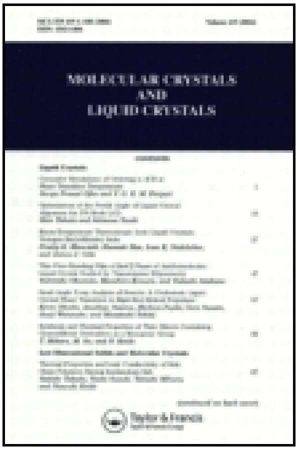

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Photochemically Stable Novel Yellow Developing Photochromic Compounds Having a Thiazole Group

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Photochemically Stable Novel Yellow Developing Photochromic Compounds Having a Thiazole Group

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Diarylethene derivatives having a thiazole ring as the aryl group ***1a****,* ***2a****, and* ***3a*** *have been synthesized in an attempt to obtain photochromic compounds which change the color from colorless to yellow, and have low photocycloreversion quantum yields and high absorption coefficients of the colored isomers. Compounds* ***1*** *and* ***3*** *exhibited reversible photochromic reactions in hexane solution. The closed-ring isomers* ***1b*** *and* ***3b*** *showed orange and yellow colors, respectively. The* ε *value of* ***3b*** *at the absorption maximum is* $18400\,M^{-1}cm^{-1}$*, which is much larger than those of* ***1b*** ($\varepsilon = 10000\,M^{-1}cm^{-1}$) *and* ***2b*** ($\varepsilon = 11400\,M^{-1}cm^{-1}$)*. The photocyclization/cycloreversion quantum yields of* ***3*** *were determined to be 0.19 and 0.0014, respectively. The yellow color was sufficiently photochemically stable under room light.*

Keywords: absorption coefficient; diarylethene; photochromism; photocycloreversion quantum yield; yellow photochromic dye

INTRODUCTION

Photochromic compounds have attracted much attention because of their potential ability for optical memory media, photo-optical

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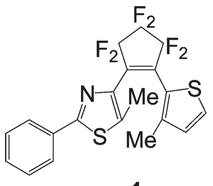
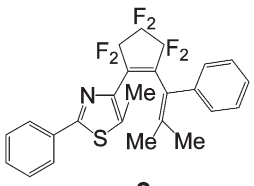
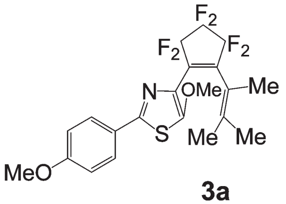
switching and display devices [1]. Among them diarylethenes with heterocyclic aryl groups, such as thiophene or benzothiophene groups, are the most promising candidates for the applications [2] because of their fatigue resistant and thermally irreversible photochromic performance [3]. For the application to a full color display it is indispensable to prepare red and yellow developing diarylethene derivatives [4]. When the thiophene rings of 1,2-bis(2-methyl-5-phenyl-3-thienyl) perfluorocyclopentenes [4] are replaced with thiazole rings, the absorption maximum of the closed-ring isomer shifts from 575 nm (blue) to 525 nm (red) [5]. Another approach to further shift the absorption band to shorter wavelength (yellow) is to attach the thiophene rings to the ethene moiety at the 2-position [6]. Very recently, oxazolylfulgides and 2,3-bis(2,3,5-trimethyl-3-thienyl)maleic imidine have been reported as yellow photochromic dyes [7]. However, These colored isomers are photochemically unstable and the photocycloreversion quantum yields are rather high. For a full color display it is strongly desired to develop yellow photochromic compounds which have low photocycloreversion quantum yields and thermal stability at room temperature. In previous papers we showed that introduction of alkoxy groups at the reactive carbons of diarylethene derivatives remarkably suppresses the photocycloreversion quantum yields [8]. Here we examined the photochromism of 1-thiazolyl-2-thienylcyclopentene derivative **1a**, a 1-thiazolyl-2-stryl cyclopentene derivative **2a**, and a 1-thiazolyl-2-vinylcyclopentene derivative **3a** having methoxy substituents to obtain yellow photochromic compounds having a low photocycloreversion quantum yield.



