Communication

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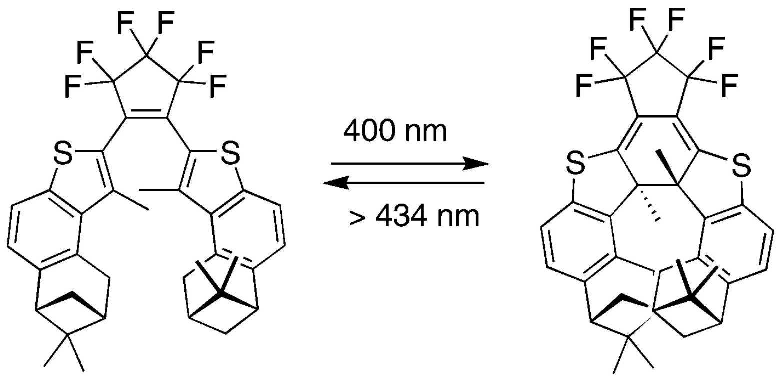

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Chiral Discrimination in Photochromic Helicenes

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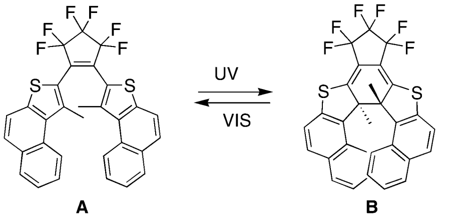
The photoregulation of chirality[1] is fundamentally significant because it has the potential to influence novel liquid crystalline materials,[2,3] nondestructive data storage,[1,4] and catalytic asymmetric synthesis. In all cases, the combination of a well-behaved photoresponsive molecular backbone and a chiral architecture that has an inherently large ability to interact and transfer its chirality to the environment is increasingly important to develop. Photochromic 1,2-dithienylethenes (DTEs) appropriately satisfy the first condition because they undergo thermally irreversible photocyclization reactions, often with minimal photofatigue.[5] They have been used with varying success in chiroptic applications.[3,4,6]

As chiral architectures, helicenes are appealing due to their large optical activities and high helical twisting powers.[7] Current systems, where helicity is modulated, are based on reversible redox chemistry,[8] coordination chemistry,[9] irradiation with circularly polarized light,[10] and stereoselective photochromism.[1] The last strategy is one of the most promising for data storage applications because the changes in optical rotation can be used as the read-out method in an all-optical memory device and because both photochromic forms are easily accessed using light rather than electricity or chemical reagents, which are often limiting when integrated in practical devices.

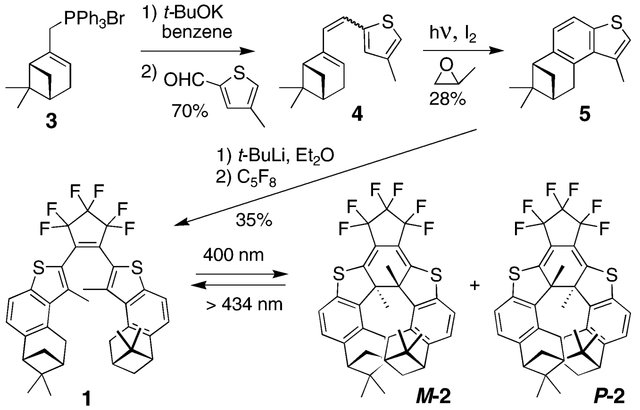


(1)

We have recently published the first example of a photochromic [7]-thiahelicene based on the 1,2-dithienylcyclopentene backbone (eq 1).[11] The steric congestion between the ends of the two arms of the photoswitch forces the ring-open form, **A**, to exist as two rapidly interconverting atropisomers. The ring-closed form **B**, on the other hand, is locked into a strict chiral structure. The ring-closed form also has two newly created stereogenic centers at the carbons involved in forming the new C−C single bond. The configuration around these centers is coupled to the helical chirality as a whole.

