

# Novel Photochromic Compounds Based on the 1-Thienyl-2-vinylcyclopentene Backbone

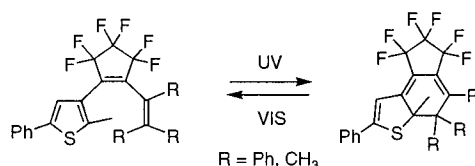
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## ABSTRACT

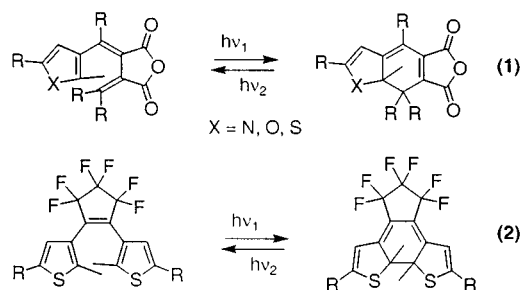


A new class of photochromic compounds based on the hexatriene backbone has been developed. The backbone, composed of a thiophene ring, a perfluorocyclopentene ring, and a trisubstituted olefin, undergoes reversible ring-opening and ring-closing photoisomerization reactions when irradiated with ultraviolet and visible light, respectively.

If organic photochromic compounds are to find widespread use in photonic device applications such as erasable memory media and optical switching, several mandatory properties must be met. Foremost are thermal irreversibility, photo-fatigue resistance, and high efficiency in a rapid photoconversion processes.<sup>1</sup> An additional factor that cannot be downplayed is the ability to tailor the physical and chemical properties of the photochromic backbone in a facile, flexible, and modular manner. This can only be accomplished by designing photochromic compounds that possess many different locations on their molecular skeletons where functional groups can be anchored.

The most promising organic photochromic compounds are based on the fulgide<sup>2</sup> (eq 1) and 1,2-dithienylcyclopentene<sup>3</sup> (eq 2) backbones, which contain 1,3,5-hexatriene skeletons

that undergo reversible  $6\pi$ -electrocyclization reactions. Both classes of compounds, however, have drawbacks that limit the scope of their use in optical device applications.



Fulgides present many sites for potential synthetic modification as well as flexibility in the choice of the heterocycle. Their synthesis, however, most often involves the Stobbe condensation, which does not always provide the desired product in high yield, particularly when the components are

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(1) (a) *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Gugliemetti, R. J., Eds.; Plenum: New York, 1999; Vols. 1 and 2. (b) Irie, M., Ed. *Chem. Rev.* **2000**, *100*, 1685–1890.

(2) (a) Fan, M. G.; Yu, L.; Zhao, W. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Gugliemetti, R. J., Eds.; Plenum: New York, 1999; Vol. 1, pp 141–206. (b) Yokoyama, Y. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001; pp 107–121. (c) Yokoyama, Y. *Chem. Rev.* **2000**, *100*, 1717–1739.

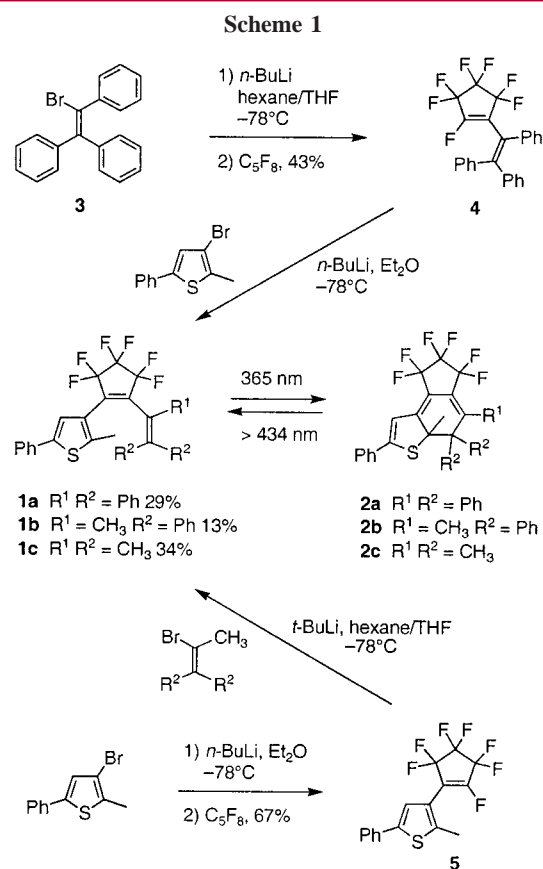
(3) (a) Irie M. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Gugliemetti, R. J., Eds.; Plenum: New York, 1999; Vol. 1, pp 207–222. (b) Irie M. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001; pp 37–62.

