A Liquid Crystal Opto-optical Switch: Nondestructive Information Retrieval Based on a Photochromic Fulgide as Trigger

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Abstract: Liquid crystals are a unique medium for sensing small structural changes in their environment. Cholesteric liquid crystals respond to these forces by changing their pitch. A photochromic dopant in a cholesteric liquid crystal was used to translate optical input to observable pitch change. The change is reversible solely by action of light, and a cyclic mode of operation is demonstrated. The information encoded by light can be read optically without its destruction. The doped liquid crystal system does not show fatigue during the course of these experiments.

Photochromic compounds have been investigated as functional elements in opto-optical switches.[1] In such a device, the position of the switch is transposed with light and sensed with light by a change in its absorption spectrum. A fundamental problem with this approach has been destructive readout. That is, reading the position of the switch, ultimately, erases it.

The optical properties of cholesteric liquid crystals depend, in part, on their pitch. The magnitude of the pitch can be sensed by measurement of reflection bands and optical rotation or by optical microscopy of oriented films.[2] Pitch can be altered by changing the structure of the liquid crystal itself or by admixing an auxiliary that changes the helical alignment of the molecules of the cholesteric liquid crystal.[3] By altering the structure of the auxiliary, one can vary how it interacts with the liquid crystal, thus changing the pitch and, in turn, the optical properties of the medium. Thus, liquid crystals provide a unique medium that can amplify small changes in composition, structure, or environment.

In this work, an opto-optical switch is constructed on the basis of the sensitivity of a cholesteric liquid crystal pitch to structural changes resulting from an admixed photochromic compound. The opto-optical switch modulates an incident beam of light through the change of optical properties induced by a second beam of light. Significantly, the position of the switch may be read at a nonabsorbed wavelength nondestructively. If changes in the incident beam are larger than those of the controlling beam, the switch will become a "light amplifier".

Previous work[4] demonstrated that a photosensitive auxiliary can affect the optical properties of cholesteric liquid crystals. Our strategy is to construct a photochromic[6] dopant whose structure is capable of significant reversible alteration upon the action of light. The forward and reverse reactions can thus be independently initiated at different irradiation wavelengths. A mixture containing such a photochromic compound in a cholesteric liquid crystal might be able to control the optical properties of the medium.

To date, no reports have been published on reversible,[5] long-lasting changes in the optical properties of cholesteric liquid crystals that are both imposed and reversed solely by the action of light. We report herein a system consisting of a photochromic fulgide dissolved in a photochemically inert cholesteric liquid crystal that is bistable and switchable by repetitive application of ultraviolet and visible light, and fatigue resistant over the course of the experiment.

Results and Discussion

Selection of the Photochromic Additive. Optical Properties. A compound capable of reversible photoswitching should have the following properties: (i) photochemical stability allowing for repetitive cycles without the loss of optical properties, e.g. fatigue resistant, (ii) its photoreaction must not be thermally reversible at the temperature of the experiment, (iii) the photoreaction must proceed with reasonable photochemical yield, and (iv) the two forms must absorb in different spectral regions, preferably where convenient light sources exist. Fulgides,[6] exemplified by **1** (see Scheme 1), are a class of compounds, some of which fulfill these design criteria. Fulgides are photochromic, where the open form **1** absorbs in the near-UV region of the spectrum and the closed form **2** absorbs visible light. Both forms of several fulgides are known to be thermally stable, and a few are reported to be fatigue resistant.[7,8] The fulgide chosen for this initial study is the previously described indole **3**.[8] The absorption maximum of the open form of **3** is at $\lambda_{\max} = 385$ nm, and the closed form **4** absorbs at $\lambda_{\max} = 584$