The limitation with our first-generation [7]-thiahelicene is that the ring-closing reaction produces a racemate. In this communication, we show that the attachment of chirality at the end of the two arms of a new photoswitch **1** results in a high level of stereoselectivity in the ring-closing reaction (**1**→**2**). We also describe how this system has a dramatic change in optical rotation and how this property can be reversibly photomodulated.

Scheme 1



The synthesis of the ring-open form of the photoswitch is outlined in Scheme 1 and starts by coupling the phosphonium salt of (1*S*)-bromo-β-pinene **3** with 4-methylthiophene-2-carboxaldehyde.[12] Photolysis of the product of the Wittig reaction (**4**) generates the chiral thianaphthene **5** as long as iodine and propylene oxide are added to the reaction mixture. The final assembly of the hexatriene structure in **1** necessary for photocyclization is accomplished by reacting the anion of **5** with octafluorocyclopentene. At no point in this three-step synthesis is resolution required, and chiral HPLC (CHIRACEL-OD, hexanes) of samples of **1** reveals the existence of only a single stereoisomer.

The reversible photochromism (**1**⇆**2**) is best shown by the changes in the UV−vis absorption spectra when a benzene solution of the compound is irradiated with appropriate wavelengths of light (Figure 1). Irradiation with light ranging from 300 to 450 nm drives the cyclization reaction (**1**→**2**), and the higher-energy absorption peaks ($\lambda = 278$ and 342 nm) for the ring-open isomer reduce in intensity with the concomitant appearance of an absorption peak in the visible region ($\lambda = 489$ nm) as the orange-colored ring-closed stereoisomers ***M*-2** and ***P*-2** are produced. The photocyclization is optimized using 400 nm light to generate a photostationary state (PSS) consisting of 40% of only a single ring-closed stereoisomer as measured first by ^{1}H NMR spectroscopy, which shows only a single set of new signals and then by chiral HPLC.[12] Although this PSS is rather disappointing, it is more than adequate for use in chiroptic applications. This stems from the large twisting power of the helicene backbone, especially when the photocyclization produces only one stereoisomer. The orange solution can be photobleached by using light at wavelengths greater than 434 nm, which converts **2** back to **1** and regenerates the original absorption spectrum. This photoreaction can be cycled numerous times without any observable degradation.

While we have not yet succeeded in isolating single crystals of the ring-closed isomer generated in this highly stereoselective photoreaction and have, therefore, not fully characterized the absolute configuration of the product, we believe it is the ***M*-2** stereoisomer. This is supported by molecular modeling,[13] which predicts this isomer to be more stable than its counterpart ***P*-2**. This is further supported by its circular dichroism (CD) characteristics.

The circular dichroism spectra are shown in the inset of Figure 1 and display significant differences throughout the 350−550 nm

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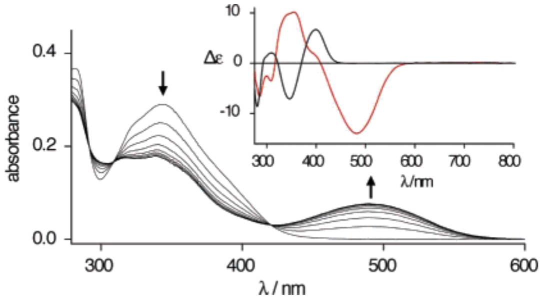

Figure 1. Changes in the UV−vis absorption spectra of a solution of **1** (2×10^{-5} M) in benzene upon irradiation with 400 nm light for a total of 240 s. The inset shows the CD spectra measured on a solution of **1** (2×10^{-4} M) in benzene (black trace) and the photostationary state (red trace) generated with 400 nm light.