highly substituted. In addition, as fulgides contain a reactive anhydride moiety, further modifications on the photochromic backbone are limited. Fulgide derivatives are also plagued by photoinduced *cis*–*trans* isomerization of the double bond connecting the heterocycle to the rest of the photochromic backbone. This process competes with photocyclization reaction as only the isomer where the three conjugated double bonds are lying in the *s-cis-cis-s-cis* manner are capable of forming the new C–C single bond. To overcome this energy-wasting drawback, large groups must be attached to the remaining free site on the alkene, where their steric bulk can influence the *E*–*Z* isomerization and populate the active (*Z*)-isomer.<sup>4</sup> This comes with a price, however, because the syntheses of these modified compounds tend to be more difficult.

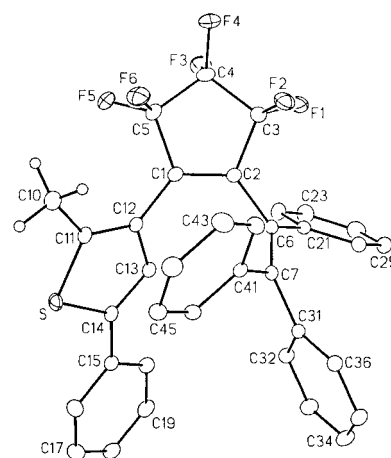
Dithienylcyclopentene derivatives, on the other hand, do not undergo competing *E*–*Z* isomerization reactions. Two rotomers, parallel and antiparallel, coexist in solution, and these rotomers, unless there are substituents attached onto the 4-position of the heterocycle or benzothiophenes are used in place of thiophene, are rapidly interconverting. Dithienylalkenes are relatively easy to synthesize due to the manner in which the thiophene rings are connected onto the cyclopentene ring at their 2- or 3-positions. However, there is a limited number of sites where functional groups may be attached (primarily the 2- and 5-positions of the heterocycles), and in many cases, introducing particular functional groups at these locations results in thermal reversibility<sup>5</sup> or poor efficiency of the photoreactions.<sup>6</sup>

One of our research goals is to prepare novel photochromic backbones that take advantage of the appealing properties of both the fulgides and dithienylalkenes without being hampered by their limitations. Here we describe three new hexatriene systems **1a**–**c** that show good photochromic behavior. They are similar in structure to 1,2-dithienylalkenes except that one of the thiophene rings has been replaced with a substituted olefin. It is this olefin that provides the functional group versatility of fulgides without sacrificing the synthetic ease at which the 1,2-dithienylethenes can be prepared.<sup>7</sup>

Photochromic compounds **1a**–**c** are prepared as shown in Scheme 1 using the same approach as used for preparing 1,2-dithienylalkene derivatives except that one of the anionic heterocycles has been replaced with a lithiated olefin. Lithiation of the known triphenylvinylbromide<sup>8</sup> **3** followed by addition of excess octafluorocyclopentene generates



compound **4**, which can be further treated with the anion generated from 3-bromo-2-methyl-5-phenylthiophene<sup>9</sup> to yield hexatriene **1a** (Figure 1).<sup>10</sup> Compounds **1b** and **1c** are better prepared by an alternate route in which the heterocycle is attached to the octafluorocyclopentene prior to addition of the substituted olefin portion. This is a preferred route because the reaction of the appropriate vinylbromide to the octafluorocyclopentene affords oils, which are much less



