THE JOURNAL OF PHYSICAL CHEMISTRY



Phototropic Guest-Host Liquid Crystal Systems: Environmental **Effects on Naphthopyran Kinetics**

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Supporting Information

ABSTRACT: Photoinduced isothermal and order-increasing phase transitions can be observed in guest-host liquid crystal mixtures containing naphthopyran derivatives. The changes are attributed to the different geometry and a less energetically favorable interaction with the liquid crystal molecules for the ground state naphthopyran species with respect to the photoproduct. In this study, we have investigated the thermal relaxation of the naphthopyran photoproduct back to the initial species as a function of temperature and excitation conditions. It was found that the thermal relaxation is typically first-order and its characteristic rate has a temperature dependence that is different in the anisotropic and isotropic states of the mesogenic solvents. In particular,



the activation energy for thermal relaxation is larger in the ordered phases of mesogenic solvents relative to their isotropic phase. The findings suggests that the naphthopyran relaxation is hindered by the organization of the host environment. These results will be useful to build a more complete understanding of the mutual guest-host interactions in naphthopyran-containing guesthost LC systems.

INTRODUCTION

Photochromic material systems assume different colorations in the dark and with exposure to light. The change in color is usually associated with a photoinduced reaction or isomerization that leads to a photoproduct with different energy levels than the initial species.^{1,2} Depending on the chemical species involved, the photoreaction can be reversible (thermally or photochemically) or irreversible. Photochromic materials have found applications in various areas, including optical filters, optical data storage systems, and ophthalmic lenses.^{1,3,4}

Naphthopyrans (also known as benzochromenes) are a wellstudied class of organic photochromic materials widely employed in variable transmission ophthalmic lenses.^{3,4} These compounds are typically colorless in the dark, having absorption bands in the UV region of the electromagnetic spectrum. The structure of a 2*H*-naphtho[1,2-b]pyran (or 2*H*-benzo[h]chromene) is shown on the left side of Scheme 1 (closed form of the chromophore). Under exposure to UV light, a ring opening reaction takes place at the C-O bond leading to the structure in the center of Scheme 1 and to merocyanine-like isomers (open form of the chromophore) after rotation around C-C bonds.^{5,6} The merocyanine isomers, which differ in the conformation of the single and double C-C bonds in the polymethine chain (two are shown on the right side of Scheme 1), typically absorb in the visible range of the spectrum. 3H-Naphtho[2,1-b]pyrans and 2H-naphtho[2,3-b]pyrans, as well as benzopyrans, undergo a photoinduced ring opening reaction in a similar manner.^o

Generally, the photoreaction proceeds from the excited singlet state of the closed form.^{7,8} The reaction schemes can involve multiple isomers, the population of which is known to depend on the specific naphthopyran family, the substituents on the pyran unit or the naphthalene unit, and the solvent environment.^{6,9,10} Two open form isomers are often thought to be present during the coloration and decoloration dynamics of naphthopyrans, and they can interconvert with each other or decay back thermally to the closed form.^{8,11,12} NMR has been used to assign isomer conformations to spectral signatures and lifetimes obtained by optical methods.^{13,14} First-order relaxation dynamics has also been observed in some cases or temperature ranges.^{11,15} Findings on the kinetics of photoinduced ring opening and thermal relaxation cannot be easily transferred from one group of derivatives to another and to different environments.

When naphthopyrans are dissolved in liquid crystal (LC) systems, the naphthopyran photochemistry can trigger isothermal phase transitions (phototropic phase transitions).^{16,17} The photoinduced changes in guest-host LC mixtures containing naphthopyrans are order-increasing,^{16,18} similar to those observed for spiropyrans¹⁹ and fulgides²⁰ but opposite to the behavior of azobenzene mesogens or LCs mixed with nonmesogenic azobenzene derivatives.^{21–23} The changes observed in naphthopyran guest-host LCs are attributable to a

Received: October 4, 2016 Revised: November 17, 2016 Published: November 18, 2016

Isomers Obtained after Ring Opening (center and right)



Scheme 2. Molecular Structures of the Naphthopyran Guest Molecule (G1) and Liquid Crystalline Hosts *n*-Pentyl-cyanobiphenyl (SCB) and *n*-Octyl-cyanobiphenyl (8CB)



better compatibility of the open form with the liquid crystal environment in contrast to the closed form. The LC phase transition temperatures are lower when the naphthopyran guest is in the closed form than the open form.^{16,18}

Due to the anisotropic nature of the ordered phases of LCs, these materials have been used to conduct mechanistic studies of chemical reactions.²⁴ Various cases have been identified in which the dynamics of a chemical or photochemical process was influenced by the presence and type of order of the LC phase, such as the atropisomerization of 1,1'-binaphthyl,²⁵ the thermal isomerization of *cis-N,N'*-diacetylindigo,²⁶ or the photodimerization of acenaphthylene.²⁷ However, it has also been found that unimolecular processes in which the change in geometry between the reactant and the product are relatively small usually do not exhibit different kinetics in ordered and isotropic media.²⁴

Here we report an investigation of the kinetics of the naphthopyran open-form to closed-form relaxation, which is thermally activated in the dark. We studied the thermal relaxation of a 2H-naphtho[1,2-b]pyran derivative (compound G1 in Scheme 2) in mesogenic (5CB and 8CB) and nonmesogenic (toluene) solvents for various temperatures and excitation intensities. We show that the relaxation is slower in ordered than in disordered phases, suggesting that the presence of order in the solvent environment stabilizes to some extent the open form of the naphthopyran.

EXPERIMENTAL METHODS

The molecular structure of the naphthopyran guest species considered in this study (G1) is shown in Scheme 2. This is one of the two molecules examined in our previous work.¹⁸ G1 was kindly provided by Alpha Micron Inc. (Kent, OH). The host materials employed here were toluene, 5CB, and 8CB. The molecular structures of the liquid crystalline hosts are also shown in Scheme 2. 5CB and 8CB are well-characterized mesogens that differ in the length of the alkyl chain attached to the biphenyl moiety. We have used 5CB and 8CB as hosts in earlier studies of G1 and related compounds, and it is already known that phase transitions can be photoinduced in these guest—host systems.^{16,18} Both 5CB and 8CB exhibit a nematic phase, but 8CB also has an underlying smectic A phase. The difference in phase sequence and phase transition temperatures for the two hosts should provide a sufficient parameter space for studying the

effect of temperature and order on the naphthopyran kinetics without large changes in intermolecular interactions.