1a



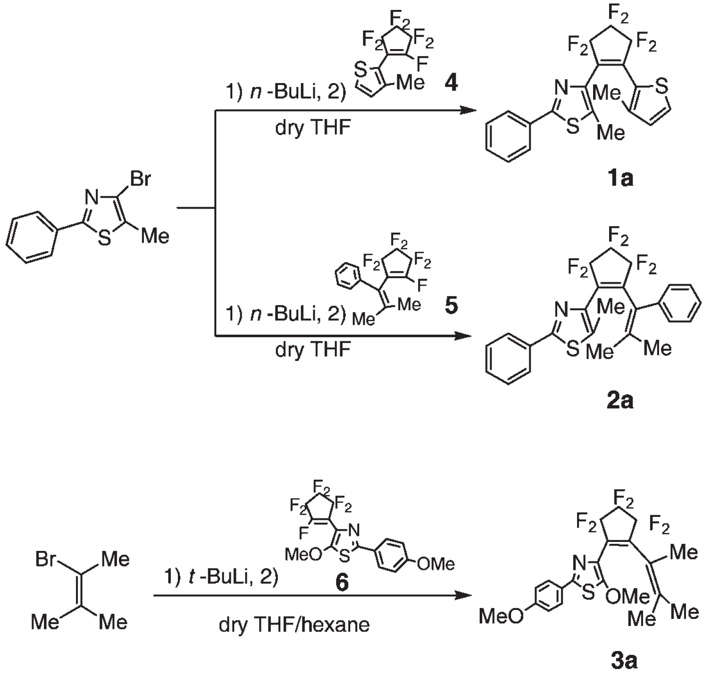
2a



3a

EXPERIMENTAL

Compound **1a** [9] and **2a** [10] were synthesized by the reaction of 4-bromo-5-methyl-2-phenylthiazole [5] with **4** and **5** by bromine-lithium exchange followed by nucleophilic displacement of fluoride, respectively. Compound **3a** [11] was synthesized by the coupling reaction of **6** and 2-bromo-3-methyl-2-butene [9]. The structures of all compounds were confirmed by ^{1}H NMR, mass spectroscopy, and elemental analysis.



SCHEME 1 Syntheses of compounds **1a**, **2a**, and **3a**.

RESULTS AND DISCUSSIONS

4-Thiazolyl [5] and 2-thienyl [6] chromophores were chosen as the aryl groups of diarylethenes to shift the absorption maximum of the closed-ring isomers to shorter wavelengths. Upon irradiation with 313 nm light, the colorless solution of **1a** turned orange, in which a visible absorption band was observed at 483 nm. The orange color is due to the closed-ring isomer **1**. When the orange solution was irradiated with visible light ($\lambda > 440$ nm), the spectrum readily returned back to the original one. The conversion from **1a** to **1b** in the photostationary state under irradiation with 313 nm light was 66%. The bathochromic shifts of **1b** are not large enough to exhibit yellow color. Therefore, the 2-thienyl group [6] was replaced with a stryl and an ethylene units to further shift the absorption band of the closed-ring isomer to shorter wavelengths.

First, we investigated the photochromic reaction of compound **2a** with stryl and thiazole groups. Upon irradiation with 313 nm light, the colorless solution turned yellow, in which a visible absorption band was observed at 426 nm. The yellow color is due to the closed-ring isomer **2b**. However, when the yellow solution was irradiated with visible light ($\lambda > 440\,\mathrm{nm}$), the spectrum did not return back to the original one. Although **2b** showed yellow color, the photo side-product was formed in the photochromic reaction.

Next, we designed a derivative **3a**, which has methoxy substituents at the *para*-position of the phenyl ring and 5-position of the thiazole ring. When the stryl unit of compound **2a** is replaced with a ethylene unit, the absorption maximum of the closed-ring isomer is expected to shift to a wavelength much shorter absorption maximum of **2b** (424 nm). In order to obtain yellow colored closed-ring isomer, it is required to introduce substituents [11]. Both methoxy substituents are effective to induce bathochromic shift. The methoxy group at the 5-position is also known to decrease the photocycloreversion quantum yield. Upon irradiation with 313 nm light the colorless hexane solution of **3a** slowly turned yellow, showing an absorption maxima at 410 nm. The photostationary spectrum is almost the same as the colored isomer, indicating a high conversion from the colorless to the colored isomers by irradiation with 313 nm light. The yellow colored solution slowly returned back to the initial colorless solution upon prolonged irradiation with visible light.

