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# Photochromism of a Diarylethene with Methoxymethyl Groups at Reactive Carbons: Thermal Irreversible Reaction of the Closed-ring Isomer

Daichi Kitagawa and Seiya Kobatake*
*Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585*

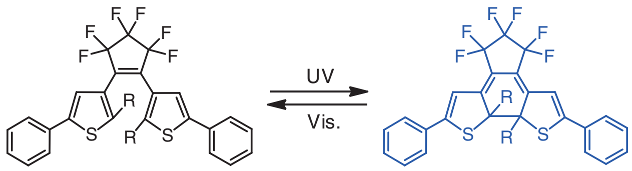
(Received November 5, 2010; CL-100931; E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp)

A photochromic diarylethene having methoxymethyl groups at the reactive carbons was synthesized, and the thermal stability of the closed-ring isomer was examined. The closed-ring isomer of the diarylethene caused both the thermal cycloreversion and a thermally irreversible reaction at 120 °C. The structure of the thermal product was determined by $^1$H NMR, MS, and X-ray crystallographic analysis.

Photochromism refers to chromatic change upon photoirradiation.[1,2] Photochromic compounds change not only their molecular structures but also their physical properties including absorption spectra, refractive indices, dielectric constants, and oxidation–reduction potentials. Various types of photochromic compounds have been synthesized and researched in an attempt to apply them to optical memories and photooptical switching devices. Among them, diarylethene derivatives are the most promising compounds for application because of some excellent characteristics, such as the thermal stability of both isomers and fatigue-resistant properties.[3–7] Such materials can potentially be used in applications such as optical memory media,[8–10] switching devices,[11–17] display materials,[18,19] and photomechanical actuators,[20–23] because of the thermal irreversibility at room temperature.

The substituents at the reactive carbons of diarylethenes can control the thermal and photochemical cycloreversion reactivities of the closed-ring isomers.[24–32] For example, introduction of bulky substituents at the reactive carbons enhances the thermal cycloreversion reactivity.[24–27] The photocycloreversion quantum yield is strongly suppressed by introduction of methoxy groups at the reactive carbons.[28] By introduction of cyclohexyloxy groups instead of methoxy groups, the photostable diarylethene-closed-ring isomers return to their initial colorless open-ring isomers by heating at temperatures above 100 °C.[29,30] Cyano groups contribute to the increase in the photocycloreversion quantum yield.[31] When trimethylsilyl groups are introduced at the reactive carbons, the colored isomer immediately and irreversibly changes to a colorless by-product by heating at 100 °C.[32] As various types of substituents have been already introduced at the reactive carbons, introduction of substituents at the reactive carbons of diarylethenes gives us encouragement to make novel photochromic functions.

Here, we introduce methoxymethyl groups at the reactive carbons of diarylethenes. 1,2-Bis(2-methoxymethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) was newly synthesized and examined for the thermal stability of the closed-ring isomer **1b**. During the course of the study on the thermal stability of the closed-ring isomer, we found that it changes to another product, which is different from the open-ring isomer, by heating at 120 °C. The structure of the by-product is clearly discussed in this letter.



**1a**: R = $CH_2OCH_3$ **1b**: R = $CH_2OCH_3$

**Scheme 1.**

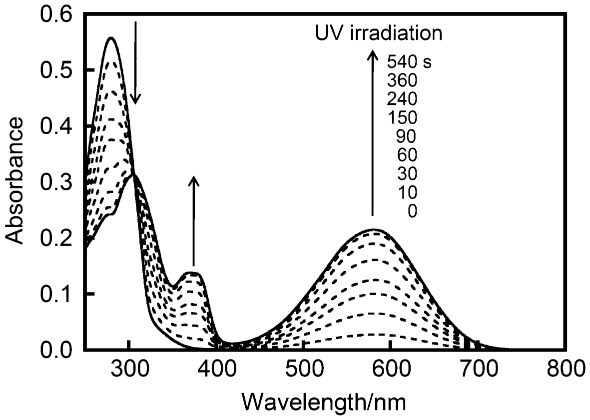


**Figure 1.** Absorption spectral change of diarylethene **1a** ($1.4 \times 10^{-5}$ mol dm$^{-3}$) in hexane upon irradiation with 313-nm light. Upon UV irradiation for 540 s, the solution of **1a** reached in the photostationary state.