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Alignment cells were prepared with glass or ITO-coated glass substrates. The substrates were coated with polyimide layers rubbed in antiparallel directions to provide homogeneous alignment conditions. The thicknesses of the cells were in the range $3-10 \ \mu\text{m}$, controlled by the inclusion of glass rod spacers in the adhesive layer. The **G1** concentration in the guest-host mixtures was between 3.8 and 4.1 wt %. Samples of **G1** in toluene, 5CB, and 8CB are labeled throughout the paper as **G1**-**tol**, **G1**-**5CB**, and **G1**-**8CB**, respectively. The mixtures in LC hosts were heated to the isotropic phase and stirred before filling the cells. The cells used for the **G1**-**tol** mixtures were sealed after filling to reduce the solvent evaporation during experimentation.

Spectra of the mixtures before exposure to UV light were collected at room temperature on an Agilent Cary 5000 spectrophotometer. Measurements as a function of temperature and in the presence of irradiation at wavelength λ_{exc} = 365 nm were taken with a spectrometer system consisting of a white light source (halogen lamp), optical fibers, lenses, and a linear CCD sensor (Ocean Optics USB2000+). A Glan-Laser calcite polarizer was placed before the sample to select the polarization state of the probing light. The collection time for the spectra measured in the kinetics study was 5 ms. The interval between subsequent spectra was 50-60 ms (spectra acquisition performed using the OOIBase32 software by Ocean Optics). The white light probe beam was normal to the sample substrates. Unless otherwise noted, absorption spectra were collected with polarization (P) of the probing light parallel or perpendicular to the rubbing direction (R). In the absorption range of the G1 open form, the spectra were corrected for reflection losses at the substrate interfaces by subtracting the effective absorbances measured for the same sample before exposure to UV light for temperatures other than those yielding a mixed nematicisotropic phase. For the mixed nematic-isotropic phase range, the spectra measured for the same sample in the dark at 25 °C were used for the subtraction.

The sample temperature was controlled using a heating stage (HCS402, Intec). The samples were allowed to equilibrate at a target temperature for about 5 min before the start of the data collection. Temperature fluctuations during the measurement time were typically within ± 0.05 °C. Phase transition temperatures were obtained from observation of the sample trans-



Figure 1. (a–c) Absorption coefficient α as a function of wavelength for (a) G1–5CB, (b) G1–8CB, and (c) G1–tol at room temperature and 4 wt % G1 concentration. The spectra displayed in blue with symbols were collected prior to exposure of the samples to UV light and thus probed only the G1 closed form. The spectra displayed in red and with no symbols were obtained at the photostationary state during exposure to 365 nm light at 4.5 mW/ cm². Solid lines, P || R; dashed lines, P \perp R; dotted line, orientational average. The host contribution has been subtracted from all spectra. (d) Absorption spectra normalized at the maximum for the G1 closed form (black, obtained with UV light off) and open form (green, obtained with UV light on) in toluene (lines with diamonds), 5CB (lines with triangles facing left), and 8CB (lines with triangles facing right). The orientational average is shown for 5CB and 8CB. For clarity, the open-form spectra in part d have been smoothed (running average of data points over 7 nm).



Figure 2. (a) Transition temperatures for 5CB, G1–5CB, 8CB, and G1–8CB, as measured during heating at 1.0 °C/min. For the mixtures, results for samples in the dark and at the photostationary state during UV exposure (9 mW/cm²) are included. "1" and "2" are the onset and the completion, respectively, of the transition from the smectic (if present) to the nematic phase; "3" is the onset of the nematic-to-isotropic transition; the samples are fully isotropic above "4". (b) Dichroic ratio D_g of the guest molecules open form as a function of temperature for G1–5CB (squares) and G1–8CB (diamonds) measured isothermally at the photostationary state (8.9 mW/cm² for G1–5CB and 4.5 mW/cm² for G1–8CB). All data obtained for cells with $L \cong 5 \mu m$.

mittance with R at 45° to the crossed polarizer and analyzer during heating at 1.0 °C/min.

The source of UV light was a LED with emission centered at 365 nm (OmniCure LX400+, Lumen Dynamics) and a bandwidth of 10 nm (full width at half-maximum, fwhm). The UV beam formed an angle of ca. 20° with the white probe beam

and had a fwhm diameter of 27 mm at the sample. The fwhm diameter of the white light probe upon the sample was 6 mm. The irradiance for the UV light incident on the front substrate of the LC cells was in the range $1-16 \text{ mW/cm}^2$. The UV pump beam reaching the LC mixture is reduced relative to this value by



Figure 3. Polarized optical micrographs of closed-form G1–8CB with homogeneous alignment (4.5 μ m thickness): (a, b) Smectic A phase at 25 °C, (c, d) nematic phase at 30 °C. The arrows indicate the transmission direction of the polarizer (P) and analyzer (A), and the rubbing direction (R). The image dimensions are 580 μ m × 435 μ m.

reflection losses at the glass interface, while absorption from the substrate is negligible.

Micrographs under cross polarizers were recorded on a polarizing microscope (Nikon Eclipse 50iPOL) equipped with a Lumenera Infinity 2-1C camera and using a 10× objective.

RESULTS

The absorption spectra for the closed form of compound **G1** in the three hosts are shown in Figure 1a,b, and c (lines with symbols). The ordinate scale in the graphs is the absorption coefficient $\alpha = (A \ln(10))/L$, where *A* is the absorbance of the guest and *L* the sample thickness. The lowest energy absorption maximum of **G1** in 5CB, 8CB, and toluene is at 354, 354, and 349 nm, respectively. The band shape is similar in all solvents, but a small bathochromic shift (5 nm) was observed in the mesogenic solvents relative to toluene (see also Figure 1d), possibly because of the difference in solvent polarity.

The transition temperatures observed for G1–5CB and G1– 8CB and for the neat hosts are shown in Figure 2a. The onset of the nematic to isotropic transition occurs at 28.3 °C for G1–5CB and 33.1 °C for G1–8CB. G1–8CB exhibits the same phase sequence as neat 8CB (crystal, smectic A, nematic, isotropic on heating). The temperature of the smectic A to nematic transition onset for the G1–8CB mixture is 27.8 °C. The transition temperatures for G1–5CB and G1–8CB in the dark are lower than those for 5CB and 8CB, respectively, due to the impurity effect of G1 on the LC host. At room temperature, G1–5CB is in the nematic phase and G1–8CB is in the smectic A phase. Images of a G1–8CB sample at 25 and 30 °C from a polarizing optical microscope are shown in Figure 3. At both temperatures, the sample is birefringent and the texture appears uniform when the rubbing direction R bisects the angle between crossed polarizers (Figure 3a,c). However, a difference in texture can be seen when the sample is rotated close to the extinction condition: striations approximately along R can be seen at 25 °C (Figure 3b) but not at 30 °C (Figure 3d). The former are due to the focal conic structure of the smectic A phase. The transition temperatures are higher when the samples are exposed to UV light than in the dark (Figure 2a), because the G1 open form is more compatible with the liquid crystal environment that the closed form, as previously reported.^{16,18} The transition temperatures for the samples under UV exposure depend on the intensity of the UV light (decreasing and approaching the transition temperatures for the samples in the dark when the intensity decreases), as this determines the fraction of G1 molecules in the open form at the photostationary state.²⁸

