S_g values from the dichroic ratio of the guests. The estimated uncertainty in the values of S and S_g is also shown.

Eq. (4)]. As indicated in Fig. 7 (filled symbols), the trend in S_g with guest concentration is similar to that of S obtained from birefringence, although $S > S_g$ in all cases. If the angular distribution of the guest and host molecules orientation is similar, the angle θ between the transition dipole moment of a guest molecule and the LC director can be estimated from the values of S and S_g [40]. The data in Fig. 7 yield $\theta = 23^\circ - 27^\circ$. The decrease in order observed in the mixtures is a consequence of the unfavorable intermolecular interactions between the host and guest molecules. Because of the change in order with composition, the absorbance of G-i measured with linearly polarized light exhibited a sublinear increase as a function of guest content (Fig. SM1 [39]).

B. Phase diagrams without and with UV exposure

The primary goal of this study was the determination of the effect of conformational changes of the guest molecules on the stability of the ordered phase. The temperatures for the transition from the nematic to the isotropic phase T_{NI} , determined while heating the samples at a constant rate and monitoring the transmission with R at 45° with respect to crossed polarizers, are shown in Fig. 9. For 5CB, the measured T_{NI} was 35.5°C , in good agreement with the literature [30]. All guest-host samples in absence of UV exposure exhibit a nematic phase. In these samples, we observed that the nematic and isotropic phases coexist over a narrow temperature range between the ordered and disordered states. Coexisting phases are often observed in mixtures of mesogens or of mesogenic and nonmesogenic molecules [41] and have been described theoretically [42]. The onset of this mixed region during heating is usually characterized by the appearance of small isotropic droplets within the nematic domain. With increasing temperature, the droplets increase in size, then merge and finally extend to the whole sample. In our experimental configuration, we identify the onset of the T_{NI} transition, $T_{NI}(\text{onset})$, as the temperature at which the magnitude of the transmittance maxima under cross polarizers starts to decrease due to scattering from the droplets. The temperature at which the maxima of the transmission spectra are indistinguishable from the zero baseline was identified as the end point of the transition range, $T_{NI}(\text{end})$ (one example of changes in spectral features is shown in the Supplemental Material, Fig. SM2 [39]). $T_{NI}(\text{onset})$ and $T_{NI}(\text{end})$ for the mixed samples are lower than the T_{NI} of 5CB [43]. The decrease in transition temperature is approximately linear with guest content and the values are similar for G-1 and G-2. The depression of the transition temperature is a manifestation of the impurity effect. The temperature range of the mixed phase $T_{NI}(\text{end}) - T_{NI}(\text{onset})$ increases with guest content and is slightly larger than 2°C at $f = 4\%$ (the value is expected to depend on the heating rate).