Diarylethene **1a** showed reversible photoisomerizations upon alternating irradiation with ultraviolet (UV) and visible light at room temperature (Scheme 1). Figure 1 shows the absorption spectral change of **1a**. Diarylethene **1a** has the absorption maximum at 280 nm in hexane. Upon irradiation with 313-nm light, the colorless solution turned blue, in which the visible absorption maximum was observed at 580 nm. This spectral change is ascribed to the photoisomerization from the open-ring isomer to the closed-ring isomer. The blue color disappeared by irradiation with visible light ($\lambda > 500$ nm) and the absorption spectrum returned to that of **1a**. The photocyclization and photocycloreversion quantum yields were determined to be 0.53 and 0.0055, respectively.[33] The photoisomerization conversion from **1a** to **1b** was 95% in hexane upon irradiation with 313-nm light. The open-ring isomer **1a** and the closed-ring isomer **1b** were stable at room temperature. These photochromic properties are similar to those of diarylethene having methyl groups at the reactive carbons.[34]

Next, the thermal stability of the closed-ring isomer was examined. The closed-ring isomer **1b**[35] in toluene, which was

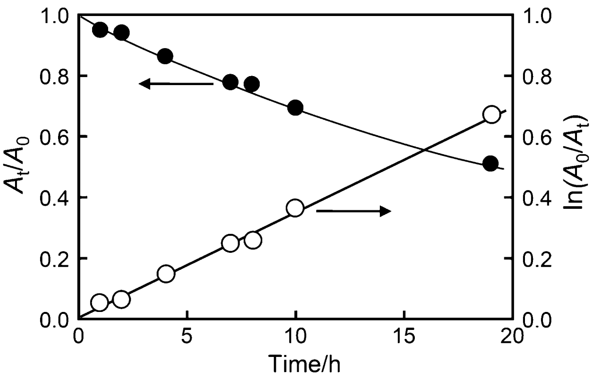


**Figure 2.** Decay curve and the first-order plot for thermal reaction of **1b** at 120 °C.

degassed and sealed off under vacuum in an optical quartz cell, was heated at 120 °C. Figure 2 shows a decay curve of absorbance of **1b** at 120 °C. The decay curve followed the first-order kinetics. The rate constant ($k$) of the thermal bleaching reaction was estimated to be $9.7 \times 10^{-6}\,\mathrm{s}^{-1}$ from the slope of the first-order kinetic plots. The value is similar to that of 1,2-bis(2-methoxy-5-phenyl-3-thienyl)perfluorocyclopentene.[29]

When the thermal bleaching solution was irradiated with UV light again, the performance of the coloration was reduced. This indicates that a by-product was produced by repeating the cycle of UV irradiation and heating at 120 °C. The closed-ring isomer **1b** was heated in toluene for 70 h at 120 °C. Then the blue color was largely bleached by the thermal reactions. The disappearance of the closed-ring isomer was estimated to be ca. 92% conversion from the change in absorbance of **1b** at 580 nm. When the remaining blue color was bleached by irradiation with visible light to give the open-ring isomer **1a**, the color of the solution turned to pale yellow, which is different from those of **1a** and **1b**. This also indicates that the by-product was produced by heating the closed-ring isomer **1b** at 120 °C.

To identify the structure of the thermally produced product, the solution was analyzed by high-performance liquid chromatography (HPLC) connected with a normal phase silica gel column using a hexane/ethyl acetate (9:1) mixture as the eluent. Figure 3 shows the chromatograph of the solution after heating for 70 h at 120 °C, followed by irradiation with visible light in toluene. The open-ring isomer **1a** was eluted at 20 min, and the new peak appeared at 42 min, which is different from the closed-ring isomer **1b**. This indicates that the closed-ring isomer **1b** gave the open-ring isomer **1a** and the by-product **1c**. The by-product eluted at 42 min was separated by HPLC to identify the structure.

The structure of the by-product **1c** was analyzed by $^1$H NMR, MS, and X-ray crystallographic analysis (see Supporting Information).[36] Two types of methoxymethyl groups exist in the $^1$H NMR spectrum of **1c**. The mass spectrum of **1c** indicates that the by-product has the same mass as the open- and closed-ring isomers. However, the structure of **1c** could not be determined conclusively by NMR and mass spectra. Finally, we established the structure of **1c** by X-ray crystallographic analysis.