For both G1–5CB and G1–8CB, dichroism is observed for the G1 closed-form absorption band (Figure 1a and b), indicating that the naphthopyran molecules are aligned within the sample. At room temperature, the dichroic ratio of the guest molecules, $D_{\rm g} = \alpha_{\rm P||R}/\alpha_{\rm P\perp R}$ (where $\alpha_{\rm P||R}$ and $\alpha_{\rm P\perp R}$ are the absorption coefficients measured with the polarization of the probing light parallel or perpendicular, respectively, to R) was 2.5 for G1–5CB and 4.8 for G1–8CB. The dichroic ratio is larger in the 8CB host relative to 5CB because the smectic phase is more ordered that the nematic phase.

The effect of order on the absorption spectra can be removed by calculating the orientational average of $\alpha_{P\parallel R}$ and $\alpha_{P\perp R}$, $\overline{\alpha} = (\alpha_{P\parallel R} + 2\alpha_{P\perp R})/3$, which corresponds to the absorption coefficient the sample would exhibit if it were isotropic ($D_g = 1$; order parameter = 0). The orientational averages $\overline{\alpha}$ are shown as dotted lines in the graphs of Figure 1a and b. It can be seen that



Figure 4. Absorbance of **G1–5CB** at 510 nm as a function of time (cell thicknesses = $4.8-5.1 \mu$ m). The UV pump light was on between time 0 and 60.0 s. The intensity for each exposure is shown in the legend. Data was recorded at 35 °C. (a) Behavior at the onset of the closed-form to open-form conversion; (b) behavior during the thermal relaxation from the photostationary state. (c, d) The same data as in parts a and b after normalization to the absorbance at the photostationary state for each exposure intensity.

the average absorption coefficient for the **G1** closed form is similar in 5CB and 8CB and similar to the value measured in the nonmesogenic host. The value at the maximum of the band is $0.19-0.24 \ \mu m^{-1}$ at 4 wt % doping.

The absorption spectrum of the G1 open form, measured during exposure to UV light, exhibits a maximum at 502 nm in 5CB, 498 nm in 8CB, and 489 nm in toluene. The bathochromic shift of the G1 open form in the two liquid crystalline solvents relative to toluene is slightly larger than that for the closed form. The solvatochromism of the open form has been seen in other naphthopyrans.²⁹ The direction of the solvatochromic shift is consistent with that expected in weakly polar merocyanine-like structures.³⁰ The band shapes are almost identical in 5CB and 8CB for both closed and open forms (Figure 1d). At the photostationary state under exposure at 4.5 mW/cm², the dichroic ratio for the guest molecules, $D_{\rm g}$, at 25 °C was 4.2 in 5CB and 7.7 in 8CB (see also Figure 2b). In both hosts, these values are larger than those of the samples in the dark, consistent with the expected photoinduced increase in order in this type of system^{16,18} and the different orientation of the transition dipole moment of the closed and open forms relative to the long axis of the molecules. The dichroic ratio decreases with increasing temperature and becomes equal to 1 in the isotropic phase (Figure 2b). For G1–8CB, a large decrease in D_{σ} is seen between 32 and 34 °C, across the transition from the smectic A to the nematic phase under UV illumination (Figure 2a). In their respective nematic phases, G1-5CB and G1-8CB exhibit similar values of D_{g} .

As will be shown below, the thermal relaxation rates for the G1 open form are different in different solvents. As a consequence,

the composition of the photostationary state at a given excitation intensity and temperature (the fraction of molecules in the open form, $f_{\rm open} = N_{\rm open}/(N_{\rm open} + N_{\rm closed}) = N_{\rm open}/N_{\rm total})$ is not necessarily the same for the three hosts considered here. In the definition of $f_{\rm open}$, $N_{\rm total}$ is the number density of **G1** molecules in the mixture. $N_{\rm open}$ and $N_{\rm closed}$ are the number densities for the open and closed form only, respectively. The change in $f_{\rm open}$ is the main reason for the different apparent absorption coefficients $\overline{\alpha}$ for the open-form cases shown in Figure 1a, b, and c. A small solvent dependence of the extinction coefficient in the three hosts cannot be excluded, but it is expected to be minimal relative to the difference in $f_{\rm open}$ in the steady state.

In order to study the dynamics of the photoconversion of **G1** from the closed to the open form, sample spectra were collected at various times during 365 nm exposure. Examples of the transient behavior for **G1–5CB** are shown in Figure 4a. Absorption due to the **G1** open form is observed when the pump light is turned on, starting at time t = 0 s, and the absorbance progressively increases with time until a constant steady state value is reached. In other naphthopyran and pyran derivatives, the ring opening reaction has been reported to occur in the ns or sub- μ s time scale,^{7,8} much faster than the resolution of our experimental setup. The characteristic time required to reach steady state is on the order of seconds for the cases of Figure 4a. These characteristic times depend on the excitation rate of the **G1** molecules in the sample and the thermal decay rate from the open to the closed form.

The fraction of molecules excited under the experimental conditions used here can be estimated as follows. At the front face of the sample, the rate equation for the excitation of **G1** molecules at 365 nm can be written as

$$\frac{\mathrm{d}N_{\mathrm{closed}}}{\mathrm{d}t} = -\sigma^{(c)}(365 \text{ nm})\phi_{\mathrm{in}}N_{\mathrm{closed}} \tag{1}$$

where $\sigma^{(c)}(365 \text{ nm})$ is the closed-form absorption cross section at 365 nm and ϕ_{in} is the incident photon flux. At short irradiation times, before any significant conversion to the open form, N_{closed} $\cong N_{\text{total}}$. The density of 5CB is about 1.02 g/cm³, ³¹ and a G1 content of 4 wt % corresponds to a molar concentration of C = 5.57×10^{-2} M and a number density of $N_{\text{total}} = 3.35 \times 10^{19}$ cm⁻³. The cross section can then be obtained from the closed-form absorption coefficient in Figure 1a (for this estimate, the orientational average values is used): $\sigma^{(c)}(365 \text{ nm}) = \alpha^{(c)}(365 \text{ nm})/N_{\text{total}} = 6.26 \times 10^{-17} \text{ cm}^2$. For $\lambda_{\text{exc}} = 365 \text{ nm}$ and an incident intensity of $I_{\text{in}} = 5.0 \text{ mW/cm}^2$, the photon flux is $\phi_{\text{in}} = I_{\text{in}}/E_{\text{ph}} =$ $9.2 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, where $E_{\text{ph}} = 5.442 \times 10^{-19} \text{ J}$ is the photon energy. From eq 1, the initial fraction of closed-form molecules excited is $|dN_{\text{closed}}/N_{\text{total}}| = (6.26 \times 10^{-17} \text{ cm}^2)(9.2 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}) dt = (0.58 \text{ s}^{-1}) dt$. Over 50 ms, the approximate time between adjacent data points in our time-resolved experiment, | $dN_{\text{closed}}/N_{\text{total}}| \cong 3\%$.

