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Reversible [7]-Thiahelicene Formation Using a 1,2-Dithienylcyclopentene Photochrome

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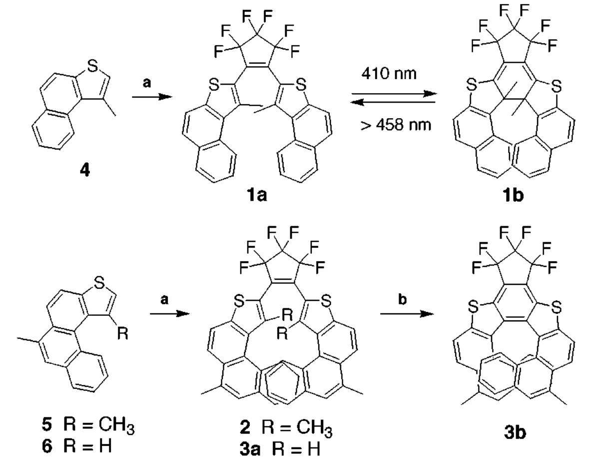
Structure is intimately related to function at the molecular level, just as it is at the macroscopic level. Tailoring precise molecular architecture is, therefore, a necessity to successfully design molecules that will translate their topological properties into the nanoscale realm. Substantial ongoing research is being dedicated to the formation of molecular systems based on the helix as an architectural motif.[1] Helicenes are a specific class of helical molecules comprised of *ortho*-condensed aromatic rings that form unique twisted nonplanar π-electron systems.[2] It is this inherently dissymmetric backbone that, among other features, makes helicenes structurally intriguing for application to the areas of asymmetric molecular recognition[3] and cataylsis,[4] liquid crystal technology,[5] and nonlinear optics[6] and as components for molecular machinery.[7]

Several groups have recently taken advantage of photochromic scaffolds to modulate helical topology,[8] most notably as potential chiroptical information storage devices.[9] However, we are unaware of any reports describing the incorporation of a photochrome directly into a helicene backbone. Here we report the first example of a [7]-thiahelicene:dithienylethene hybrid (**1**) and how the photochrome provides a convenient mechanism to modulate helical topology.

Our design involves the lesser known dithienylethene photochrome in which the 3-methylthiophene heterocycles are linked to the perfluorinated cyclopentene at their 2-ring positions.[10] This particular photochrome has a structural advantage over its more commonly used 3-thienyl-linked counterpart[11] as it directs the individual naphthalene arms toward one another where photocyclization can ultimately yield a helical architecture. A rigid nonplanar helical backbone is created when **1a** is converted to **1b**. The closed form represents an excellent photochromic mimic of the [7]-thiahelicene originally reported by Wynberg and coworkers.[12] Regeneration of the open form by photochemically cleaving the bridging C−C bond linking the two flanking arms of the helicene destroys the extended helicene backbone.

Scheme 1[a]



[a] Reaction conditions: (a) *t*-BuLi, hexane (hexane/THF for **6**), −78 °C, then C_5F_8; (b) *hν*, I_2, propylene oxide, benzene.

Photochrome **1a** was prepared by coupling the known thianaphthalene **4**[13] to octafluorocyclopentene (Scheme 1). The photoswitch can be conveniently toggled between its open (**1a**) and closed (**1b**) states by alternate irradiation with appropriately tuned wavelengths of light. Irradiation of CH_2Cl_2 solutions of **1a** at 410 nm[14] resulted in an immediate increase in the absorption intensity in the visible spectral region (430−580 nm) due to the appearance of the closed isomer, **1b** (Figure 1). This photostationary state was identified by ^1H NMR spectroscopy as consisting of 74% of the closed isomer, **1b**. Irradiation of **1a** at wavelengths even slightly greater than or less than 410 nm resulted in a decrease in the amount of closed isomer **1b** at the photostationary state. Irradiation of **1b** at wavelengths greater than 458 nm resulted in the rapid ring-opening photoreaction and the regeneration of the original absorption spectrum corresponding to **1a**.

Single crystals of **1a**, suitable for X-ray crystallographic analysis, were grown by slowly cooling a hot hexane solution of the photochrome. The crystal contains the two enantiomeric forms of **1a**, and consequently, the crystal as a whole is racemic. When the photostationary state was treated under identical conditions, single crystals of both **1a** (yellow crystals) and **1b** (orange crystals) could be isolated. The structure of the closed isomer in the crystal (Figure 2) highlights the molecule's helical nature, which originates as a result of the steric crowding between the naphthalene arms of the helicene skeleton. The direct overlap of carbons C20 and C40 defines the 3.47 Å distance between opposing terminal benzene rings and completes one helical turn.

The conrotatory ring-closing reaction dictates that only two of the four possible stereoisomers of **1b** are produced in the

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(14) The monochromatic light used to carry out the ring-closing reaction was generated from a Spectral Energy lamp (1000 W Xe/Hg source) and monochromator assembly. The ring-opening reaction was carried out using the light of a 150-W tungsten source that was passed through a 458-nm cutoff filter to eliminate higher energy light.

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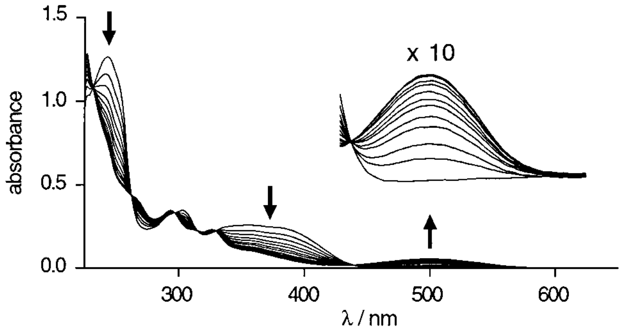

Figure 1. Changes in the UV−vis absorption spectra of a CH_2Cl_2 solution of **1a** (2×10^{-5} M) upon irradiation with 410-nm light. Irradiation periods are 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, and 100 s.

