

# Linked Photoswitches Where Both Photochromes Open and Close

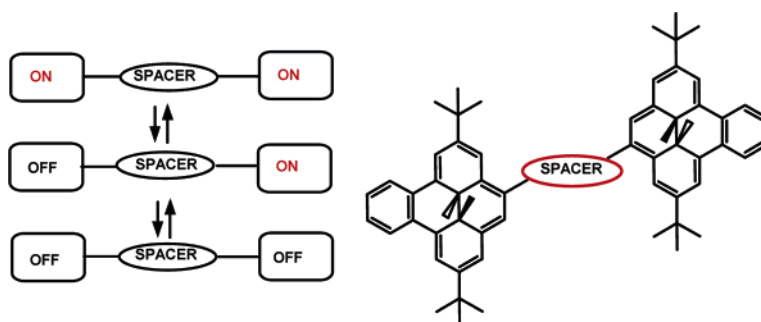
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## ABSTRACT

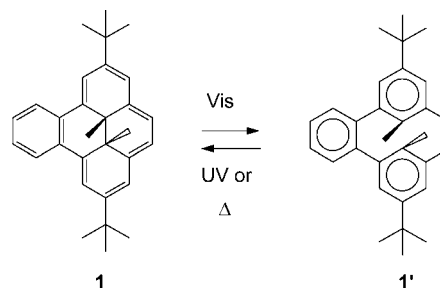


In the dithienylethene photochrome series, linking two photochromes together directly, or with an ethynyl spacer, shuts down the photoswitching of one of the photochromes. We report here, that for dihydropyrenes, two photochromes can be linked together without affecting the ability of either to photoswitch.

Recently, photochromic systems have attracted much attention because of their potential use in optoelectronic devices.<sup>1</sup> Irie<sup>2</sup> and Branda<sup>3</sup> have extensively studied the 1,2-dithienylethenes, and these are the most important members of the diarylethene class of photochromes because of their thermal irreversibility. This makes them useful building blocks for photochromic materials. Fulgides and spiropyrans are examples<sup>4</sup> of other important photochrome classes. A less well-known example of the diarylethene class are the dihydropyrenes. They are different from the dithienylethenes in that they are negative or inverse photochromes in which the thermally stable form is colored and which, on irradiation, becomes colorless. They do not, as yet, show complete thermal irreversibility. For example,  $\tau_{1/2}$  for the thermal

reversion of **1'** to **1** is about 1 week at 20 °C (Scheme 1). They are however, completely photoswitchable, 100% of either photoisomer being easily attainable.<sup>5</sup>

**Scheme 1.** Benzodihydropyrene Photochrome



It is interesting to link or couple photochromes, because then the possibility exists that each photochrome can exist in an open (O) or closed (C) state, and so, if two identical photochromes are coupled, three states, closed–closed (C–

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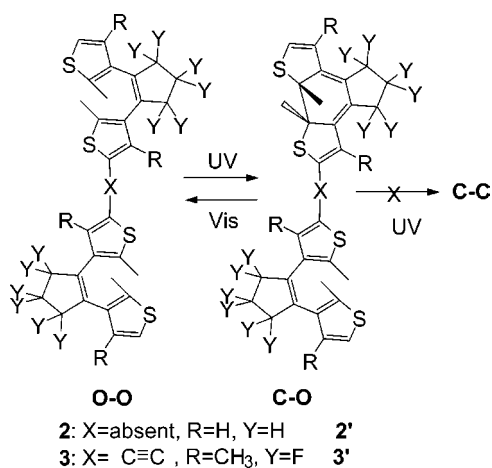
(2) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.

(3) (a) Murguly, E.; Norsten, T. B.; Branda, N. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1752–1755. (b) Myles, A. J.; Branda, N. R. *Adv. Funct. Mater.* **2002**, *12*, 167–173. (c) Myles, A. J.; Branda, N. R. *Macromolecules* **2003**, *36*, 298–303.