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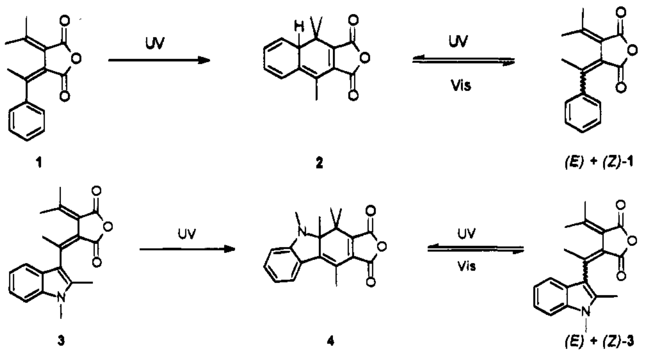
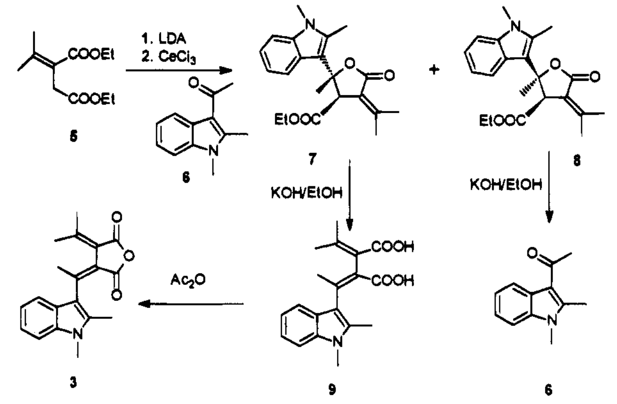
Scheme 1. Photochemistry of Fulgides



Scheme 2. Synthesis of Fulgide 3



nm, making possible the use of a Rayonet photoreactor equipped with 300 nm lamps for the coloration process (3 → 4) and an incandescent lamp for the bleaching process (4 → 3). The reported[8] photochemical yields for coloration ($\Phi_{403} = 0.040$) and bleaching processes ($\Phi_{608} = 0.051$) are acceptable.

Since the synthesis (see Scheme 2) and properties of the fulgide **3** and its intermediates were only briefly mentioned in a single paper,[8] full experimental details of the synthesis are included in this work. The initial diethyl isopropylidenesuccinate (**5**)[9] was treated with lithium diisopropylamide in THF[8,10] and added to a suspension of cerium chloride in THF followed by addition of indole ketone **6**.[11] Analysis of the reaction products by NMR spectroscopy revealed a mixture of isomeric lactones **7** and **8** in a 1:2 ratio. In the original paper, the mixture of **7** and **8** was reported as a single diastereoisomer.[8] The separated isomers were each hydrolyzed with ethanolic potassium hydroxide with the *trans* isomer, producing the expected succinic acid **9** in 41% yield. By contrast, the *cis* isomer underwent a retroaldol reaction, regenerating the starting ketone **6**, which explains the poor yield of the hydrolysis reported in the original paper.[8] The diacid **9** was dehydrated with acetic anhydride, producing the final fulgide **3** in 82% yield.

The UV–vis spectra of the **3** and **4** in toluene are shown in Figure 1. To test the thermal stability of the colored form **4**, the solution, after irradiation with UV light, was heated at 70 °C for 24 h in the absence of light. The optical density of this solution did not change within experimental error, thus demonstrating that this form is stable over the time of the measurement.

