



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Chiral power change upon photoisomerization in twisted nematic liquid crystals



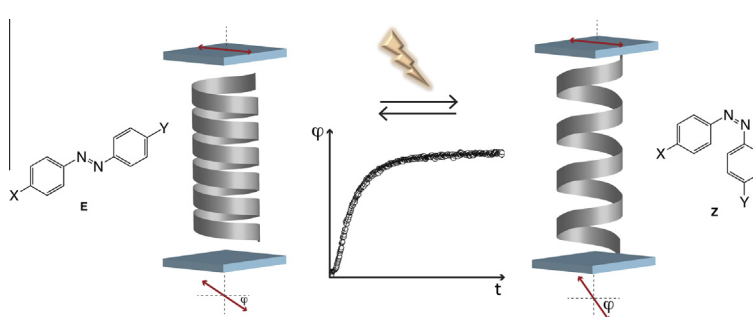
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HIGHLIGHTS

- Photoisomerization induces rotatory dispersion change in nematic liquid crystals.
- Dimethylamino azobenzene is the most effective dopant tested for this purpose.
- Isomerization and chiral change display the same dynamics.
- The liquid crystal pitch change is the reason of the variation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 October 2014

Received in revised form 14 January 2015

Accepted 18 January 2015

Available online 7 February 2015

Keywords:

Photoisomerization
 Liquid crystals
 Chiral power change
 Photochromism
 Azobenzenes
 Spirooxazine

ABSTRACT

In this work, we use the photoisomerization of azobenzenes, a phenanthrospiropoxazine, and a fulgide in a twisted nematic liquid crystalline phase to change the chiral twisting power of the system. The changes are probed by the rotatory power of linearly polarized light. Time resolved and steady state experiments are carried out. The chiral change and the photoisomerization process have similar characteristic recovery times and activation energy, thus probing that the change is induced by the modification in the chemical composition of the photochromic dopant system. The amplitude of the light twisting power change correlates with the order change in the liquid crystal (LC) but not with the modification in the absorption characteristics of the system. This indicates that the driving force of the chiral change is the microscopic order modification in the LC phase that affects the helical pitch of the phase.

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Introduction

All-optical storage-read systems are interesting devices because of the possibility of wireless remote control. To achieve the opera-

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tion of such a device, a photosensitive material must provide the state change of the system that can be tested by a suitable optical signal. In this regard, photochromic molecular systems are adequate to operate as the commanding element. They have been tested in many optical storage and photoswitching devices [1–4]. In particular, a photochromic system, lacking thermal interconversion reactions, could provide a long-term memory, that can be read and erased with light. However, very few systems show this feature: namely some diarylethenes and fulgides [5]. In all cases, a writing and an erasing wavelength has to be used in the suited

range for the transformation in each direction to occur. On the other hand, systems with one photochemical conversion pathway and thermal reversion to the original state are also attractive because they offer the possibility of periodic excitation with a frequency limited by the inverse of the decay lifetime of the metastable state. In this perspective, there is no need of an erasing wavelength, whereas the readout must be performed during the lifetime of the metastable state. These requirements are fulfilled by a vast variety of systems, particularly azobenzenes and related compounds [6–10] that display a great light stability and allow many excitation cycles. Nonetheless, readout is also a concern in these systems. Signals based on absorption of the metastable isomer can cause destructive reading (reversion of the signal) as readout and erasing wavelength ranges coincide, with the difference being that readout is performed at a much lower incident light power. Hereof, the use of light signals that are not based on absorption is an interesting alternative because they only cause small perturbations in the device, especially if the photochemically sensitive element is not involved.