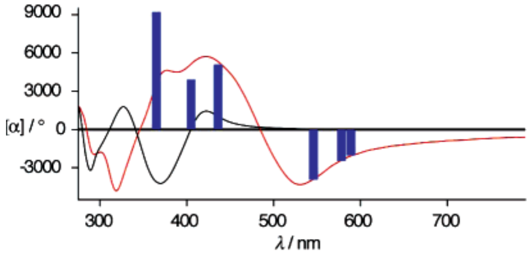

Figure 2. ORD spectra measured on a solution of **1** (2×10^{-4} M) in benzene (black trace) and the photostationary state (PSS) (red trace). The changes in optical rotation ($[\alpha]_{\mathbf{PSS}} - [\alpha]_{\mathbf{1}}$) measured at six wavelengths with a polarimeter are highlighted by the blue bars.

region. The inset reveals how the strong bisignate bands can be photomodulated. The CD spectrum for the PSS also correlates well with those for other helicenes of known "handedness".[14] This supports our claim that ***M*-2** is the only stereoisomer produced in the ring-closing reaction. The ring-open isomer **1** displays Cotton effects ($\Delta\epsilon_{347} = -7$, $\Delta\epsilon_{400} = +7$), which at this time, we can only attribute to positive exciton chirality between the two arms of the compound.[15] This chirality may result from the existence a dominant chiral conformer of **1**; however, the dominance of such an isomer could not be predicted with molecular modeling.[16] A more likely explanation is that the transition moments are asymmetrically oriented in some of the conformers but not in others.

Nondestructive optical memory media are approachable using photochromic DTE compounds as long as the interrogating stimuli needed to induce a read-out signal do not trigger or interfere with the reversible photocyclization reactions. Using changes in optical rotation is a practical strategy, and the reactions of **1** and ***M*-2** represent a functional example because the isomers display large differences in how they interact with plane-polarized light, as shown by the changes in the optical rotary dispersion spectra (Figure 2). The magnitudes of the specific rotation [α] throughout the UV−vis spectrum can be photomodulated when the ring-open isomer (in benzene) is converted to the PSS containing 40% ***M*-2**. The most notable changes are in the 350−600 nm range. The largest signal for the PSS appears at 422 nm ($[\alpha] = 5725°$), and the most significant difference between the signal for the PSS and that for the ring-open form **1** is at 373 nm ($\Delta[\alpha] = 8698°$). Efforts are underway to increase the amount of ring-closed isomer in the PSS and to further investigate the effects of environment, concentration, and aggregation.

This novel system satisfies the requirements of a successful chiroptical photoswitch. It is thermally stable in both its states, it displays high stereoselectivity in its photocyclization reactions, and it exhibits large changes in its CD and ORD spectral properties.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Canadian Research Chairs Program, and Simon Fraser University for financial support of this research. We thank Nippon Zeon Corporation for supplying the octafluorocyclopentene needed to prepare the photochromic compound. We are grateful to the reviewers for their helpful comments and suggestions.

Supporting Information Available: Synthetic details, photochemical reactions, and structural and optical characterizations for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Performed using a CHIRALCEL-OD column (1.0 mL/min, hexanes). This column has been successfully used to separate the enantiomers of compound **B** and other thiahelicenes. See ref 14 and Supporting Information for details.
(13) Semiempirical calculations (AM1) using Spartan '02 from Wavefuntion, Inc. estimate that the ***M*-2** stereoisomer is ∼16 kcal/mol more stable than the ***P*-2** stereoisomer.
(14) It is accepted that the trends in the CD spectra are consistent for a series of compounds of similar structure and chirality. *M*-Helicenes typically exhibit positive Δϵ values in the higher-energy regions and negative values at the lower-energy regions of the CD spectra. Wachsmann, C.; Weber, E.; Czugler, M.; Seichter, W. *Eur. J. Org. Chem.* **2003**, 2863. Caronna, T.; Sinisi, R.; Catellani, M.; Luzzati, S.; Abbate, S.; Longhi, G. *Synth. Met.* **2001**, *119*, 79. Groen, M. B.; Wynberg, H. *J. Am. Chem. Soc.* **1971**, *93*, 2968.
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(16) The arm of isomer **1** does not show Cotton effects. The coexistence of four equal-energy conformers is predicted by molecular modeling (Spartan AM1).

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