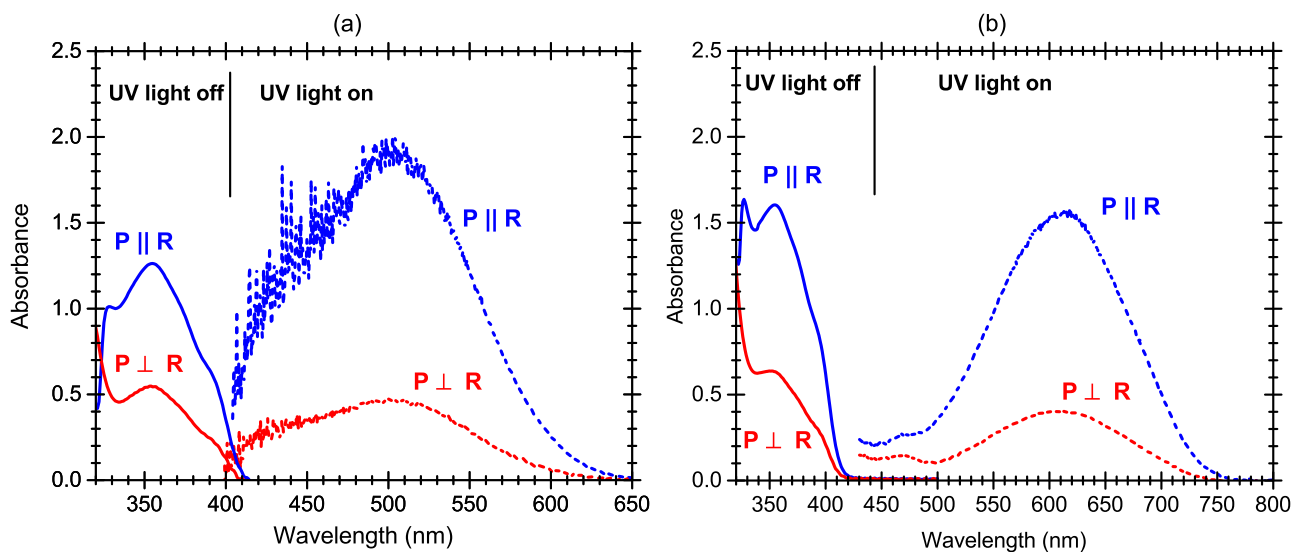


FIG. 8. Absorption spectra of G-i in 5CB (ca. 4% guest concentration) measured in LC cells of $\sim 10 \mu\text{m}$ thickness with light linearly polarized parallel and perpendicular to R : (a) G-1; (b) G-2. Solid lines: measurement in the dark; dashed lines: measurement during exposure at 365 nm, $9 \text{ mW}/\text{cm}^2$. The contribution of 5CB to the measured signal has been subtracted from all spectra and the data are reported in absorbance units.

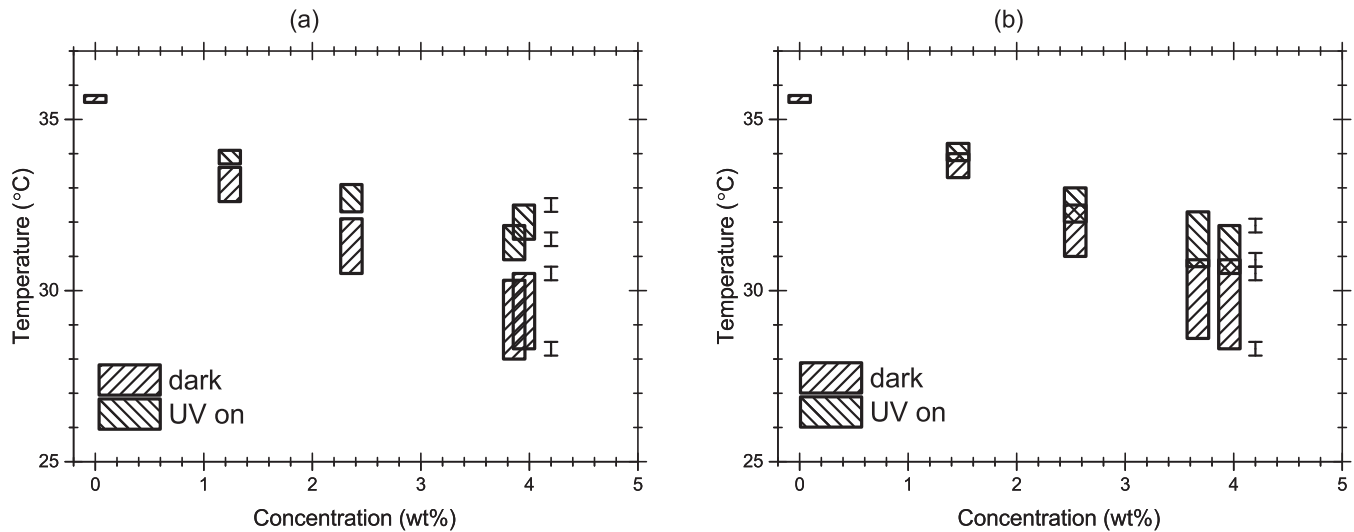


FIG. 9. Nematic-to-isotropic transition temperature of G-i-5CB mixtures in planar LC cells as prepared (dark; rectangles with striations from bottom left to top right) and during UV exposure to 365-nm light (rectangles with striation from top left to bottom right). For each sample and conditions, the bottom of a rectangle in the graph represents $T_{NI}(\text{onset})$; the top of the rectangle $T_{NI}(\text{end})$. Data obtained on heating of the samples at 1.0 °C/min: (a) G-1; (b) G-2. The error bars for $T_{NI}(\text{onset})$ and $T_{NI}(\text{end})$ are shown for the 4% sample on the right side of the actual data. The uncertainty in the temperature values is the same for the other samples.