Figure 1 shows the absorption spectra of these closed-ring isomers **1b**, **2b**, and **3b** in hexane. The absorption maximum of **3b** shows yellow color, which is a hypsochromic shift as much as 80 nm in comparison with that of **1b**. The ε value of **3b** at the absorption maximum is $18400\,\mathrm{M^{-1}cm^{-1}}$, which is much larger than those of **1b** ($\varepsilon = 10000\,\mathrm{M^{-1}cm^{-1}}$) and **2b** ($\varepsilon = 11400\,\mathrm{M^{-1}cm^{-1}}$).

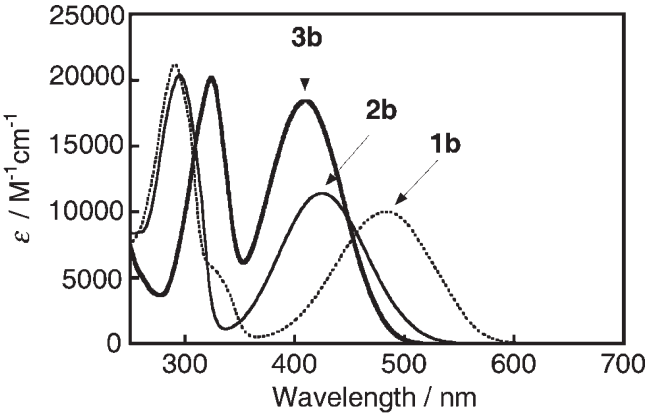


FIGURE 1 Absorption spectra of the closed-ring isomers **1b** (dotted line), **2b** (solid line), and **3b** (bold solid line) in hexane.

The photocyclization/cycloreversion quantum yields of **1** were 0.36 and 0.16, respectively. The cyclization quantum yield of **3a** was 0.19. On the other hand, the photocycloreversion quantum yield of **3b** was remarkably suppressed to 0.0014. The yellow colored isomer **3b** was found to be sufficiently photochemically stable under room light. The absorption coefficient of **3b** was obtained to be 18400 $M^{-1}cm^{-1}$, which is much larger than that of the closed-ring isomers of yellow developing diarylethenes. The large absorption coefficient of **3b** is due to the methoxy group at the *para*-position of the phenyl ring [12]. Compound **3** is a useful candidate as a yellow photochromic dye.

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[9] Data for compound **1a**: **1a** (14%) as a colorless solid after elution from silica gel with 10% ethyl acetate in hexane, m.p. = 107–108°C. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.80$ (s, 3H), 1.98 (s, 3H), 6.86 (d, $J = 5.0$ Hz, 1H), 7.44 (m, 4H), 7.88 (m, 2H). MS (m/z) 445 (M^+), Anal. Found: C, 53.96; H, 2.85; N, 3.00%. Calcd for $C_{20}H_{13}F_6NS_2$: C, 53.93; H, 2.94; N, 3.14%.
[10] Data for compound **2a**: **2a** (11%) as a colorless solid after elution from silica gel with 10% ethyl acetate in hexane, ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.67$ (s, 3H), 1.75 (s, 3H), 2.39 (s, 3H), 7.34–7.16 (m, 5H), 7.42–7.34 (m, 3H), 7.85–7.76 (m, 2H). MS (m/z) 479 (M^+), Anal. Found: C, 62.62; H, 3.99; N, 2.92%. Calcd for $C_{25}H_{19}F_6NS$: C, 62.64; H, 4.02; N, 2.96%.
[11] Data for compound **3a**: **3a** (5%) as a colorless oil after elution from silica gel with 30% ethyl acetate in hexane, m.p. = 93–94°C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.49$ (s, 3H), 1.75 (s, 3H), 1.93 (s, 3H), 3.86 (s, 3H), 4.01 (s, 3H), 6.93 (d, $J = 9.0$ Hz, 2H), 7.71 (d, $J = 9.0$ Hz, 2H). MS (m/z) 463 (M^+). Anal. Found: C, 54.30; H, 4.20; N, 3.18%. Calcd for $C_{21}H_{19}F_6NO_2S_2$: C, 54.42; H, 4.13; N, 3.02%.
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