**Figure 1.** Molecular structure of **1a** in the crystal. Thermal ellipsoids are drawn at the 20% probability level.

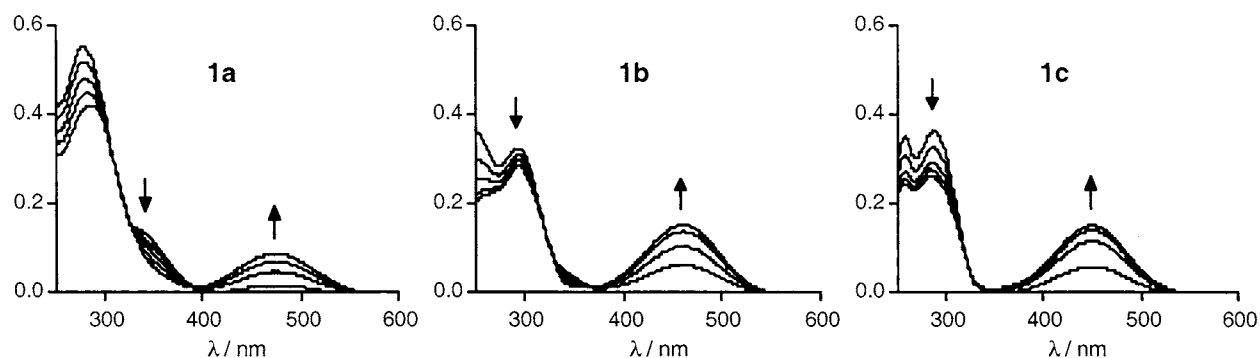
(4) Yokoyama, Y.; Goto, T.; Inoue, T.; Yokoyama, M.; Kurita, Y. *Chem. Lett.* **1988**, 1049. Yokoyama, Y.; Inoue, T.; Yokoyama, M.; Goto, T.; Iwai, T.; Kera, N.; Hitomi, I.; Kurita, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3297. Yokoyama, Y.; Kurita, Y. *Mol. Cryst. Liq. Cryst., Sect. A* **1994**, *246*, 87.

(5) Uchida, K.; Tsuchida, E.; Aoi, Y.; Nakamura, S.; Irie, M. *Chem. Lett.* **1999**, 63. Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Lett.* **2000**, 1340.

(6) Takami, S.; Kawai, T.; Irie, M. *Eur. J. Org. Chem.* **2002**, 3796. Morimitsu, K.; Shibata, K.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2002**, *67*, 4574.

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(8) Gilman, H.; Fothergill, R. E. *J. Am. Chem. Soc.* **1929**, *51*, 3149. Lomas, J. S.; Fain, D.; Briand, S. *J. Org. Chem.* **1990**, *55*, 1052. Koelsch, C. F. *J. Am. Chem. Soc.* **1932**, *54*, 2045.



**Figure 2.** Changes in the UV–vis absorption spectra of **1a–c** upon irradiation with 365 nm light. Irradiation periods are 10, 30, 60, and 120 s. All spectra are of  $\text{CH}_2\text{Cl}_2$  solutions at  $2 \times 10^{-5}$  M.

convenient to handle than the solid diene **5**. Monothiophene **5** reacts with the anions of 1,1-diphenylpropene and 3-methyl-2-butene<sup>11</sup> to produce hexatrienes **1b** and **1c**, respectively.

All three compounds **1a–c** exhibit good photochromic properties and can be toggled between their colorless ring-open (**1a–c**) and colored ring-closed (**2a–c**) forms by alternate irradiation with ultraviolet and visible light<sup>12</sup> as monitored using UV–vis absorption and <sup>1</sup>H NMR spectroscopy. When  $\text{CH}_2\text{Cl}_2$  solutions ( $2 \times 10^{-5}$  M) of the colorless ring-open forms are irradiated with 365 nm light, absorption bands in the visible region appear and the solutions turn orange as a result of the ring-closing reactions to produce **2a–c** (Figure 2 and Table 1). <sup>1</sup>H NMR spectroscopic studies

and 64% for **2c**, respectively. All the solutions of **2a–c** can be decolorized by irradiating them with visible light of wavelengths greater than 434 nm to induce the ring-opening reactions and regenerate **1a–c**. In the absence of visible light, the color persisted, attesting to the thermal stability of the photochromic compounds.