When these mixtures are illuminated with 365-nm light, a fraction of the guest molecules are interconverted to the open form, which has a strong absorption band in the visible range, peaking at 500 nm for G-1 and 610 nm for G-2 (see Fig. 8, dashed lines, for steady-state spectra at $f = 4\%$). For these samples, a steady-state population of the photoisomer is obtained in 10–20 s of exposure in the temperature range 25 °C–35 °C (see Supplemental Material, Fig. SM3 [39] for examples of isothermal photoconversion dynamics in G-1 at 25 °C and 35 °C) [44]. When the UV light is turned off, the molecules relax back to the closed form. The relaxation rate is temperature dependent and for G-1 the open-form decay is complete in about 150 s at 25 °C and 30 s at 35 °C. A complete analysis and discussion of switch-on and switch-off times for these materials systems will be reported separately. For experiments during a heating ramp, the samples were exposed to UV light for a few minutes at the initial temperature, to allow steady-state conditions to be reached before the start of the heating step. No changes in the spectra of the cell with neat 5CB are observed. For each guest-host sample, both $T_{NI}(\text{onset})$ and $T_{NI}(\text{end})$ increase under UV exposure (Fig. 9, rectangles with stripes oriented from top left to bottom right). This is consistent with the interpretation that the open-form configuration of the guest molecules has a more energetically favorable interaction with the ordered liquid crystal environment than the closed form [20]. The magnitude of the shift in transition temperature increases with guest concentration. The largest change measured for 9 mW/cm² exposure was observed for the 3.9% G-1 sample, with $\Delta T_{NI} = T_{NI-\text{UV}}(\text{onset}) - T_{NI-\text{dark}}(\text{onset}) = 2.9$ °C. The width of the mixed region for any of the compositions was found to be smaller for the exposed sample than for the sample in the dark, also suggesting better compatibility of the open-form molecules with the liquid crystal host. The experimental findings also show that some of the samples exhibit an overlap between the mixed phase existence range in the dark and

with UV exposure [i.e. $T_{NI-\text{dark}}(\text{end}) > T_{NI-\text{UV}}(\text{onset})$; see crosshatched regions in Fig. 9(b)]. This poses a limitation for the use of these materials in practical applications, as it may reduce the dynamic range of a device (either the initial or photoinduced final state would have a mixed phase).

A brief comparison of these results with those of previously investigated materials that exhibit photoinduced disorder-to-order transitions helps put these findings in perspective. In the pioneering work by Kurihara *et al.* [17], an isothermal phase transition in a spiropyran-5CB sample was observed at a reduced temperature of 1.005, corresponding to $\Delta T_{NI} \geq 1.5$ °C. The lower limit is smaller than the ΔT_{NI} value obtained for the 4 wt % G-i samples. The material described in Ref. [17], however, performed better than G-i-5CB if samples with the same guest content are compared. The largest ΔT_{NI} reported by Allison and Gleeson [18] was 1.2 °C for a thiophene fulgide at 2 wt % in the host E7 (reduced temperature = 1.004), comparable to our results at the same guest concentration.

C. Changes in order parameter with composition and exposure

In this final section, the effect of the presence of naphthopyran conformers on the order of the samples away from the transition temperature is examined. This was accomplished by determining the effective birefringence of the samples as a function of temperature with and without UV illumination using a simplified approach (the method is described in the Supplemental Material and birefringence data for G-1-containing samples are given in Fig. SM4 [39]) and then converting the birefringence to order parameter values using Eq. (4).

The results for the G-1-5CB sample with $f = 2.4\%$ in the dark are given in Fig. 10 (solid triangles). The order parameter progressively decreases with increasing temperature from 0.47 at 25 °C to 0.32 at the $T_{NI-\text{dark}}(\text{onset})$. This trend of decreasing S approaching T_{NI} is typical for the nematic