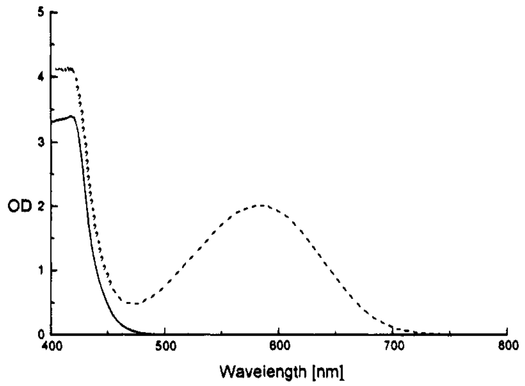
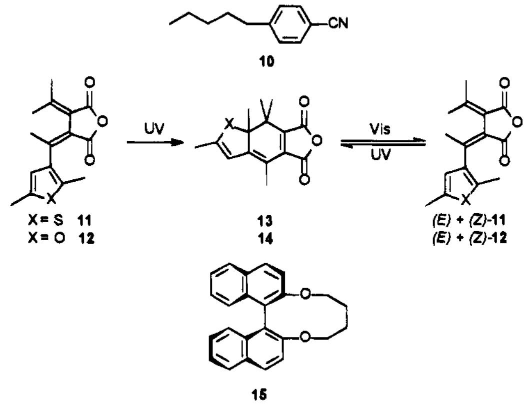


Figure 1. UV spectra of a 1.12 mM solution of fulgide **3** in toluene before irradiation (solid line) and after irradiation with UV (dashed line).

Scheme 3. Liquid Crystals and Dopants



Interaction with the Liquid Crystal. The liquid crystal chosen for investigation as an opto-optical switch is K-15 (4-cyano-4′-pentylbiphenyl, **10**, Scheme 3) which is nematic at room temperature. We tested the fulgide for significant interactions with the liquid crystal by observing the change of the nematic to isotropic phase transition temperature. In the only published work on this topic, Allinson and Gleeson[12] report measuring the phase transition temperatures of a liquid crystal with a fulgide dopant. These authors investigated the influence of fulgides **11** and **12** on order parameter variation and on the nematic to isotropic phase transition temperature of E7 (a eutectic mixture of liquid crystals based on biphenyl compounds). Only marginal variation of the phase transition temperatures and biphasic temperature ranges were reported upon irradiation of the solutions at a concentration of 1% of **11** and **12** in E7. After increasing the concentration of **11** to 2%, the changes in the phase transition temperatures and biphasic temperature ranges were significant. For solutions of the closed form **13**, the phase transition temperature is higher by more then a degree and the biphasic temperature ranges are narrower by about a degree when compared with those of the **11**/E7 solution. These authors speculate that the observed increased stability of the nematic phase of the solution of **13** compared with the nematic phase of the solution of the open form **11** can be attributed to the more planar structure of the closed form **13**.

At concentrations up to 2% w/w of **3** in K-15, no noticeable effect of the dopant on the phase behavior was detected. At a concentration of approximately 5%, the liquid crystal mixture shows a phase transition temperature dependence on the structure of the additive. In one experiment, a 5.6% solution

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Table 1. Phase Transition Temperature for a 5.6% Solution of Fulgide **3** in K-15 (**10**)

sample	process	$T_{N/N+I}$[a] (°C)	$T_{N+I/I}$[b] (°C)	ΔT[c] (°C)
nonirradiated	heating	25.4	27.1	1.7
	cooling	21.3	25.6	4.3
UV-irradiated	heating	25.5	28.0	2.5
	cooling	22.6	25.9	3.3

[a] The temperature of onset (on heating) or disappearance (on cooling) of the isotropic phase. [b] The temperature of onset (on cooling) or disappearance (on heating) of the nematic phase. [c] $\Delta T = T_{N+I/I} - T_{N/N+I}$.

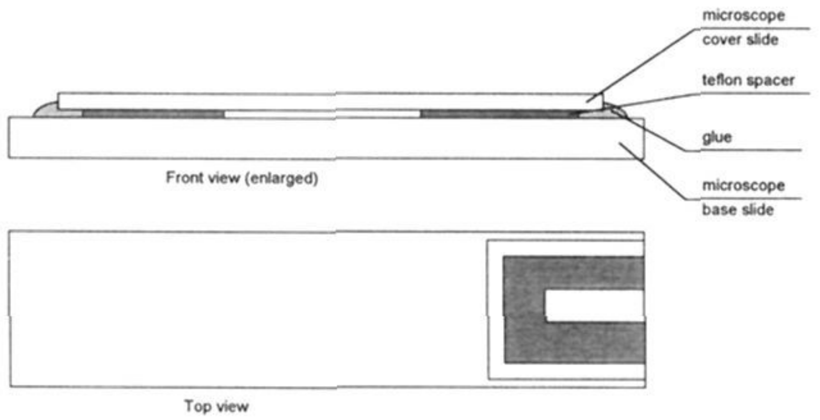

Figure 2. Cell for cholesteric phase pitch measurements. Not to scale.