Changes in open- and closed-form populations are faster for larger fluxes (see eq 1). As a consequence, the steady state is expected to be reached in shorter times at high flux. For example, at 35 °C, the time to reach 90% of the steady state value is 3 s while pumping at 16 mW/cm² and 8 s at 1.6 mW/cm² (see Figure 4c, where the data are shown on a normalized scale).

Information on thermal decay rates could be obtained from a detailed analysis of the absorbance data while the UV pump is on. Depending on the number of active species, their absorption characteristics, and the experimental configuration used, it is not always possible to solve the rate and propagation equations analytically, especially if λ_{exc} is not an isosbestic point. In the ordered phase of mesogenic solvents, there is one additional complicating factor: if the order changes during exposure, as is the case in phototropic systems, the fraction of light absorbed by the sample can vary not only because of the change in the relative population of the absorbing species during exposure but also because the effective absorption coefficient of the species depends on the order of the system. This potential issue can be avoided by measuring the thermal relaxation rate from the behavior of the sample after the pumping light has been turned off. The thermal decay of G1 after turning off irradiation is shown in Figure 4b. The absorbance of the G1 open form decreases from the steady state values toward zero. If the absorbance data are normalized to the steady state absorbance values, all the traces closely overlap (see Figure 4d).³² The similarity between the traces in Figure 4d indicates that their relaxation dynamics is the same. This would be the case if only one G1 open form species were generated during the photoinduced conversion and the dark relaxation back to the closed form did not involve intermediates, that is, if the thermal relaxation were described by a single decay constant. On the basis of these observations, the guest-host mixtures can be described by the simplified mechanism illustrated in Scheme 3.

First-order relaxation dynamics has been reported in a few naphthopyrans.^{11,15} In a wider range of derivatives, though, reaction mechanisms involving the closed form and more than one open-form isomer have been observed.^{9,12,14,33} Either the reaction mechanism is intrinsically different for 2*H*-naphtho[1,2-b]pyrans with the substitution pattern of **G1**, or the thermal

Scheme 3. Mechanism for the Photoinduced Ring Opening and Thermal Relaxation Consistent with the Dynamics Observed for $G1^a$



"The reaction from left to right is photoinduced using excitation at λ_{exc} it has efficiency η , and it does not occur thermally at T = 25-60 °C. The reaction from right to left occurs thermally, and it is characterized by the relaxation rate k_{Δ} .

relaxation shown in Scheme 3 represents the rate limiting step and other processes have significantly different rates.

Given the reaction mechanism of Scheme 3, the population of the G1 open form (N_{open}) at time *t* once the UV pump is turned off is described by the following rate equation

$$\frac{\mathrm{d}N_{\mathrm{open}}(t,z)}{\mathrm{d}t} = -k_{\Delta}N_{\mathrm{open}}(t,z) \tag{2}$$

with the boundary condition that the population is $N_{\text{open}}(t_{\text{off}}, z)$ when the pump is turned off at $t = t_{off}$. k_{Δ} is the rate of the thermal relaxation process. We have written eq 2 for a generic case where the open-form population is not uniform and depends on the depth in the sample, z. Because attenuation of the pump beam is non-negligible in our experimental conditions, there is a gradient of excitation rate through the sample thickness during UV exposure. In addition, the viscosity of the host may be large enough to prevent efficient redistribution of the photoproducts. The dynamics of photoreactions in solution is often studied with vigorous stirring to achieve a reasonably uniform distribution of photoproducts in the sample. Stirring is not possible in the sample configurations explored here. We will assume, however, that N_{open} is uniform in the plane of the sample at each depth z within the probe area (within which the pump intensity is uniform to a good approximation).

The solution of eq 2 for the boundary condition given above is

$$N_{\text{open}}(t, z) = N_{\text{open}}(t_{\text{off}}, z) e^{-k_{\Delta}(t-t_{\text{off}})}$$
(3)

If the sample in an ordered phase is probed in the visible range where there is no absorption of the **G1** closed form, the attenuation of the probe beam of flux ϕ_{probe} due to absorption from the **G1** open form between depth z and z + dz is expressed (for polarization parallel or perpendicular to the rubbing direction) as

$$d\phi_{\text{probe},P\parallelR}(t,z) = -\phi_{\text{probe},P\parallelR}(t,z)\sigma_{P\parallelR}^{(o)}(\lambda')N_{\text{open}}(t,z) dz$$
$$d\phi_{\text{probe},P\perpR}(t,z) = -\phi_{\text{probe},P\perpR}(t,z)\sigma_{P\perpR}^{(o)}(\lambda')N_{\text{open}}(t,z) dz$$
(4)

where $\sigma_{P||R}^{(o)}(\lambda')$ and $\sigma_{PLR}^{(o)}(\lambda')$ are the absorption cross sections of the open form at λ' for the polarization conditions in the subscript. These terms are related to the orientation average cross section $\overline{\sigma}^{(o)}$ and the order parameter *S*, which is time dependent, and are thus not constant during the decay:

$$\sigma_{\mathbf{P}\parallel\mathbf{R}}^{(\mathrm{o})}(\lambda') = (2S(t)+1)\overline{\sigma}^{(\mathrm{o})}(\lambda')$$
(5a)

$$\sigma_{P\perp R}^{(o)}(\lambda') = (1 - S(t))\overline{\sigma}^{(o)}(\lambda')$$
(5b)



Figure 5. (a) The decay of **G1** open form from the photostationary state: orientational average absorbance at 510 nm of **G1–5CB** at 27 °C (blue symbols), 30 °C (brown symbols; scattering due to the occurrence of a nematic-to-isotropic phase transition starting at t = 72 s contributes to the data points in the "scattering range" indicated by the double-headed arrow, see text for details), and 40 °C (red symbols) as a function of time. The UV pump light at 8.9 mW/cm² was turned off at $t_{off} = 60.0$ s. The best fits to single exponential decays for each trace are shown as black lines. Cell thickness: $4.9 \,\mu$ m. (b–g) Polarized optical micrographs of **G1–5CB** ($4.8 \,\mu$ m thickness) at 30 °C at steady state under UV light (b) and at various times after switching off the UV pump light: $t - t_{off} = 5$ s (c), 19 s (d), 28 s (e) 42 s (f), 430 s (g). The transmission directions for the polarizer and analyzer and the rubbing direction are shown in part b and are the same for the other images. The image dimensions are 580 μ m × 435 μ m.