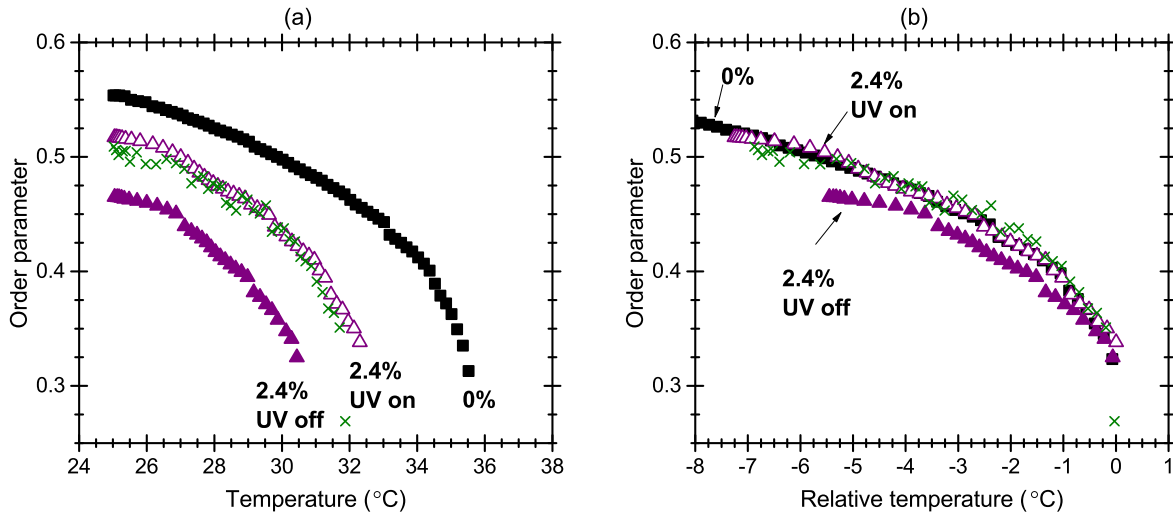


FIG. 10. Order parameter as a function of temperature for a 2.4% G-1-5CB mixture in a $\sim 10\text{-}\mu\text{m}$ planar LC cell. Filled triangles: sample in the dark (S from birefringence); open triangles: sample during exposure to 365-nm light (from birefringence). The corresponding data (from birefringence) for neat 5CB are included for comparison (filled squares). For the G-1-5CB mixture with UV exposure, the order parameter S_g estimated from the dichroic ratio of the guest open form is also included (crosses). All data obtained on heating of the samples at $1.0\text{ }^\circ\text{C}/\text{min}$. (a) Absolute temperature scale; (b) temperature scale relative to $T_{NI}(\text{onset})$ of each sample and illumination condition.

phase of rodlike molecules. Previous modifications of the Landau-de Gennes theory for the nematic-isotropic phase transition lead to the following expression for the order parameter for $T < T_{NI}$ [41,45]:

$$S = B(T^* - T)^\beta, \quad (6)$$

where $\beta = 1/4$, B is a constant, and T^* is a critical temperature close to but above T_{NI} (the temperature at which S would reach zero if Eq. (6) were valid above T_{NI}). $S = 0$ for $T \geq T_{NI}$. Experimentally, many LCs follow this power law over the full nematic range with $\beta = 0.18 - 0.23$ [34]. Our results for 5CB show the same general behavior (solid squares in Fig. 10) and are in good agreement with the literature data [36,46]. The qualitative agreement supports the use of the simplified method for the birefringence estimate. At every temperature in the nematic range, S is significantly smaller for G-1-5CB than for neat 5CB.

The order parameter has the same trend with temperature when the G-1-5CB sample is illuminated [open triangles in Fig. 10(a)]. Because of the photoinduced shift in transition temperature, the order parameter curve for the UV-exposed sample is located between that of the same sample before illumination and neat 5CB. If the sample were to be held at any fixed temperature below $T_{NI-\text{dark}}(\text{onset})$, exposure to UV light would always lead to an increase in the local order of the sample. For example, at $28.0\text{ }^\circ\text{C}$, $S = 0.42$ for the sample in the dark and $S = 0.48$ with exposure to UV light at $9\text{ mW}/\text{cm}^2$ (after steady state is reached). The corresponding change in birefringence at 700 nm is 0.018 . These order and birefringence changes are significant and comparable to those between samples at different G-i content in the series.