of **3** in K-15 was investigated. The effects of light on the phase transition temperature and the biphasic temperature ranges, ΔT, of this mixture are summarized in Table 1. These data show that a measurable difference exists in the interactions of the open (**3**) and closed (**4**) forms with the liquid crystal. Similar to the Gleeson report,[12] the phase transition temperatures are higher for the UV-irradiated solution, which indicates that the nematic phase is more stable in the presence of the closed form of fulgides. The observed biphasic temperature range changes, however, are not uniform. The biphasic temperature range upon heating is wider for the closed, more planar, and presumably less disrupting **4**, which is contrary to the reported results for **13**. As the structures of **4** and **13** are very similar, we cannot offer any satisfying explanation as to which structural features contribute to the observed effect. However, the change of the interaction is measurable and can be used to control the phase of a liquid crystal.

Pitch Change Induction. In the previous experiments we found that **3** and **4** differed substantially in their interactions with K-15. A relevant issue thus is whether this difference is sufficient to drive a measurable change in the pitch of a cholesteric liquid crystal. Since K-15 interacts with fulgide **3**, we chose to induce a cholesteric phase in K-15 rather than search for another suitable cholesteric liquid crystal material. K-15 was admixed with a small amount of the chiral binaphthyl ether **15** which is photostable,[13] known to have a large twisting power (β_M), and is easily obtained.[14] Upon addition of 1.35% w/w of **15** to K-15, a permanent cholesteric phase is induced with a pitch length of 37 ± 1 μm.

The pitch of the cholesteric liquid crystal was directly observed as a fingerprint pattern under a light microscope. A typical cell for the pitch measurement is shown in Figure 2. A thin Teflon spacer separated the cover and base microscope slides. To induce formation of the fingerprint pattern, a monolayer of C_{18} chains was deposited and chemically bound to the glass surfaces.[15] The cell was filled with test mixtures by capillary force.

Table 2. Cholesteric Phase Pitch Size of 5.2% Fulgide **3** and a 1.35% Solution of **15** in K-15 (**10**) upon Alternating Irradiation with UV and Visible Light

irradiation	pitch (μm)	irradiation	pitch (μm)
none	26 ± 1	Vis	42 ± 1
UV	30 ± 1	UV	30 ± 1
Vis	42 ± 1	Vis	42 ± 1
UV	30 ± 1		

To observe its effect upon the liquid crystal pitch, fulgide **3** was added to the mixture of dopant **15** and liquid crystal **10**. The addition of **3** modified the helical alignment of the liquid crystal molecules, resulting in a pitch change. The closed form **4** has a different interaction with the medium than that of the open form **3**. Coloring and bleaching of **3** results in alternating changes of the **3**:**4** ratio which in turn results in variation of the interaction of the mixture of **3** and **4** with the liquid crystal phase. This variation manifests itself macroscopically as a pitch change measured[15] by observing the fingerprint pattern of the cholesteric phase in thin layers with an optical microscope. The pattern was observed between crossed polarizers at 100× magnification.[16] The pitch and fingerprint pattern did not change during the measurement, thus demonstrating that the readout proceeds without destruction. These studies are summarized in Table 2.

As in the previous experiments with the nematic liquid crystal, no effect is seen when the concentration of **3** is below 2% w/w. At concentrations of approximately 5% w/w, the pitch changes with the structure of the additive. Alternating irradiation of this mixture with visible and UV light leads to a pitch change of ca. 30%. The pitch changes are reproducible, again indicating that the photoreaction is reversible.