be derived from eq 4 after separating the variables and integrating over the sample thickness L. After substituting eq 5a and 5b for the cross sections, the following expression for the absorbances

The absorbances at λ' for the two polarization conditions can

parallel and perpendicular to R are obtained:

$$\begin{split} A_{P\parallel R}(\lambda', t) &= \frac{1}{\ln 10} \ln \frac{\phi_{\text{probe}, P\parallel R}(t, 0)}{\phi_{\text{probe}, P\parallel R}(t, L)} \\ &= \frac{(2S(t) + 1)\overline{\sigma}^{(o)}(\lambda')}{\ln 10} e^{-k_{\Delta}(t - t_{\text{off}})} \\ &\int_{0}^{L} N_{\text{open}}(t_{\text{off}}, z) \, dz \end{split}$$
(6a)

$$A_{P\perp R}(\lambda', t) = \frac{1}{\ln 10} \ln \frac{\phi_{\text{probe}, P\perp R}(t, 0)}{\phi_{\text{probe}, P\perp R}(t, L)}$$
$$= \frac{(1 - S(t))\overline{\sigma}^{(o)}(\lambda')}{\ln 10} e^{-k_{\Delta}(t - t_{\text{off}})}$$
$$\int_{0}^{L} N_{\text{open}}(t_{\text{off}}, z) dz$$
(6b)

The orientational average of eqs 6a and 6b is

$$\overline{A}(\lambda', t) = (A_{P\parallel R}(\lambda', t) + 2A_{P\perp R}(\lambda', t))/3$$
$$= \frac{\overline{\sigma}^{(o)}(\lambda')}{\ln 10} e^{-k_{\Delta}(t-t_{off})} \int_{0}^{L} N_{open}(t_{off}, z) dz$$
(7)

Thus, $\overline{A}(\lambda', t)$ exhibits a monoexponential decay with a decay rate independent of $N_{\text{open}}(t_{\text{off}}, z)$. The time dependence of $\overline{A}(\lambda', t)$ in ordered phases is the same as that in an isotropic sample. In contrast, $A_{P\parallel R}$ and $A_{P\perp R}$ in eq 6 have a more complex dependence on time because *S* is not constant. In the general case for an anisotropic solvent, the absorbance measured with unpolarized

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Та	ble	1.	Thermal	D)ecay	Rates	k_{Δ}	for	the	Op	en	Form	of	G	1
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<i>T</i> (°C)	k_{Δ} (s ⁻¹) for G1–5CB ^{<i>a,b</i>}	k_{Δ} (s ⁻¹) for G1–8CB ^{<i>b,c</i>}	k_{Δ} (s ⁻¹) for G1–tol ^c
25.0	N: 3.89×10^{-2}	S: 1.38×10^{-2}	1.84×10^{-1}
27.0	N: 5.32×10^{-2}	S: 1.90×10^{-2}	2.15×10^{-1}
29.0	N: 7.24×10^{-2}	S: 2.70×10^{-2}	2.55×10^{-1}
31.0	N: 9.12×10^{-2}	S: 3.70×10^{-2}	3.04×10^{-1}
31.0	I: 1.04×10^{-1}	N: 5.06×10^{-2}	
32.0	N: 9.67×10^{-2}	S: 4.45×10^{-2}	
32.0	I: 1.29×10^{-1}	N: 6.04×10^{-2}	
33.0	I: 1.49×10^{-1}		3.56×10^{-1}
35.0	I: 1.83×10^{-1}	N: 9.33×10^{-2}	4.16×10^{-1}
37.0		I: 2.07×10^{-1}	5.00×10^{-1}
40.0	I: 3.19×10^{-1}	I: 2.94×10^{-1}	6.42×10^{-1}
50.0	I: 7.83×10^{-1}	I: 7.53×10^{-1}	1.45×10^{0}

^{*a*}Data for decay from the photostationary state at 8.9 mW/cm². ^{*b*}The letter in front of the k_{Δ} value indicates the phase of the sample in which that rate was determined: S (smectic A), N (nematic), I (isotropic). ^{*c*}Data for decay from the photostationary state at 4.5 mW/cm².



Figure 6. G1 open-form decay from the photostationary state: orientational average absorbance, normalized to the photostationary state value, of G1– **5CB** (red symbols), **G1–8CB** (green symbols), and **G1–tol** (black symbols) as a function of time at (a) 25 °C and (b) 40 °C. The UV pump light (4.5 mW/cm²) was turned off at t = 60.0 s.

light (that is,

$$A_{\text{unpol}}(\lambda', t) = -\log\left(\frac{1}{2}10^{-A_{p\parallel R}(\lambda't)} + \frac{1}{2}10^{-A_{p\perp R}(\lambda't)}\right) \text{ would}$$

not exhibit a strictly monoexponential decay.

The decay rates k_{Δ} were thus estimated by determining the best fit to monoexponential functions (eq 7) for the experimental orientational averages $\overline{A}(\lambda', t)$ obtained for the various samples and temperatures. A few examples of experimental data and fitting curves are shown in Figure 5a for **G1–5CB**. Good fits to the experimental data were obtained at temperatures for which no isothermal phase changes occurred (27 and 40 °C cases in Figure 5a), indicating that the experimental data are consistent with the first-order kinetics illustrated in Scheme 3.

The trace at 30 °C in Figure 5a, where the absorbance values exhibit a nonmonotonic trend after the light irradiation is removed, can be explained as follows. At 30 °C, the steady state of the **G1–5CB** sample under UV exposure at 8.9 mW/cm² is in the nematic phase (Figure 5b). The sample in the dark, however, exhibits a coexistence of isotropic and nematic phases (see also Figure 2a). The sample is in the nematic state when the UV light is turned off at t = 60 s. The **G1** open form starts to decay back to the closed form. Correspondingly, the order parameter and the birefringence of the sample decrease relative to the steady state, as evidenced by the change in interference colors when the sample is viewed under crossed polarizers (Figure 5c). When N_{open} reaches a critical value, a phase transition starts to occur, small droplets appear, and the sample becomes highly scattering (Figure 5d). Scattering is responsible for the change in trend of

the absorbance trace starting at 72 s (arrow in Figure 5a). After this time, the measured quantity is actually the total optical loss through the sample (absorption and scattering). The droplets then develop into isotropic domains that increase in size over time (Figure 5e,f). At this temperature, some nematic domains persist for several minutes after the transition onset, when the G1 closed form has already fully recovered and the sample is at equilibrium (Figure 5g). The absorbance trace follows a monoexponential decay at times before the onset of scattering (the dashed line in Figure 5a was obtained from fitting the data for t = 60-72 s; values for t > 72 s are the extrapolation of the fitting results). For all the experiments discussed in this paper, data points for times during which the samples became scattering due to a phase transition were excluded from the model fitting. The behavior near the isothermal phase transitions will be addressed in more detail later.