<sup>1</sup>H NMR spectroscopy studies also show that the conversion of **1a** to **2a** results in the generation of a photo side-product, which has yet to be isolated or characterized. We suggest that this side-product could possibly be due to the cyclization followed by oxidation of the stilbene fragment to generate a phenanthrene system.<sup>13</sup> The side-product formation can also be monitored by luminescence spectroscopy. Solutions of the ring-open isomer **1a** exhibit no observable emission when they are excited with ultraviolet light ( $\lambda_{\text{max}} = 300$  nm). Solutions of the ring-closed isomer **2a**, however, did produce intense emission at 400 nm when excited at the same wavelength (300 nm). Photobleaching of the solutions using visible light ( $>434$  nm) resulted in the disappearance of the band centered at 473 nm in the absorption spectrum; however, the emission at 400 nm remained. Subsequent irradiation of the resulting solution with 365 nm light triggered a further increase of the band in the luminescence spectrum, indicating that some photodegradation was occurring upon cyclization of **1a** to **2a**. Compounds **1b** and **1c** showed clean conversion to compounds **2b** and **2c**, respectively, as monitored by <sup>1</sup>H NMR spectroscopy.

We have succeeded in preparing several photochromic compounds based on a modified hexatriene skeleton. This novel molecular scaffold offers the chance to decorate

**Table 1.** UV–vis Absorption Data for All Photochromic New Compounds in Their Ring-Open and Ring-Closed Forms

compound	$\lambda_{\text{max}}$ (nm)	$\epsilon$ ( $\text{L mol}^{-1} \text{cm}^{-1}$ )
<b>1a</b>	279	27 600
<b>2a<sup>a</sup></b>	473	4470
<b>1b</b>	294	16 200
<b>2b<sup>a</sup></b>	460	7860
<b>1c</b>	288	18 200
<b>2c<sup>a</sup></b>	450	7580

<sup>a</sup> Measured at the photostationary states obtained by irradiating  $\text{CH}_2\text{Cl}_2$  solutions ( $2 \times 10^{-5}$  M) of the ring-open forms with 365 nm light for 140 s (**2a**), 180 s (**2b**), and 120 s (**2c**).

performed on  $\text{CD}_2\text{Cl}_2$  ( $1 \times 10^{-3}$  M) solutions of **1a–c** reveal that the photostationary states are 47% for **2a**, 75% for **2b**,

(9) Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871.

(10) X-ray-quality single crystals were grown by slow evaporation from a hexane solution. Crystal data for **1a**:  $\text{C}_{36}\text{H}_{24}\text{F}_6\text{S}$ ,  $M = 602.61$ , triclinic, space group  $P1$  (No. 2),  $a = 10.8285(14)$ ,  $b = 11.9726(16)$ ,  $c = 12.5721(16)$  Å,  $\alpha = 98.094(3)$ ,  $\beta = 115.285(3)$ ,  $\gamma = 95.371(2)$ ,  $V = 1437.4(3)$  Å<sup>3</sup>,  $T = -80$  °C,  $Z = 2$ ,  $\mu = 0.177 \text{ mm}^{-1}$ , 7193 reflections measured, 5779 unique,  $R_1(F) = 0.0431$ ,  $wR_2(F^2) = 0.1190$  (all data).

(11) These anions are prepared from their respective bromides. 2-Bromo-1,1-diphenylpropene: Koelsch, C. F.; White, R. V. *J. Org. Chem.* **1941**, *6*, 602. 2-Bromo-3-methyl-2-butene: Patel, B. A.; Kim, J.-I. I.; Bender, D. D.; Kao, L.-C.; Heck, R. F. *J. Org. Chem.* **1981**, *46*, 1061.

(12) Standard lamps used for visualizing TLC plates (Spectroline E-series, 365 nm, 470 mW/cm<sup>2</sup>) were used to carry out the ring-closing reaction of all photochromic compounds in this study. The ring-opening reactions were carried out using the light of a 150 W tungsten source that was passed through a 434 nm cutoff filter to eliminate higher energy light.

(13) Irie has reported that bis(thienyl)ethenes lacking substituents on the C-4 positions of the thiophene rings produce photo byproducts after prolonged irradiation with UV light (Irie, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2389). In the present cases, a side-product was only observed after short irradiation periods, and only for **1a**. We, therefore, believe that the side-product is more likely the phenanthroline derivative, although the other possibility cannot be ruled out.

photoresponsive systems with a wide range of functional groups without sacrificing photochromic behavior. The use of this backbone in materials applications as well as the precise nature of the photo side-product in the case of **1a** is currently underway and will be reported in due time.

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of Alberta, and Simon Fraser University. Special thanks go to Nippon Zeon Corporation for supplying the octafluorocyclopentene.

**Supporting Information Available:** Experimental procedures for preparation of compounds **1a–c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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