Conclusions

We have shown that the pitch of a cholesteric liquid crystal can be controlled photochemically by a photochromic fulgide dopant. The pitch changes are measurable at reasonable fulgide concentrations, and both states of the liquid crystal/fulgide mixture are thermally stable under the conditions tested. The change of the pitch is bidirectional and reversible and is controlled with light of suitable wavelength. The pitch of the liquid crystal can be read optically without affecting the recorded information. These properties are unique and are suitable for development of an opto-optical switch.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400 spectrometer. The chemical shifts in $CDCl_3$ are reported in δ (ppm) relative to internal tetramethylsilane. UV spectra were recorded on a Varian Cary-1E spectrometer. A Hewlett-Packard 5970 Series mass selective detector was used with a Hewlett-Packard 5890 GC for GC−MS analyses which were performed at 70 eV with a 0.25 mm × 12 m HP-1 capillary column programmed at 100 °C for 5 min and then heated to 250 °C at the rate of 20 °C min^{-1}. Analytical GC separations were performed with a Varian 3700 GC equipped with a flame ionization detector, an HP 3390A reporting integrator, and a 0.25 mm × 6 m HP-1 capillary column programmed at 100 °C for 3 min and then heated to 250 °C at the rate of 15 °C min^{-1}. Elemental analyses were performed by the Microanalytical Laboratory at the University of Illinois. The temperature during the observations of liquid crystals was controlled by a Mettler Model FP82 hot stage attached to a Mettler Model FP80 central processor. The liquid crystal patterns were observed through a Micromaster Model E microscope from Fisher Scientific equipped with light polarizers and a NEC color CCD camera, model NC-15. The total magnification of the optical system was 100×. A 720 nm cutoff filter was installed on the microscope's light source

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for the measurement involving the colored form **4**. The output from the CCD camera was observed on an S-VHS monitor, model PM-1971S, from NEC and recorded as photographs taken from the screen.

Materials. All solvents and reagents were obtained from commercial vendors and used without further purification unless otherwise noted. Diethyl ether (ether) and tetrahydrofuran (THF) were distilled from Na^+/benzophenone ketyl; toluene was distilled from CaH_2. Samples of Teflon FEP film were donated by DuPont.

Synthesis. The 1,2-dimethylindole,[17] diethyl isopropylidenesuccinate[9] (**5**), and binaphthyl ether[14] **15** were prepared following literature procedures.

3-Acetyl-1,2-dimethylindole (6).[11] The purity of 1,2-dimethylindole is crucial for successful preparation. Commercial product (Aldrich) contained impurities that could not be separated and caused the yield of the final product to drop to 60%. The 1,2-dimethylindole was synthesized from *N*-methylphenylhydrazine and acetone by Fisher indole synthesis in 31% yield.[17] The product was sublimed twice until all the colored impurities were removed, and used immediately. Tetrafluoroboric acid ethyl ether complex solution in ether (8.8 mL, 9.7 g, 85%, 60 mmol) was added dropwise to a solution of triethyl orthoacetate (11 mL, 9.7 g, 60 mmol) in 20 mL of dry methylene chloride at −13 °C and stirred at constant temperature for 20 min. The mixture was added dropwise to a solution of 7.2 g of 1,2-dimethylindole in 170 mL of CH_2Cl_2 at −13 °C over a period of 20 min. During the addition, an off-white precipitate formed. The solution was warmed to room temperature and stirred for an additional 30 min. Ether (300 mL) was added and the resulting tan precipitate filtered and washed with ether until the filtrate was approximately colorless. The precipitate was suspended in a mixture of 200 mL of 5% aqueous solution of sodium hydroxide and 1000 mL of ether. After 1 h of vigorous stirring, the precipitate dissolved and the organic layer separated and was washed with water. The aqueous layer was washed twice with ether. The combined etheral extracts were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The resulting solid was sublimed at 113 °C (10^{-5} mmHg) to yield 8.6 g of white crystalline product (92.5% yield): mp 140−140.5 °C (lit.[11] 139−140 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (s, 3 H), 2.68 (s, 3 H), 3.58 (s, 3 H), 7.21−7.25 (m, 3 H), 7.93−7.95 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 29.4, 31.7, 109.9, 121.1, 122.4, 122.5, 126.8, 137.2, 145.8, 195.4. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.96; H, 7.00; N, 7.48.