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C), closed–open (C–O), and open–open (O–O), might exist. With more than a simple on–off switch, higher logic operations become possible. We were the first to report<sup>6</sup> a bis-photochrome, and both photochromes opened and closed. Both Branda<sup>7</sup> and Irie<sup>8</sup> have reported bis-photochromes where in each case both photochromes would not close. Our photochromes had two dihydropyrenes fused to a chrysene spacer, whereas Irie and Branda's systems were linked via a linear spacer. Branda's system (**2/2'** in Scheme 2) had no

**Scheme 2.** Branda and Irie's Linked Photochromes



spacer group, **X**. When **2** was irradiated with 365 nm broadband light, only one of the photochromic dithienylethene units underwent photocyclization to give **2'**. Prolonged irradiation resulted in irreversible destruction of the system by way of a rearranged side product. Irradiation of **2'** with longer wavelength light at 434 nm returned **2**. Irie's system (**3/3'** in Scheme 2) had an ethynyl group as the spacer **X**. Again, on irradiation of the O–O form **3** with 320 nm light, only one dithienylethene photochrome closed to give **3'**. When they studied the fluorescence spectra of the two forms, they found that the O–O form fluoresced at 440 nm when excited at 320 nm, whereas the O–C form did not. The absorption spectrum of the O–C form overlaps with the fluorescence spectrum of the O–O form, and so they state that it is possible that on irradiation of the O–C form with UV light, it transfers energy within the molecule and prevents further cyclization. The failure in these two systems to close both dithienylethenes intrigued us and stimulated us to investigate similarly linked dihydropyrenes. In our systems, Irie's hypothesis concerning the fluorescence overlap with the absorption spectra of the other isomer may not affect

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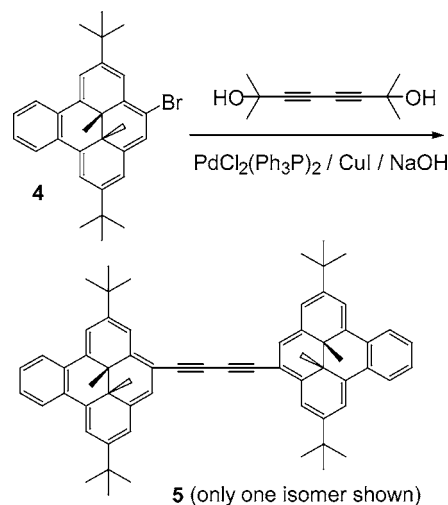
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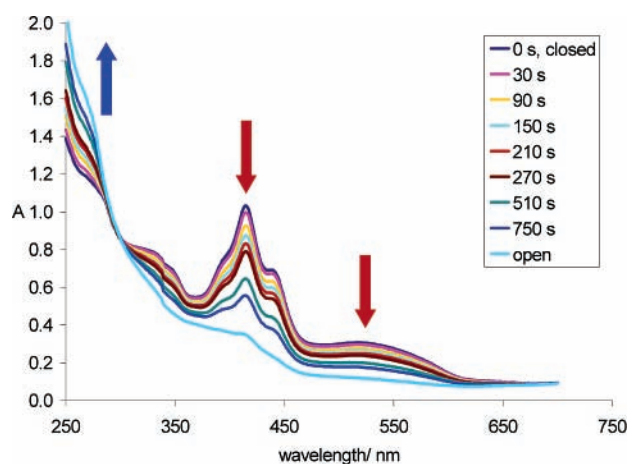
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dihydropyrenes because the thermally stable isomers are already closed and, as well, the dihydropyrenes show only extremely weak fluorescence.<sup>9</sup> We thus synthesized a bis-dihydropyrene system, having a bis-ethynyl spacer, **5** (Scheme 3).

**Scheme 3.** Synthesis of Our Linked Photochrome



The bis-photochrome **5** was synthesized from the bromo-benzodihydropyrene **4**<sup>9</sup> in a single step using a Sonogashira coupling reaction in which the butadiyne unit was generated in situ.<sup>10</sup> Diyne **5** was obtained in about 30% yield as dark reddish-brown crystals, mp 168–169 °C. Full experimental details and characterization are given in Supporting Information. Only one isomer is shown in Scheme 3; however, an equal mixture of the isomer shown and the diastereomer in which the right-hand set of internal methyl groups are reversed (but still are trans) is expected. As has been the case in other similar dihydropyrenes,<sup>5</sup> only two internal methyl proton peaks and one carbon peak are seen in the <sup>1</sup>H

