Chiroptical Switching between Liquid Crystalline Phases

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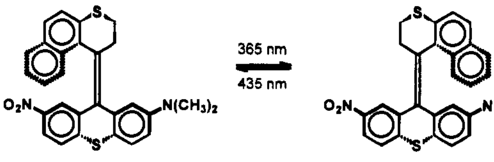
The modulation of the mesophases and physical properties of liquid crystalline (LC) materials by reversible photochemical reactions,[1] *i.e.*, photoswitching of LC phases, is a major challenge for information technology. The photochromic behavior of organic molecules has also attracted renewed interest with a view to the development of materials for optical data storage and molecular optical devices.[2] It is well-known that small amounts of optically active guest molecules added to a nematic host induce a cholesteric phase and that the helical pitch in the twisted nematic phase is very sensitive to chemical modifications in the chiral guest molecule.[3]

Reversible switching of a liquid crystal between a twisted and a nontwisted phase by photochemical modification[4] of the chirality of the doping molecule, although predicted,[5–7] has thus far not been realized. In their pioneering efforts to develop a chiral liquid crystalline phototrigger, Schuster and co-workers[6] showed that photoracemization of optically active binaphthyl derivatives induces a cholesteric to nematic transition in a doped phase.

We describe herein the first successful demonstration of the reversible photochemical modulation of the helical pitch of a twisted nematic LC phase and the reversible transition between cholesteric and nematic phases using as dopant an optically active photoresponsive molecule. The chiroptical molecular switch[8] employed is based on the donor–acceptor substituted inherently dissymmetric alkenes *cis*- and *trans*-2-nitro-7-(dimethylamino)-9-(2′,3′-dihydro-1′*H*-naphtho[2,1-*b*]thiopyran-1′-ylidene)-9*H*-thioxanthene (**1** and **2**) (Scheme 1).[9] Addition of 1 wt % of enantiomerically pure P-*trans*-**2**[10] to the nematic phase, obtained from 4′-(pentyloxy)-4-biphenylcarbonitrile **3**,[11] converts it to a cholesteric phase.[12] With M-*trans*-**2** a similar induced cholesteric phase is observed, with opposite screw sense.

Scheme 1. Photoisomerization of M-**1** and P-**2**



M-1 (cis-nitro)

P-2 (trans-nitro)

When the Grandjean–Cano method[13] is employed on a wedged-shaped sample, disclinating lines are clearly observed in a cholesteric fingerprint structure under the microscope (ca. 150× magnification) through crossed polarizers. A stereoselective photochemical interconversion of the pseudoenantiomers P-trans $\rightleftharpoons$ M-cis,[14] accompanied by reversal of helicity, is known to occur upon irradiation at 365 nm (30:70 ratio, M-**1**:P-**2**) and 435 nm (90:10 ratio, M-**1**:P-**2**) (Scheme 1).[9,15] Irradiation of a thin film of **3**,[16] doped with 1 wt % of P-*trans*-**2**, at 435 nm for 15 s resulted in a stable cholesteric phase[12] (cholesteric I), as shown in Figure 1a. This indicates that the photostationary state P-*trans*-**2** $\rightleftharpoons$ M-*cis*-**1** is also readily reached in the LC phase. Irradiation of this thin film of **3** containing M-**1** in excess over P-**2** at 365 nm for 5 min results in a distinct decrease in the pitch as is seen in a change in distance between two consecutive steps in the fingerprint texture (cholesteric phase II, Figure 1b).[17] Upon irradiation at 435 nm the pitch reverts to the original value. In a related experiment using the Grandjean–Cano method the pitch alternates from 12.29 μm (cholesteric I) to 5.31 μm (cholesteric II).[18,19] Alternating irradiation with 435 and 365 nm light (irradiation time 5 min) results in a photomodulation (increase at 435 nm, decrease at 365 nm) of the pitch in the induced cholesteric phase. The pitch modulation was perfectly stable during eight switching cycles. The control of the helix pitch, depending on the wavelength used, is in accordance with the inversion of helicity of the inherently dissymmetric alkenes M-**1** and P-**2** (Scheme 1). Furthermore, when the same set of experiments was repeated starting with M-*trans*-**2**, reverse