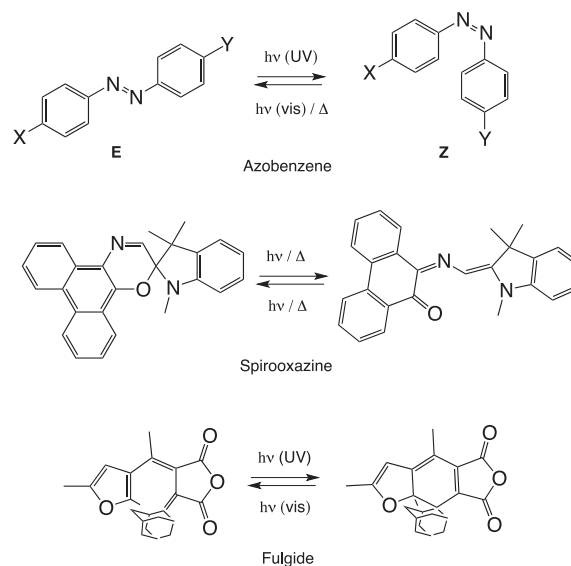
Liquid crystals (LC) are ideal media as hosts for photochromic systems. LC combine anisotropic properties of the solid state with the fluidity and solvation capability of the liquid state. The twisted nematic cell is the key element in LC displays. There are many reports on the use of LC doped with photochromic molecules [8,11–16]. In this approach, the light transformation of the photochrome is used to induce changes in the LC environment that are amplified by the susceptibility of the metastable phase. The optical features of the liquid crystals were used to test the state of the system in most of the cases by the change in the reflection [13–15] signal of twisted nematic phases. This testing does not involve absorption of the photochromic element. Another way of testing that does not imply destructive reading is based on refractive index changes, particularly in the optical rotatory dispersion in chiral phases, which can be monitored by the rotation of the plane of linearly polarized light. This specific approach avoids the need of spectral detection or of a different wavelength of the probe light for every system. For this reason optical probing of the state of the system based on refractive index changes is an interesting possibility.

Photochromic transformation is accompanied by a change in the affinity of the photoproducted isomer and the mesophase, which modifies the state of the labile LC. The particular aim of this work is the study of changes in the chiral power of a twisted nematic LC induced by the photoisomerization of photochromic compounds. Accordingly, we used three types of photochromic compounds. Their structures are shown in Scheme 1. Azobenzenes, having an E–Z phototransformation with a thermally metastable Z isomer. The geometry change upon this isomerization greatly perturbs the LC phase. A spirooxazine with a great shape and spectral absorption range change upon photoisomerization was the second family. Finally, we used a fulgide with absence of back thermal isomerization at room temperature and a very small shape change.

Material and methods

Materials

The following chemicals were used as received: Azobenzene (AB) (Aldrich), 4-(N,N-dimethylamino) azobenzene (DAB) (Aldrich), 2,3-dihydro-1,3,3-trimethylspiro[indoline-2,2'-[2H]phenanthro[9,10b][1,4]oxazine] (SO) (Aldrich), E- α -(2,5-dimethyl-3-furyl ethylidene)-(adamantylidene)-succinic anhydride (AFU) (Chemos GmbH), commercial liquid crystal mixtures ZLI-1132 (Licristal/Merck) and S-811 chiral inductor (CI), compatible with ZLI-1132 phase and with a helical twisting power (HTP) of $-13.9 \mu\text{m}^{-1} \text{M}^{-1}$,



Scheme 1. Molecular structure of the photochromic compounds used in this work and their photochromic reactions.

was also from Licristal/Merck. 4-(N,N-dimethylamino)-4'-nitroazobenzene (N-DAB) was synthesized according to literature [17]. Cells of parallel polyimide rubbed layers, coated with indium tin oxide (ITO), spaced $10 \mu\text{m}$ apart were purchased from E.H.C. Co., Ltd. (Japan).

Sample preparation

Mixtures of the twisted nematic phase were prepared by weighting ZLI1132, S-811, the photochromic dye and then stirring for at least 6 h at $\sim 40\text{--}50^\circ\text{C}$ in the dark. Typically, the amount of the chiral inductor was adjusted between 5% and 15% w/w to tune the cholesteric reflection band in the NIR far from the absorption bands of the dyes and from the probe laser wavelength. Cells were filled at room temperature by capillary effect, and orientation was verified by polarized microscopy.

Methods

Absorption

A Shimadzu UV3101PC spectrophotometer was used for the absorption measurements. When necessary, the sample was irradiated immediately before the measurement.

Polarized light microscopy

Phase transition temperatures were recorded by observation of the disappearance and appearance of the typical cholesteric phase texture, when heating and cooling the samples, respectively. A transmission microscope (Leitz DMR) equipped with a heating stage (Leitz 1350) was used. The sample was placed between two crossed film polarizers (Melles Griot). The temperature, for which the sample starts showing isotropic phase, is determined by the appearance of the first black point in the sample. The disappearance of the last bright spot determines the end of the phase transition temperature range, $T_{\text{CH-I}}$. Determination of the $T_{\text{CH-I}}$ was performed in quadruplicate and the results were comparable within experimental uncertainty.

Chiral power

We setup an optical arrangement to measure the intensity of linearly polarized light transmitted through the sample as a function of time and angle of the analyzer. Briefly, the sample

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