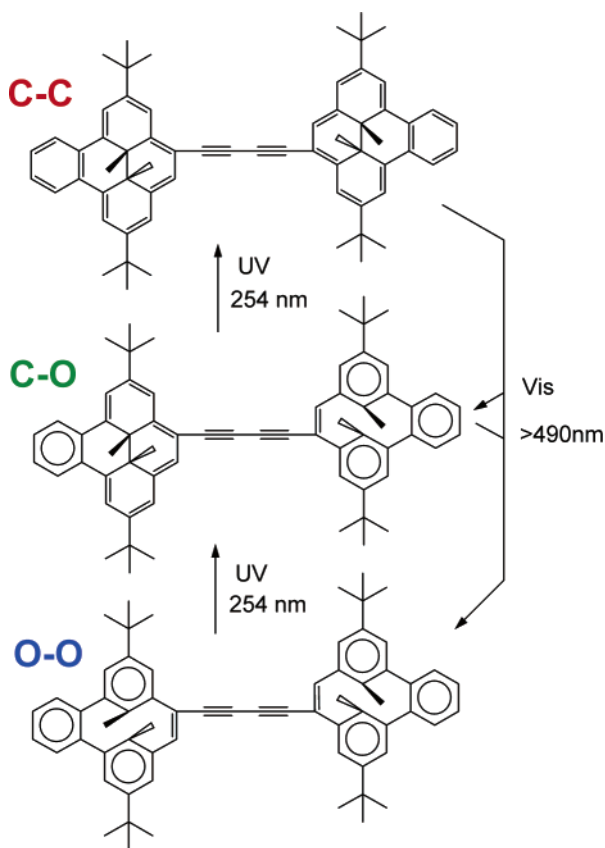


**Figure 1.** Absorption spectra of the opening of C–C **5** with visible light,  $\lambda > 490$  nm, in cyclohexane.

and  $^{13}\text{C}$  NMR spectra, at  $\delta -1.38$  and  $-1.40$  and at  $\delta 18.25$ , respectively.

When a degassed solution of the bis-dihydropyrene **5** was irradiated with visible light of wavelength  $>490$  nm (white light from a tungsten household bulb with an orange plastic 490 nm cut off filter), the brownish-red solution bleached to very pale yellow. The UV-vis absorption spectrum was recorded at successive intervals and is shown in Figure 1. As irradiation continued, the characteristic peaks for a benzodihydropyrene at 525 and 415 nm decreased and the benzenoid bands for a cyclophanediene below 300 nm increased. The disappearance of the visible bands is consistent with conversion of the C-C bis-dihydropyrene form to the O-O bis-cyclophanediene form (Scheme 4). This was

**Scheme 4.** Three States of Photochrome **5**

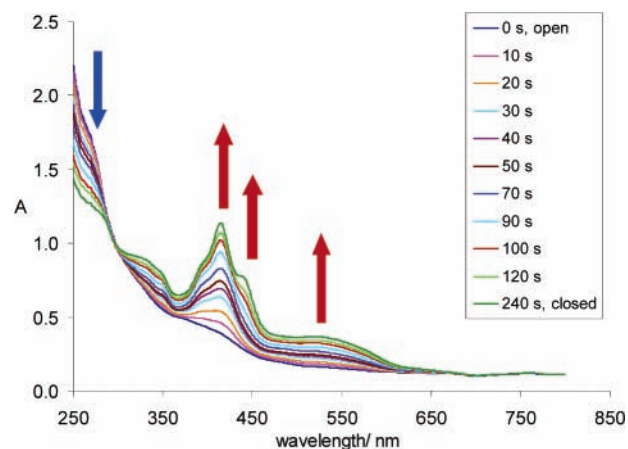


confirmed by both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and is essentially complete by NMR. Note that the O-O isomer does have an extensive tail that extends to  $\sim 460$  nm.

The internal methyl proton and carbon peaks of the initial C-C isomer at  $\delta -1.38$  and  $-1.40$  and at  $\delta 18.25$ , respectively, are completely replaced on irradiation with new peaks at  $\delta 1.20$  and  $1.17$  and at  $\delta 19.4$  and  $18.7$ , respectively, corresponding to the internal methyl group protons and

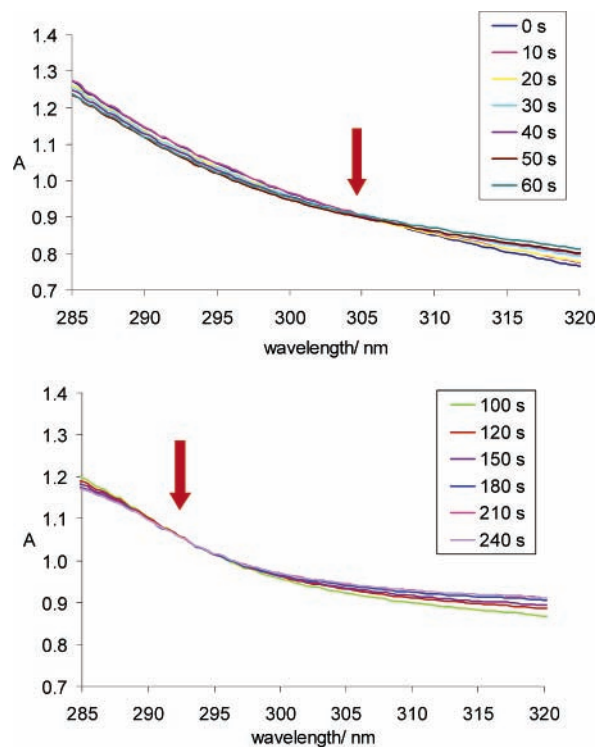
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**Figure 2.** Absorption spectra of the closing of O-O **5** with UV light,  $\lambda = 254$  nm, in cyclohexane.