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(10) Enantiomerically pure M-**1** (*cis*-nitro), P-**1** (*cis*-nitro), M-**2** (*trans*-nitro), and P-**2** (*trans*-nitro) were obtained as described previously (ref 9) and were stable toward thermal (ΔG = 122.2 + 0.5 kJ mol^{-1}) and photochemical racemization under the conditions employed (HPLC, CD analysis).

(11) 4′-(Pentyloxy)-4-biphenylcarbonitrile (Aldrich), mp (C–N) 48 °C, (N-I) 67 °C; after doping of 1 wt % P-**2** mp (C–N) 40 °C, (N-I) 63 °C.

(12) At this concentration the dopant P-**2** is fully compatible with **3**; a "stable cholesteric phase" indicates constant pitch irrespective of longer irradiation times.

(13) Grandjean, F. *C. R. Hebd. Seances Acad. Sci.* **1921**, *172*, 71. Cano, R. *Bull. Soc. Fr. Mineral*, **1968**, *91*, 20. See also ref 3.

(14) The term pseudoenantiomers is used in this context to indicate the opposite helicity of P-**2** and M-**1**.

(15) Ratios determined in *n*-hexane (HPLC); the isomeric composition at the photostationary states and the extrema in the UV/vis difference spectra of **1** and **2** in the LC phase may well deviate slightly from those in solution.

(16) A wedge-shaped sample was prepared by gluing a glass hair onto a microscope slide and resting one side of the cover slip on top of the glass hair. For orientation of the mesomorphic phases the glass was rubbed after having been hydrophobized with dimethyldichlorosilane. The sample was held at 47.3 °C. Irradiations were carried out with a 200 W high-pressure mercury lamp (Oriel). The desired wavelengths were obtained using mercury line interference filters (bandwith = 10 nm). It should be noted that **3** is transparent at the wavelengths employed.

(17) It was observed in all experiments that initial irradiation for 15 s of a doped film was sufficient to reach a stable cholesteric phase (and apparently a photostationary state of the dopant). Subsequent irradiation times of 5 min were employed to interconvert cholesteric phase I to cholesteric phase II (and vice versa) and to ensure stable phase formation. We have at present no explanation for the discrepancies in initial and subsequent irradiation times required.