Indolelactones 7 and 8.[8,10] Cerium chloride (4.4 g, 18 mmol) was baked under vacuum at 140 °C for 3 h, cooled under dry N_2, suspended in 20 mL of dry THF, stirred under dry N_2 overnight, and finally cooled to −78 °C. In a separate flask, diethyl isopropylidenesuccinate[9] (3.8 g, 18 mmol) in 20 mL of dry THF was cooled to −78 °C and lithium diisopropylamide (12 mL, 1.5 M solution in cyclohexane, 18 mmol) was added over a period of 5 min. The mixture was stirred at −78 °C for 30 min and added dropwise *via* cannula (precooled with dry ice) to the cerium chloride suspension. The mixture was warmed to 0 °C over a period of 30 min, stirred at 0 °C for an additional 30 min, and recooled to −78 °C. To this mixture was added 3-acetyl-1,2-dimethylindole (3.0 g, 16 mmol), and the final solution was allowed to warm overnight. The reaction was quenched with water, and ether and 5% aqueous sulfuric acid were added. The organic layer was separated and the aqueous layer extracted twice with ether. The combined organic layers were washed with brine to neutral pH, dried over $MgSO_4$, and concentrated under reduced pressure. The isomers were separated by triple column chromatography (silica, hexane/ether, 3:1), yielding two fractions, which were each independently crystallized from dry ethanol. Two isomers were obtained: *trans*-**7** (2.9 g, 48% yield) and *cis*-**8** (1.3 g, 22% yield).

trans-**7**: mp 144.5−145.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, 3 H, $J = 7.1$ Hz), 1.7 (s, 3 H), 1.83 (s, 3 H), 2.24 (s, 3 H), 2.56 (s, 3 H), 3.61 (s, 3 H), 4.33 (q, 2 H, $J = 7.1$ Hz), 4.45 (s, 1 H), 7.14−7.24 (m, 2 H), 7.26−7.27 (m, 1 H), 7.83−7.85 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1, 14.0, 20.0, 24.1, 25.0, 29.0, 56.6, 61.3, 82.8, 109.3, 115.0, 119.2, 119.9, 121.0, 121.3, 125.0, 133.2, 137.0, 154.5, 169.4, 171.4. Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94. Found: C, 70.91; H, 7.14; N, 4.08.

cis-**8**: mp 137−138 °C; the proton spectrum shows a mixture of two conformers; only partial coalescence occurs at elevated temperatures (up to 105 °C in toluene-d_8); ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ 0.32 (t, 1.1 H, $J = 7.3$ Hz), 0.45 (t, 1.9 H, $J = 7.1$ Hz), 1.77 (s, 1.1 H), 1.88 (s, 1.9 H), 1.96 (s, 3 H), 2.37 (s, 3 H), 2.44 (s, 1.1 H), 2.59 (s, 1.9 H), 3.38−3.50 (m, 1.3 H), 3.54−3.61 (m, 0.7 H), 3.62 (s, 3 H), 4.12 (s, 0.3 H), 4.26 (s, 0.7 H), 7.03−7.20 (m, 3 H), 7.53−7.54 (m, 0.7 H), 8.17−8.19) (m, 0.3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1, 14.0, 19.9, 24.1, 25.0, 29.0, 56.6, 61.3, 82.8, 109.3, 115.0, 119.2, 119.9, 121.0, 121.3, 125.0, 133.2, 137.1, 154.5, 169.4, 171.4. Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94. Found: C, 70.80; H, 7.12; N, 3.93.