The k_{Δ} estimates for **G1** in 5CB, 8CB, and toluene are collected in Table 1. For the mesogenic solvents, the phase of the sample at the various temperatures is indicated in front of each decay value. It can be seen that the decay rates are host dependent and that they increase with increasing temperature.

At 25 °C, the thermal relaxation is slower in the smectic A phase of 8CB than in the nematic phase of 5CB (Figure 6a). Both are significantly slower than in the isotropic solvent, toluene. At 40 °C (Figure 6b), the relaxation is faster than at 25 °C in each of the hosts. All samples are isotropic at 40 °C, and the relaxation is slightly faster in toluene than in the mesogenic solvents.

Differences in solvent polarity, polarizability, and viscosity could be responsible for the change.

DISCUSSION

An increase in decay constants with increasing temperature is common and is often associated with an Arrhenius behavior of the chemical process involved

$$k_{\Lambda} = P \mathrm{e}^{-E_{\mathrm{a}}/(RT)} \tag{8}$$

where E_a is the activation energy, *R* is the gas constant, and *P* is the pre-exponential factor.

Figure 7a shows that log k_{Δ} for **G1–tol** exhibits a linear decrease as a function of 1/T, consistent with eq 8. From the best fit of the data, an activation energy of $E_a = 62.8$ kJ/mol is obtained (Table 2). This value is similar to those previously reported in the literature for other naphthopyran derivatives in ordinary solutions. Favaro et al. observed $E_a = 79$ kJ/mol for Reversacol Berry Red in 3-methylpentane and 82 kJ/mol in toluene.²⁹ Ottavi et al. reported activation energies in the range 60–70 kJ/mol for lapachenole³⁴ and of 60 kJ/mol for 2,2-diphenyl-5,6-benzo-(2*H*)chromene.¹²

The relaxation behavior of the photochromic molecules in mesogenic solvents is different in some critical respects relative to that in toluene. First, at any temperature, the G1 relaxation rates in 5CB and 8CB are smaller than those in toluene (Figure 7a). Second, the rates do not exhibit a simple Arrhenius behavior over the full temperature range investigated and the trend is strongly dependent on the phase of the host. For G1-5CB, the slope of the log k_{Δ} line as a function of 1/T changes going from the isotropic to the nematic phase. Distinct fits to eq 8 can be carried out in the isotropic and nematic ranges (lines ii and iii in Figure 7b). The activation energy E_a is larger in the nematic than in the isotropic phase by about 24 kJ/mol (see Table 2). For comparison, a fit for data over the full temperature range is also drawn in Figure 7b (line i). It can be seen that the k_{Δ} values on line i systematically overestimate the experimental values in the nematic range and underestimate those in the isotropic range. Figure 7b also shows that the decay rates obtained after exposures at different excitation intensities are very close, consistent with the one-open-form, one-rate relaxation mechanism in Scheme 3.

The change in behavior between the nematic and isotropic phases is more evident in the case of **G1–8CB** (Figure 7c, lines v and vi), where the activation energies are estimated to be 121 and 78 kJ/mol, respectively. In **G1–8CB**, there is also a change in behavior, albeit smaller, between the smectic and nematic phases (cf. lines iv and v in Figure 7c). The temperature ranges over which experimental points are available for the smectic A and nematic phases are narrow, and as such, the parameters obtained in the fitting to eq 8 are affected by large errors. Nevertheless, performing the fit over the combined nematic and smectic phase would lead to oppositely signed residuals on the two sides of the phase transition. Differences in pre-exponential factors are also observed between phases, with values in ordered phases ($P \ge 10^{14} \text{ s}^{-1}$) being significantly larger than those in the isotropic phase (P on the order of 10^{12} s^{-1} or smaller).

Table 2 also lists the activation enthalpy ΔH^{\dagger} and entropy ΔS^{\dagger} for the **G1** open form thermal relaxation process of the **G1** open form from the Eyring equation

$$k_{\Delta} = \frac{k_{\rm B}T}{h} \mathrm{e}^{-(\Delta H^{\dagger} - T\Delta S^{\dagger})/(RT)} \tag{9}$$



Figure 7. Thermal decay rates as a function of inverse temperature. (a) Results obtained for G1-tol (black), G1-5CB (red), and G1-8CB (green) after exposure at 4.5 mW/cm² (8.9 mW/cm² in 5CB). (b) Decay rates for G1-5CB and fits to eq 8: (i) fitting over all data points; (ii) fitting over data in the nematic range, (iii) fitting over data in the isotropic range; results from different excitation intensities are shown by symbols of different sizes (small, 1.6; medium, 8.9; large, 16 mW/cm²). (c) Decay rates for G1-8CB and fits to eq 8 in the smectic (iv), nematic (v), and isotropic (vi) ranges. In all graphs, data points in the isotropic phase are displayed as circles, those in the nematic phase as squares, and those in the smectic phase as diamonds.

where $k_{\rm B}$ and h are the Boltzmann and Planck's constants, respectively. The temperature dependence is different in eqs 8 and 9. Trends in experimental rates are often described equally well by both expressions if the temperature range is relatively narrow, as in our case. Graphs of k_{Δ}/T as a function of 1/T for **G1** in the three hosts are included in the Supporting Information (Figures S1, S2, and S3). From the results in Table 2, it can be seen that the ΔH^{\dagger} values follow the same trend as the activation energies, as expected. Also of note is the fact that the values of