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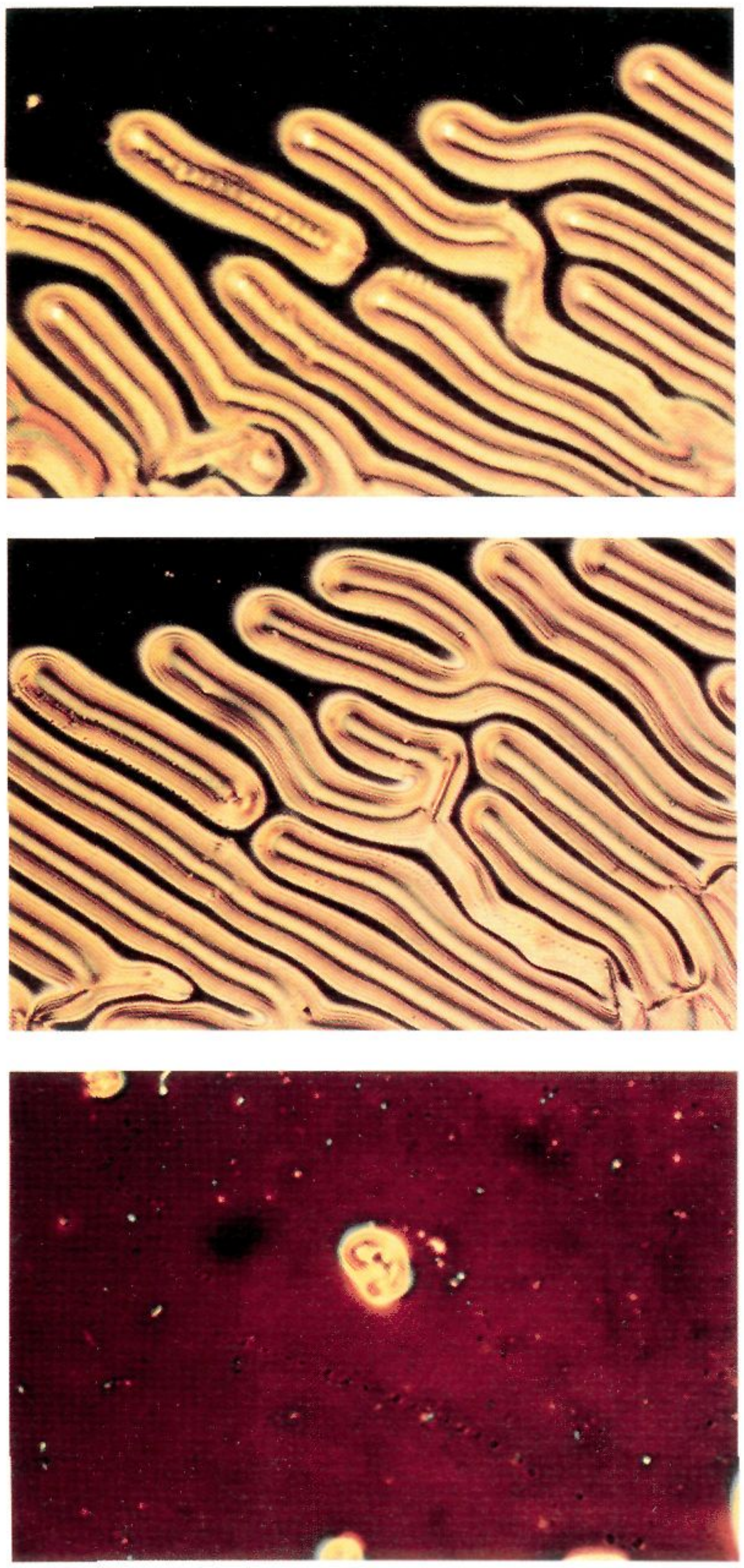
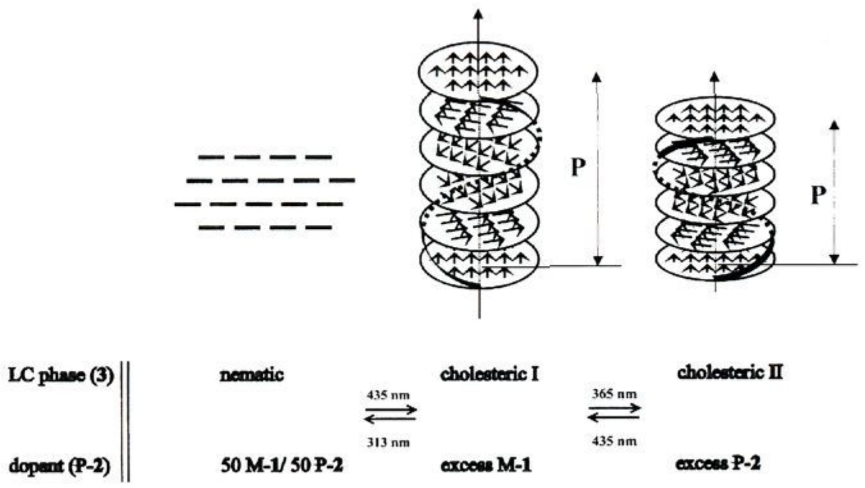