In a separate measurement, the absorption spectra in the visible range of the $f = 2.4\%$ G-1 sample were collected during heating at the same constant rate ($1\text{ }^\circ\text{C}/\text{min}$) and with exposure to UV light, for polarizations of the probing

light parallel and perpendicular to R . From these spectra, the dichroic ratio for the G-1 open form and the corresponding S_g [from Eq. (5)] were determined. Figure 10(a) shows that the S_g values (shown as crosses in the graphs) are in very good agreement with the birefringence-derived S values (open triangles) for the same exposure conditions. The similarity in magnitude of S and S_g (and not only in their trends, as was the case for the samples in the dark; see Fig. 7) implies that the transition dipole moment of the guest molecules in the open form is approximately parallel to the liquid crystal director.

The same data can be graphed on a relative temperature scale where the zero of the abscissa is $T_{NI}(\text{onset})$ for each sample and exposure condition [Fig. 10(b)]. The order parameter for the G-1-containing sample in the dark is slightly smaller than for 5CB at the same relative temperature. However, when the sample reaches the steady state under UV exposure, the S trace very nearly overlaps that of neat 5CB. This match implies that the open-form isomers are more compatible with the LC medium than the closed-form ones and their presence compensates for the loss of order due to the residual concentration of closed-form molecules (as mentioned above, the photoconversion is not complete).

It should be mentioned that in Ref. [18], Allison and Gleeson measured the order parameter as a function of temperature for E7 doped with photoresponsive fulgide derivatives. They found that all the samples exhibited the general behavior of Eq. (6), with slightly smaller S values for the doped samples relative to E7. However, no changes were detected when the samples were irradiated relative to the samples in the dark. This is different from the response of the G-1-5CB mixtures shown in Fig. 10. This could indicate that the nature of the photoinduced changes are different in the two classes of guests or that in Ref. [18] the changes in order were too small to resolve.

Other compositions were investigated and the same general behavior was observed in all G-i-5CB samples; specifically an

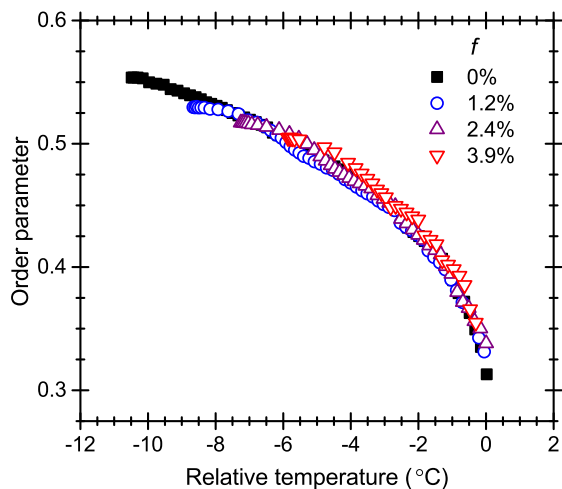


FIG. 11. Order parameter S as a function of relative temperature $[T - T_{NI}(\text{onset})]$ for G-1-5CB mixtures with various guest content during UV illumination: 1.2% (circles); 2.4% (upward triangles); 3.9% (downward triangles). Values of S for 5CB are included for comparison (solid squares).

increase in order parameter was observed when the samples were exposed to UV light in the nematic range. On a relative temperature scale, the order parameter of all the exposed samples is close to that of 5CB (see Fig. 11 for G-1-5CB and SM4 [39] for 4.0% G-2-5CB). The results suggest that a similar local environment in the photostationary state is reached irrespective of the initial guest content, resembling that of 5CB. The change in properties from the dark state to the steady state becomes larger with guest concentration.

The photoinduced increase in order is common to all G-i samples tested and we expect it to be observable in other naphthopyran derivatives apart from G-1 and G-2. The magnitude of the changes in transition temperature (Fig. 9) and the values of the order parameters of the samples in the dark (Fig. 7) or under similar exposure conditions are different for the two guests. This observation suggests that, while the difference in geometry between the closed and open forms is responsible for the effect, the interaction with the liquid crystal environment is strongly influenced by the side groups attached to the naphthopyran core. Investigations on a larger number of molecules could allow determining whether steric effects or the substituent charge distribution have a dominant influence on the local order in the dark and the photostationary state.