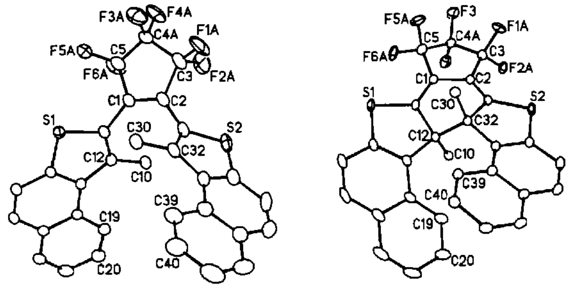

Figure 2. The structures of the *open* (left) and *closed* (right) forms of photochrome **1** in the crystal. Only selected enantiomers are depicted. The thermal ellipsoids are drawn at the 20% probability level.

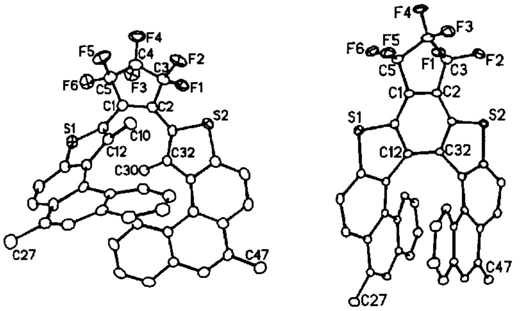

Figure 3. The structures of the *open* form of photochrome **2** (left) and [9]-thiahelicene **3b** (right) in the crystal. The thermal ellipsoids are drawn at the 20% probability level.

photocyclization of **1a**. The four stereoisomers result from the creation of two stereogenic centers and a helical screw axis. This does not, however, exclude the possibility of post-cyclization epimerization of **1b** resulting in the generation of all four stereoisomers. This is unlikely as previous studies on heptaheterohelicenes with similar backbones show limited racemization at ambient temperatures.[12] In the solid state only the *P*-SS and *M*-RR stereoisomers are observed. We attribute this stereodiscrimination to the significantly enhanced stability of these two enantiomers as compared to their diasteriomeric counterparts (*P*-RR and *M*-SS).[15]

The existence of only a single pair of enantiomeric products in solution was supported by the 600 MHz ^{1}H NMR spectrum of **1b** which displayed a single clean set of peaks throughout both the aromatic and aliphatic regions. All of the proton resonances in **1b** appear upfield from the corresponding signals for **1a**.

A more extended [9]-thiahelicene (**2**) was prepared by coupling [4]-thiahelicene **5** to octafluorocyclopentene as shown in Scheme 1. Photocyclization of **2** was expected to yield a [9]-thiahelicene with a substantial increase in the extent of overlap of the terminal aromatic rings. Surprisingly, no photocyclized product was detected when **2** was systematically irradiated throughout its absorbing spectral region (250−480 nm).

X-ray analysis of single crystals of **2** (Figure 3)[16] reveals that the individual [4]-thiahelicenes appended to the perfluorocyclopentene core are helical themselves due to the crowding caused by the methyl groups on the thiophene heterocycles.[17] In the event that the extended [4]-thiahelicene arms were preventing the photocyclization due to steric hindrance, **2** was irradiated in boiling Decalin (bp = 187 °C) where rapid epimerization of each arm can be expected. These experimental conditions also failed to yield any detectable photocyclized product.

When the methyl groups on the thiophene heterocycles in **2** were replaced by hydrogen atoms (**3a**), photocyclization followed by subsequent oxidative trapping afforded the nonphotochromic [9]-thiahelicene **3b** in 94% yield as can be seen from the X-ray structure of the isolated product (Figure 3).[16] Compounds **2** and **3a** both absorb substantially further into the visible region (extending out to 480 nm) than the corresponding photochrome **1a**. As has previously been suggested, when the absorptions of the open and closed isomers of photochromic compounds overlap substantially and the ring-opening quantum yield is greater than the cyclization quantum yield, the presence of the closed isomer at the photostationary state will be negligible.[10a] The fact that the closed form of **3a** can be trapped in high yield as the oxidized product **3b** strongly suggests that compound **2** suffers from the existence of a photostationary state that favors the open isomer at the expense of the closed isomer as opposed to steric inhibition of the photocylization reaction.

The influence that remote chiral auxiliaries will have on the stereochemical ring-closing reaction of photochromic helicene precursors is currently under investigation and will be reported in due course.

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[15] Single point energy calculations of the AM1-optimized structures of both diastereomers were performed using the GAUSSIAN 98 suite of programs and the standard 3-21G* basis set. These calculations estimate that the observed stereoisomers are more stable by 19.2 $\text{kcal mol}^{-1.}$

[16] Single crystals of **2** were grown by slow evaporation of a hexane solution. Crystals of **3b** were grown by diffusion of pentane into a benzene solution.

[17] This was previously shown to be the case for a structurally similar molecule: Musmar, M. J.; Martin, G. E.; Gampe R. T., Jr.; Lynch. V. M.; Simonsen, S. H.; Lee, M. L.; Tedjamulia, M. L.; Castle, R. N. *J. Heterocycl. Chem.* **1985**, *22*, 545.