Indole Fulgide 3.[8] The *trans*-indolelactone **7** (2.6 g, 7.4 mmol) was dissolved in a solution of 10 g of KOH, 10 mL of water, and 40 mL of ethanol and stirred at 70 °C for two days, during which time the solution turned yellow. The reaction mixture was cooled and acidified with 20% sulfuric acid, resulting in the formation of yellow precipitate which was collected by filtration and air dried. The precipitate was triturated with hot benzene to yield 0.99 g (41% yield) of crude acid which was suspended in dry toluene (10 mL) and acetic anhydride (10 mL). The mixture was stirred under reflux for 2 h, during which time the precipitate dissolved. The solution was concentrated under reduced pressure and the residue purified by column chromatography (silica, methylene chloride). The product (0.76 g, 82% yield) was isolated as a yellow solid: mp 166−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 3 H), 2.20 (s, 6 H), 2.81 (s, 3 H), 3.70 (s, 3 H), 7.14−7.16 (m, 1 H), 7.24−7.26 (m, 1 H), 7.29−7.31 (m, 1 H), 7.38−7.40 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 23.1, 24.1, 26.8, 30.4, 110.2, 120.6, 120.8, 121.8, 122.5, 123.1, 126.0, 136.3, 138.1, 147.1, 150.7, 154.4, 165.4, 189.1. Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.82; H, 6.07; N, 4.42.

Alkaline Hydrolysis of *cis*-Indolelactone 8. The hydrolysis was conducted under identical conditions as for the *trans* isomer **7** with 1.2 g (3.4 mmol) of **8**. No identifiable acidic product was isolated. The neutral benzene fraction was concentrated under reduced pressure and weighed 0.55 g. The major compound was indole ketone **6** (65% by GC) identified by comparison of its GC−MS trace with the trace of the original ketone.

Irradiation of Indole Fulgide 3 with UV Light. An indole fulgide **3** solution in toluene (3 mL, 1.12 mM) in a 1.0 cm quartz cuvette was irradiated with UV light in a Rayonet photoreactor ($\lambda_{max} = 300$ nm). The absorption at 584 nm reached its maximum after 5 min. From the UV absorption at 584 nm, the concentration of the colored form ($\epsilon_{584} = 6810$ M^{-1} cm^{-1})[8] was calculated to be 0.325 mM and the conversion found to be 29% advanced. The colored sample was heated to 70 °C in the dark for 24 h. A subsequent UV spectrum indicated no measurable decay in UV signal intensity.

Suppression of the Nematic to Isotropic Phase Transition Temperature. Indole fulgide **3** was dissolved in the liquid crystal (K-15) **10** to 5.6% w/w concentration. A thin layer of this solution was spread between the base and cover microscope slides. The slide was placed under an optical microscope in a hot stage between crossed polarizers. The CCD S-VHS camera was used as a detecting device and the light source covered with 720 nm cutoff filter for the experiments with the colored form **4**. The rate of the temperature change was 0.5 °C/min. The data in Table 1 represent the average values obtained during three consecutive heating/cooling cycles.

Cholesteric Phase Pitch Measurements. The thickness of the empty cell (Figure 2) was measured by IR interference to be 15 ± 2 μm.[18] A solution of **15** (1.35% w/w) and fulgide **3** (5.2% w/w) in K-15 (**10**) was prepared by mixing the components at approximately 40 °C. The sample was placed in the cell by capillary action. The cell was alternately irradiated with UV and visible light for 5 min and placed under the optical microscope in the hot stage after each irradiation. The temperature was maintained at 17 °C with the aid of a stream of dry ice-cooled nitrogen, where the cholesteric phase is stable. The fingerprint pattern was observed and the pitch measured.

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