It was mentioned in the previous section that when the UV light is turned off, the naphthopyran molecules relax back to the ground-state closed form. After the UV exposure during the heating experiments discussed above, the samples were cooled to room temperature and their optical properties

compared with those they exhibited before UV exposure. In the case of G-1, the initial state was completely recovered and a subsequent UV exposure resulted in the same photostationary state (Supplemental Material, Fig. SM6a [39]). For G-2, however, a small change in birefringence was observed for the sample before and after UV exposure (Fig. SM6b [39]). The change could be due to photodegradation of the sample. To quantify the changes, fresh samples were exposed to UV light for extended periods of time under conditions comparable to those used for the other experiments in this section (Supplemental Material, Fig. SM7 [39]). It was found that the absorbance in the open-form absorption band of G-1 changes by less than 1% over 10–15 min, the duration of the typical heating step. For G-2, larger changes were observed, on the order of 6%–9% over the same period. Due to the reduced stability, G-2-containing samples were refreshed after each heating with UV exposure experiment. Photodegradation due to UV exposure is known to occur in other photochromic molecules. The origin of the UV-induced photodegradation in samples containing G-i is not known at this stage, but it could be due to photoinduced side reactions, the presence of impurities in the guest or host, or singlet oxygen sensitization.

IV. CONCLUSIONS

Naphthopyran-doped 5CB mixtures become more ordered when exposed to UV light due to compatibility differences of the closed and open form of the guest molecules with the rod-shaped molecules of the liquid crystal host medium. The nematic phase of the guest-host systems is extended to higher temperatures when the samples are exposed to UV light. At the highest concentration tested, the change in transition temperature is between 2 °C and 3 °C for two separate guest molecules, which is larger than previous reports for order-increasing phototropic compounds. The increase in order with exposure to UV light extends throughout the nematic phase and is larger for a higher concentration of the guest molecules. On a relative temperature scale, the order parameter trace of samples containing a significant fraction of guest molecules in the open form, as obtained by illumination with UV light, almost overlaps with that of the 5CB host, partly canceling the impurity effect. Because of the different transition temperature and order for samples in the dark and under UV illumination, large isothermal photoinduced changes in birefringence can be obtained.

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- [1] T. Ikeda, *J. Mater. Chem.* **13**, 2037 (2003).
- [2] F. Ercole, T. P. Davis, and R. A. Evans, *Polym. Chem.* **1**, 37 (2010).
- [3] N. Tamaoki and T. Kamei, *J. Photochem. Photobiol., C* **11**, 47 (2010).

- [4] C. H. Legge and G. R. Mitchell, *J. Phys. D: Appl. Phys.* **25**, 492 (1992).
- [5] C. Leier and G. Pelzl, *J. Prakt. Chem.* **321**, 197 (1979).
- [6] U. Hrozhyk, S. Serak, N. Tabiryan, and T. J. Bunning, *Mol. Cryst. Liq. Cryst.* **454**, 235/[637] (2006).