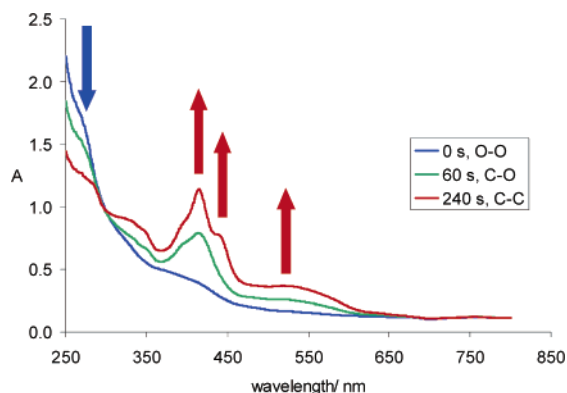
carbons of a cyclophanediene, the O-O isomer. Only a single isosbestic point was observed in the UV-vis spectra, and no peaks were observed consistent with the intermediate O-C isomer in the  $^1\text{H}$  spectra, which suggests that both dihydropyrenes of **4** open simultaneously (on our time scale). This was not changed when the irradiation was carried out with light of  $\lambda > 590$  nm and is exactly what was observed for the bis-photochrome with a fused spacer.<sup>6</sup> At this time



**Figure 3.** (a) Top: isosbestic point at 305 nm during the early part of UV irradiation of O-O **5**. (b) Bottom: isosbestic point at 293 nm during later part of UV irradiation, in cyclohexane.

we do not know whether this is a single-photon process in which the bonds of both dihydropyrene units are broken at the same time or whether the C–O form is converted to the O–O form much faster than the C–O form is made.

When the bleached O–O sample of **4** was then irradiated with a 3W 254 nm mercury lamp, the reddish color returned and the peaks corresponding to dihydropyrenes grew back (Figure 2); however, in this case, two isobestic points were observed, one at 305 nm in the first 60 s of traces and a second at 293 nm in the later (90–240 s) traces (Figures 3a and 3b). This suggests that during the UV reversal, the C–O intermediate was formed first, as was also the case with the conjugated fused spacer example reported by us previously,<sup>6</sup> which subsequently further closed to return C–C **4**. Careful inspection of Figure 2, amplified in Figure 4, reveals that the shoulder at 450 nm only develops later during the irradiation and corresponds to the more conjugated C–C



**Figure 4.** Absorption spectra of the UV closing of O–O **5** (blue) showing the intermediate spectrum of C–O **5** (green) and the final spectrum of C–C **5** (red), in cyclohexane.

form. This is less pronounced than was observed when the fused conjugated spacer chrysene was used.<sup>6</sup> We were hoping to verify this in the NMR spectra. Unfortunately, there appears to be insufficient difference in the chemical shifts of the internal methyl protons or the *tert*-butyl protons of the dihydropyrene units of C–C and C–O **5** to see sharp peaks for each individual isomer (there are two diastereomers of each), which is perhaps not so surprising considering the separation between the units, and as well, even when the spacer was a fused chrysene, which has substantially greater conjugation, the shift difference of these peaks was in each case <0.1 ppm.<sup>6</sup> Currently, we have not been able to separate by chromatography the three isomers; however, we will pursue the search for good intermediate spectra in the future. The NMR data though *leaves no doubt* that both dihydropyrenes fully open and close, unlike the two dithienylethenes, **2** and **3**. The lack of significant fluorescence in the case of the dihydropyrenes may thus be a real advantage if linked photochromes are desired. We are currently synthesizing dihydropyrenes linked with other nonfused spacers such as 1,4-phenylene-, 1,2-ethynyl-, 1,1-carbonyl-, and 1,2-ethenyl- to further explore the photochromicity of linked dihydropyrenes and compare them to dithienylethene types recently reported.<sup>11</sup>

**Acknowledgment.** We thank Science and Engineering Research Canada and the University of Victoria for financial support.

**Supporting Information Available:** Experimental procedure for the synthesis of **5** and its irradiation and spectroscopic information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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