Tabl	e 2.	Arr	henius	and	Eyring	Parameters	for	G1	Thermal	Relaxation	l
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sample ^a	phase ^b	P^{c} (s ⁻¹)	E_{a}^{c} (kJ/mol)	$\Delta H^{\dagger \ d} \ (\mathrm{kJ/mol})$	$\Delta S^{\dagger \ d} \left(\mathrm{J}/(\mathrm{mol}\ \mathrm{K}) \right)$
G1-tol (4.5 mW/cm^2)	Ι	$(1.98 \pm 0.65) \times 10^{10}$	62.8 ± 0.9	60.3 ± 0.8	-56.3 ± 2.5
G1-5CB (8.9 mW/cm ²)	I and N	$(5.14 \pm 5.03) \times 10^{13}$	86.8 ± 2.7	83.1 ± 2.1	9.5 ± 7.0
G1-5CB (8.9 mW/cm ²)	Ν	$(0.97 \pm 1.48) \times 10^{17}$	104.9 ± 4.7	102.5 ± 3.1	72.1 ± 11.2
G1-5CB (8.9 mW/cm ²)	Ι	$(8.09 \pm 6.03) \times 10^{12}$	80.5 ± 2.0	78.0 ± 1.7	-6.3 ± 5.8
G1–5CB (1.6, 8.9, 16 mW/cm ²)	Ν	$(4.03 \pm 11.7) \times 10^{15}$	96.9 ± 8.1	93.6 ± 5.4	42.6 ± 19.8
G1–5CB (1.6, 8.9, 16 mW/cm ²)	Ι	$(1.42 \pm 0.92) \times 10^{12}$	76.0 ± 2.0	73.4 ± 1.5	-20.8 ± 4.9
G1-8CB (4.5 mW/cm ²)	S	$(2.30 \pm 2.66) \times 10^{20}$	126.7 ± 3.7	124.3 ± 2.3	136.5 ± 8.1
G1-8CB (4.5 mW/cm ²)	Ν	$(3.26 \pm 4.96) \times 10^{19}$	121.2 ± 4.9	118.6 ± 3.1	119.9 ± 10.8
G1-8CB (4.5 mW/cm^2)	Ι	$(3.07 \pm 2.37) \times 10^{12}$	78.1 ± 2.4	75.6 ± 1.9	-14.5 ± 6.1

^aThe value given in parentheses is the intensity used to generate the photostationary state. ^bPhase for data points considered in the analysis. ^cFrom the best fit of the experimental data to eq 8. ^dFrom the best fit of the experimental data to eq 9.



Figure 8. Examples of **G1** open-form thermal decay behavior near phase transitions. (a) Nematic-to-isotropic transition: **G1–5CB** at 31.0 °C after excitation at 16 mW/cm² ($L = 5.2 \mu$ m). (b) Smectic A-to-nematic transition: **G1–8CB** at 31.0 °C after excitation at 4.5 mW/cm² ($L = 4.5 \mu$ m). UV light was turned off at time 60.0 s. Bottom panels: optical loss at 800 nm (mainly due to scattering). Top panels: orientational averaged absorbance at 510 nm (black symbols; only data points for times at which scattering is negligible are shown); best fit to single exponential decays of the absorbance data for ranges I and II (dashed lines), and their combination (dotted line, case a only). The double-headed arrows indicate the extent of ranges I and II in time.

 ΔS^{\dagger} are negative in all isotropic cases and positive and relatively large in the nematic and smectic A phases. This suggests that the **G1** thermal relaxation involves a larger rearrangement of the solvating environment in the ordered phases relative to the isotropic one. There is a linear relationship between ΔH^{\dagger} and ΔS^{\dagger} values in Table 2 of the type $\Delta H^{\dagger} = \beta \Delta S^{\dagger} + C$ (where β is the isokinetic temperature and *C* is a constant; see Figure S4). This would be the case if the reaction mechanism were the same in all of the solvent environments tested. The existence of a linear relationship is, however, not sufficient to prove that the mechanism is solvent independent.

Additional supporting evidence for a phase-dependent relaxation behavior can be obtained from experiments performed at temperatures where the isothermal phase transitions occur, as shown in Figure 8. At 31.0 °C, G1-5CB is in the isotropic phase in the dark, while it is nematic under illumination at 16 mW/cm^2 . Absorbance data collected during the relaxation from this steady state are shown in the top panel of Figure 8a (t > 60 s). Similar to what was discussed above for the 30 °C data in Figure 5, a short time after the illumination is turned off, isotropic domains start to form and the sample becomes scattering (t = 65 s, see optical loss data in the bottom panel of Figure 8a). At this temperature, the phase transition is complete within a few seconds and the sample is again in a single phase (isotropic) from t = 74 s onward. The assignment of the phase is based on the observed value of D_{σ} , which is >1 in the photostationary state and for 60 s < t < 65 s (range *I* in Figure 8a) and equal to 1, within experimental error, for t > 74 s (range II in the figure). A good fit of the experimental

data points to eq 7 can be obtained independently for ranges I and II (dashed lines in the figure), and the estimated k_{Δ} value is smaller for I (0.0911 s⁻¹) than II (0.108 s⁻¹). If ranges I and II are combined in the fit attempt (dotted line in the figure), the fitted curve is systematically below the experimental data points in range I and above in range II, and thus, it is not a good description of the experimental trend.

A change in decay behavior is also seen across the smectic Anematic transition in G1-8CB. At 31.0 °C, the photostationary state for illumination at 4.5 mW/cm² is smectic, while the relaxed state in the dark is nematic (see Figure 2a). As shown in Figure 8b (top panel), a change in the trend of the G1 open-form absorbance is observed over time, as at both early decay times (t< 72 s, range I) and long decay times (t > 76 s, range II), log \overline{A} decreases linearly with time but with different slopes $(3.71 \times$ 10^{-2} s⁻¹ in range I and 5.06×10^{-2} s⁻¹ in range II). On the basis of other spectroscopic evidence, including a small change in optical loss at wavelengths outside the G1 open form absorption band (see bottom panel of Figure 8b), the smectic A-nematic phase transition during this sample's relaxation is identified as occurring between t = 72 and 74 s. For all cases in which the change in G1 open-form content in the sample before and after a phase transition could be monitored, k_{Δ} was larger in the less ordered phase than in the more ordered phase (see Figure 7b and c).