- [7] U. A. Hrozhyk, S. V. Serak, N. V. Tabiryan, L. Hoke, D. M. Steeves, B. Kimball, and G. Kedziora, *Mol. Cryst. Liq. Cryst.* **489**, 257/[583] (2008).
- [8] A. Sobolewska, J. Zawada, S. Bartkiewicz, and Z. Galewski, *J. Phys. Chem. C* **117**, 10051 (2013).
- [9] S. Tazuke, S. Kurihara, and T. Ikeda, *Chem. Lett.* **16**, 911 (1987).
- [10] E. Sackmann, *J. Am. Chem. Soc.* **93**, 7088 (1971).
- [11] A. Sobolewska, S. Bartkiewicz, and J. Mysliwiec, *Appl. Phys. Lett.* **103**, 083302 (2013).
- [12] J.-H. Son, S.-H. Lee, S.-H. Hong, W.-C. Zin, and J.-K. Song, *Liq. Cryst.* **40**, 646 (2013).
- [13] W. E. Haas, K. F. Nelson, J. E. Adams, and G. A. Dir, *J. Electrochem. Soc.* **121**, 1667 (1974).
- [14] T. J. White, M. E. McConney, and T. J. Bunning, *J. Mater. Chem.* **20**, 9832 (2010).
- [15] K. Ichimura, *Chem. Rev.* **100**, 1847 (2000).
- [16] S. K. Prasad, *Angew. Chem., Int. Ed.* **51**, 10708 (2012).
- [17] S. Kurihara, T. Ikeda, S. Tazuke, and J.-E. Seto, *J. Chem. Soc., Faraday Trans.* **87**, 3251 (1991).
- [18] H. Allison and H. F. Gleeson, *Liq. Cryst.* **14**, 1469 (1993).
- [19] S. K. Prasad and G. G. Nair, *Adv. Mater.* **13**, 40 (2001).
- [20] T. Kosa, L. Sukhomlinova, L. Su, B. Taheri, T. J. White, and T. J. Bunning, *Nature (London)* **485**, 347 (2012).
- [21] D. B. Knowles, US Patent No. 5,238,981 (Aug. 24, 1993).
- [22] B. Van Gemert, *Mol. Cryst. Liq. Cryst.* **344**, 57 (2000).
- [23] J. C. Crano, T. Flood, D. Knowles, A. Kumar, and B. Van Gemert, *Pure Appl. Chem.* **68**, 1395 (1996).
- [24] S. Jockusch, N. J. Turro, and F. R. Blackburn, *J. Phys. Chem. A* **106**, 9236 (2002).
- [25] S. Delbaere, G. Vermeersch, and J.-C. Micheau, *J. Photochem. Photobiol., C* **12**, 74 (2011).
- [26] J. C. Arnall-Culliford, Y. Teral, P. Sgarabotto, M. Campredon, and G. Giusti, *J. Photochem. Photobiol., A* **159**, 7 (2003).
- [27] L. Sukhomlinova, L. Su, T. Kosa, and B. Taheri, US Patent No. 8,697,890 B2 (Apr. 15, 2014).
- [28] L. Sukhomlinova, T. Kosa, B. Taheri, T. White, and T. Bunning, US Patent Application No. 13/990,072 (2013).
- [29] L. Sukhomlinova, L. Su, T. Kosa, and B. Taheri, US Patent Application No. 14/215,902 (2014).
- [30] P. Yeh and C. Gu, *Optics of Liquid Crystal Displays* (Wiley, New York, 1999), p. 23.
- [31] S.-T. Wu, U. Efron, and L. D. Hess, *Appl. Opt.* **23**, 3911 (1984).
- [32] The voltage-dependent measurement is needed to remove the ambiguity in the phase shift inherent in the transmission data in the homogeneous state and thus to determine the number of integer π phase shifts bounding the actual phase shift at a probing wavelength.
- [33] G. Pelzl, in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, Vol. 2A (Wiley-VCH, Weinheim, 1998), Ch. III, 2.4, p. 128.
- [34] I. Haller, *Prog. Solid State Chem.* **10**, 103 (1975).
- [35] J. Li, S. Gauza, and S.-T. Wu, *J. Appl. Phys.* **96**, 19 (2004).
- [36] R. G. Horn, *J. Phys. (Paris)* **39**, 105 (1978).
- [37] The reference value for S is reported to two significant digits, as it was obtained from a figure in Ref. [36] and this limits the absolute accuracy of the method; however, internal comparisons of S values for the samples and conditions considered here are only limited by the uncertainty on the birefringence, estimated to be about 0.003.
- [38] J. Li, C.-H. Wen, S. Gauza, R. Lu, and S.-T. Wu, *J. Disp. Technol.* **1**, 51 (2005).
- [39] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevE.93.032701> for additional figures and description of method to measure birefringence.
- [40] Using Eq. (6) in B. Bahadur, in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Wiley-VCH, Weinheim, 1998), Vol. 2A: Low Molecular Weight Liquid Crystals I, p. 269, and assuming that S is approximately equal to the order parameter for the long axis of the guest molecules.
- [41] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, Oxford, 1993).
- [42] R. L. Humphries and G. R. Luckhurst, *Proc. R. Soc. London, Ser. A* **352**, 41 (1976).
- [43] For 5CB, the onset and end transition temperature are the same within the uncertainty of our experiment, about $\pm 0.2^\circ\text{C}$, as expected for a single component mesogen.
- [44] It should be mentioned that the conversion from the closed to the open form is not complete, so that the exposed samples are effectively a mixture of three species: open form and closed form of the guest and 5CB.
- [45] P. H. Keyes, *Phys. Lett. A* **67**, 132 (1978).
- [46] M. Marinelli, F. Mercuri, U. Zammit, and F. Scudieri, *Phys. Rev. E* **58**, 5860 (1998).