Figure 4 shows an ORTEP drawing of **1c**. One of the methoxymethyl groups is attached to the sulfur atom, and the cleavage of the C–S bond is confirmed. This result is very similar to that of the trimethylsilyl derivative.[32] Cleavage of the C–S bond results in the formation of a benzene ring at the central position, followed by a methoxymethyl rearrangement. The by-product is stable under heating as well as photoirradiation due to the aromatic stability. Although the mechanism of formation of **1c** is not clear, we propose that **1c** is produced by a C–S bond cleavage, as shown in Figure 5.

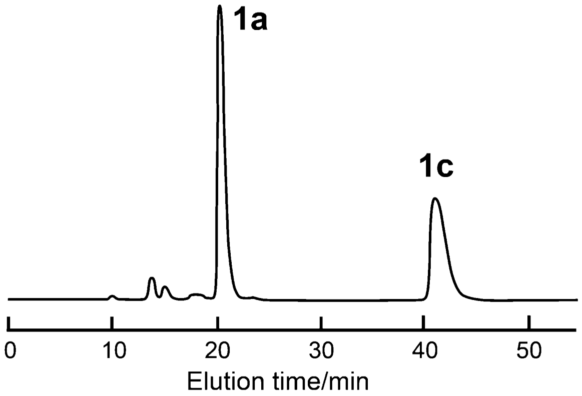


**Figure 3.** HPLC of the concentrate after heating **1b** for 70 h at 120 °C, followed by irradiation with visible light in toluene. The peak intensity was detected by absorbance at 254 nm in hexane/ethyl acetate (9:1).

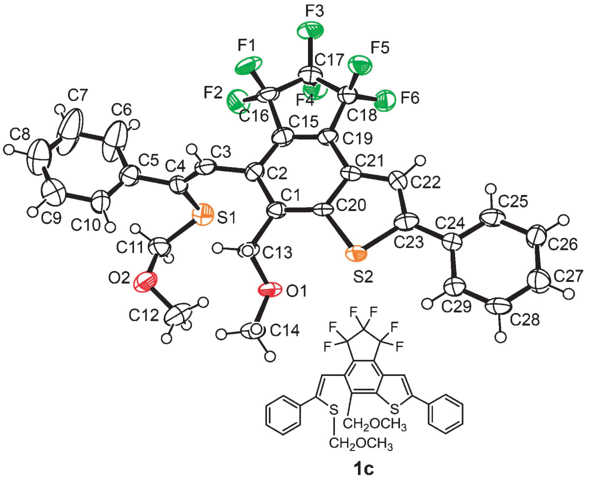


**Figure 4.** ORTEP drawing of the by-product **1c** showing 50% probability displacement ellipsoids.

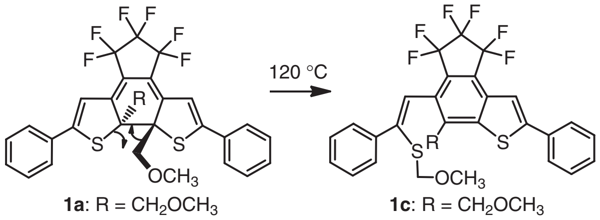


**Figure 5.** The reaction mechanism proposed for formation of **1c**.

In conclusion, we have synthesized a new diarylethene with methoxymethyl groups at the reactive carbons. Upon alternating

UV and visible light irradiation, the diarylethene showed photoreversible photochromism in solution. In addition to the photochromic reaction, we found that the closed-ring isomer **1b** irreversibly changed to a pale yellow by-product **1c** by heating at 120 °C, which is a new type of by-product. The closed-ring isomer **1b** gave 58% of **1a** and 42% of **1c** by the thermal reaction of **1b** for 70 h at 120 °C. The by-product **1c** was stable against both UV and visible light irradiation. A similar reaction was not observed in diarylethene bearing propyl groups at the reactive carbons, while the closed-ring isomer returned to the initial open-ring isomer by heating at 120 °C.[37] The results from this work can be useful for a molecular design of photochromic diarylethenes, which have novel photochromic functions.

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