Figure 1. (a) (top) Cholesteric fingerprint texture observed for 4′-(pentyloxy)-4-biphenylcarbonitrile doped with P-*trans*-**2** after irradiation with 435 nm light. (b) (middle) Cholesteric fingerprint texture observed for **3** doped with P-*trans*-**2** after irradiation with 365 nm light. (c) (bottom) Compensated nematic structure obtained after irradiation at 313 nm for 20 min of a cholesteric thin film of **3** doped with 1 wt % of P-*trans*-**2**. Viewed at ca. 150× magnification through crossed polarizers (reproduced at 50% of original size).

behavior was observed, *i.e.*, alternating irradiation at 435 and 365 nm resulted in a decrease or an increase of the pitch, respectively. In addition, we could show by determination of the cholesteric screw sense by the Grandjean−Cano method[18,19] that, as expected, the pseudoenantiomers P-**2** and M-**1** twist the nematic LC to cholesteric phases of opposite handedness, but also that the cholesteric screw sense is modulated upon irradiation at 435 and 365 nm.[20]

Scheme 2. Photochemical Switching Processes of LC-Phase (**3**) and Chiral Dopants (**1**, **2**)[a]



[a] Cholesteric phase I, negative helicity; cholesteric phase II, positive helicity.

Next the possibility of switching of the liquid crystal **3** between a twisted and a nontwisted phase was examined. The UV/vis spectra of **1** and **2** are nearly identical at 300 nm, and irradiation of either M-**1** or P-**2** at 313 nm in *n*-hexane has been shown to result in a photostationary state with equal amounts of both helices (M-**1**:P-**2** = 1).[9] Irradiation of a thin film of **3** containing 1 wt % M-**1** at 47.3 °C for 20 min using 313 nm light results in a conversion of the cholesteric to the nematic phase as is shown in Figure 1c. Apparently a (nearly) 50:50 ratio of opposite helices of the chiral guest molecule is formed in the LC phase as well as in solution at this particular wavelength, resulting in a compensated nematic phase. Much to our delight, subsequent irradiation of this film at 435 nm for 20 min restored the original cholesteric texture (Figure 1a).

Finally the switching cycles shown schematically in Scheme 2 were executed; the changes in the LC phase and the optically active dopant (chiroptical switch) are both indicated.

A thin film of **3** and 1 wt % P-**2** was irradiated at 435 nm (cholesteric phase I, negative helicity) and subsequently irradiated at 313 nm for 20 min, resulting in a compensated nematic phase. Next irradiation at 435 nm (20 min) reversed this process (cholesteric phase I, negative helicity), and subsequent irradiation at 365 nm (5 min) induced a decrease of the pitch (cholesteric phase II, positive helicity). Irradiation of this film at 435 nm (5 min) reestablished cholesteric phase I (negative helicity). This four-step switching cycle was repeated two times without appreciable deterioration of the film.[21]

In conclusion, we have demonstrated that the helically shaped photoswitchable alkenes **1** and **2** are highly effective in the reversible, light-induced, conversion of cholesteric to nematic LC phases as well as in the reversible alteration of the macroscopic helical pitch (and the screw sense) in the cholesteric phase. Both processes in this three-position switch can be controlled by modulation of the diastereomeric ratio that is produced depending on the wavelength used for irradiation.

A quantitative study of helical twisting power and wavelength dependency of these processes with other mesoscopic systems is currently in progress.

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(19) For the determination of the pitch and the helical twisting power β the distances between the concentric rings of Grandjean−Cano lines were measured using a converging lens with planar boundary conditions. To provide a concentric planar surface alignment both the converging lens and the microslide are rubbed unidirectionally, after having been coated with a polyimide. We measured the following helical twisting powers β: for P-*trans*-**2**, $\beta = 1.9$; for M-*cis*-**1**, $\beta = 7.3$.

(20) We independently determined the helical screw sense of the cholesteric phases using the Grandjean−Cano method with concentric rings.[18] P-*trans*-**2** and P-*cis*-**1** induce a positive helicity; M-*trans*-**2** and M-*cis*-**1** induce a negative helicity.

(21) In the process of irradiation slight disorders were observed at the edge of the glass slide in some cases.