To summarize, our results on the thermal relaxation of the G1 open form indicate that the process is influenced by the environment in which the molecules are embedded. Overall, the

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open-form relaxation rates are smaller in mesogenic solvents than in toluene. Part of this difference can be attributed to the effect of viscosity, which is significantly smaller for toluene than for 5CB and 8CB even in the isotropic phase (around 50 °C, the viscosity coefficient is 0.42, 14, and 18 mPas for toluene,³⁵ 5CB,³⁶ and 8CB,³⁶ respectively). For each solvent, the viscosity increases approximately exponentially as a function of 1/T and thus it would lead to a rate expressed by eq 8 in the absence of other effects. However, examples of anomalous viscosity dependence for the rates of unimolecular reactions are known. Otruba and Weiss reported that the thermal isomerization to an indolinospiropyran from its merocyanine open form was characterized by similar rates in polybutadiene when the viscosity varied over 2 orders of magnitude.³⁷ Also, the activation enthalpy for the atropisomerization of 1,1'-binaphthyl was found to be smaller in the nematic phase of E7 and in the solid phase of the mesogen p-methoxybenzylidene-p-n-butylaniline (MBBA) than in benzene or cyclohexane.²⁵

An increase in the polarity of the solvent going from toluene to 5CB and 8CB could also account for the observed change in activation energies for the G1 relaxation. An increase in reaction rate at a given temperature with solvent polarity has been seen for various isomerization processes.^{38,39} Serra and Terentjev, on the other hand, found that the isomerization rate for azobenzene is smaller in chloroform than in the less polar toluene.⁴⁰ Activation enthalpy and entropy can also vary with solvent, as the rate changes with solvent polarity depend on the relative ability of the solvent environment to screen the charges of the reactant and transition state. Görner et al. did not observe any significant solvent dependence in the dynamics of 3,3-diphenyl-3Hnaphtho[2,1-b]pyran.¹¹ However, in the thermal relaxation of other photochromic dyes, an increase in ΔH^{\dagger} and ΔS^{\dagger} in more polar solvents has often been observed.^{39,41} This is the same trend detected for G1 in the isotropic phases (Table 2). The difference in behavior relative to the case discussed by Görner et al.¹¹ could be due to the presence of polar substituents in **G1**.

We also found that **G1** relaxation rates are smaller in the ordered versus disordered phases. The activation enthalpy for the thermal relaxation reaction increases going from the isotropic to the ordered phases of the mesogen. At the same time, ΔS^{\dagger} assumes a large positive value in the ordered phases, whereas it is negative in isotropic environments.

The larger viscosity of the ordered phases of 5CB and 8CB relative to their isotropic phase can be in part responsible for the effect. However, we believe that viscosity cannot fully explain the observed behavior, based on the following considerations:

- (1) k_{Δ} values for the isotropic phase of 5CB and 8CB are the same, while the viscosity is larger in 8CB than in 5CB, as discussed above. In the ordered phase, the values of the viscosity components are at most 10% larger for 8CB than for 5CB near their respective nematic-to-isotropic transition temperature.³⁶
- (2) There have been reports in the literature in which naphthopyrans were shown to exhibit faster decay kinetics in certain solid films than in liquid solutions,²⁹ which implies that other effects can be competitive with viscosity-induced changes in this family of compounds.
- (3) A dependence of the dynamics of unimolecular reactions on the order of the solvent environment has been reported in other cases. For example, an increase of activation enthalpy in a smectic phase relative to isotropic solvents was reported in some N_iN' -diacylindigos with long

substituents.²⁴ In the ring closing of the open form of an indolinospiropyran, the E_{a} and ΔS^{\dagger} values were found to be significantly larger in the smectic phase of *n*-butyl stearate than in its isotropic phase.^{24,37} Viscosity was not believed to be the dominant factor in those changes based on the compound's behavior in various polymer matrixes. The difference was instead ascribed to the fact that the transition state was expected to have a more globular shape than the reactant.³⁷ Thus, larger rearrangements of the solvent molecules would be needed in the smectic than in the isotropic phase. At least one case of rate increase with order has been reported for the thermal cis-trans isomerization of azobenzenes in mesophases.⁴² However, a larger body of evidence suggests that azobenzene isomerization does not depend directly on the order of the solvent environment.^{24,43-43}

Thus, G1 is a molecular system in which the reaction rate is modulated by the order of the solvation sphere. In particular, the relaxation of the open form is hindered in an ordered environment. This is in part linked to the large positive value of ΔS^{\dagger} in the ordered phases. It was demonstrated that the **G1** open form is more compatible with a liquid crystalline environment than the closed form, based on changes in transition temperatures and local order of naphthopyran-LC guest-host systems at equilibrium.^{16,18} The increase in activation energy for the naphthopyran thermal relaxation in ordered phases relative to disordered ones could be a different manifestation of the same intermolecular interactions responsible for the photoinduced order increase in naphthopyran-LC mixtures. The fact that activation enthalpies and entropies are different in the nematic phase of 5CB and 8CB, which have very similar molecular structure, could indicate that the magnitude or anisotropy of the intermolecular interactions responsible for the effect are very sensitive to small changes in the relative position of guest and host molecules and in the charge distribution in the polar structure of the naphthopyran open form. It can also be related to the fact that some of the viscosity coefficients of 8CB (e.g., η_2) exhibit pretransitional effects when approaching the nematic-to-smectic A phase transition.³⁶ It should also be mentioned that effects on the G1 open form relaxation due to viscosity and order may be inherently linked in ordered phases, due to the presence of anisotropy.

CONCLUSIONS

Guest-host LC systems containing naphthopyrans are known to undergo an increase in order when exposed to UV light, resulting from the conformational change from the closed form to the open form of the guest molecules. After removal of the UV excitation, the photoinduced population of the open form reverts to the closed form. Here we have investigated the kinetics of the thermal relaxation of the naphthopyran derivative G1. The decay rate is host dependent and increases with temperature. At room temperature, the decay rate was 0.18 s^{-1} in toluene, 0.039 s^{-1} in 5CB, and 0.014 s^{-1} in 8CB. The temperature dependence followed an Arrhenius behavior within each phase of the guesthost LC systems. Larger activation energies are observed in the ordered phases of the 5CB and 8CB hosts than in their isotropic phase. In addition, relaxation rates were larger in a nonmesogenic solvent than in mesogenic ones. The results indicate that the ring-closure process of the class of naphthopyran molecules studied here is very sensitive to the nature of the environment, including the amount of local order and the viscosity. The

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observed trend in activation entropy suggests that the change in geometry from the open form to the transition state requires a larger reorganization of the solvent molecules in ordered solvents than in an isotropic environment. This could be due to a change in the free volume or of the solvation sphere around the naphthopyran molecules in a liquid crystalline environment as a result of the anisotropic nature of the guest—host intermolecular interactions.

The sensitivity of the **G1** dynamics on the type and order of the solvent could prove useful in tailoring the properties of photoresponsive systems or as means to probe perturbations to the local order of guest—host LC systems.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.6b10053.

Eyring plots for G1 thermal decay rates in toluene, 5CB, and 8CB (experimental data and fitting lines in the various phases); isokinetic plot for the thermal relaxation of the G1 open form (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Air Force Office of Scientific Research and the Materials and Manufacturing Directorate of the Air Force Research Laboratory. We gratefully acknowledge Tamas Kosa, Ludmila Sukhomlinova, and Bahman Taheri of Alpha Micron Inc. (1950 State Rt. 59, Kent, OH 44240) for providing compound **G1** and for useful discussions.

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