Systematic study on the thermal cycloreversion reactivity of diarylethenes with alkoxy and alkyl groups at the reactive carbons

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Abstract The relationship between the thermal cycloreversion reactivity of diarylethenes and the bulkiness of the substituents at the reactive carbons was systematically investigated. Two photochromic diarylethenes, 1,2-bis(2-isobutoxy-5-phenyl-3-thienyl)perfluorocyclopentene (1a) and 1,2-bis(2-neopentoxy-5-phenyl-3-thienyl)perfluorocyclopentene (2a), were newly synthesized and their optical properties and thermal cycloreversion reactivity were examined, because there is insufficient data for diarylethenes with alkoxy groups at the reactive carbons. The steric substituent constant was employed to correlate the relationship between the thermal cycloreversion reactivity of diarylethenes with alkoxy groups at the reactive carbons and the bulkiness of the substituent. A good correlation was obtained for the substituent constant using CH₂ instead of oxygen in the alkoxy groups. The results indicate that this is a very useful strategy for the design of novel diarylethenes with desired thermal cycloreversion reactivity.

Keywords Photochemistry \cdot Photochromism \cdot Diarylethene \cdot Thermal bleaching reaction

Introduction

Photochromism is the phenomenon of chromatic change due to the reversible photoisomerization between two isomers having different absorption spectra [1, 2]. Compounds that have such a property are called photochromic compounds and can reversibly change not only their molecular structures but also their refractive indices, dielectric constants, oxidation–reduction potentials, and geometrical structures.

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While various types of photochromic compounds have been reported to date, they are classified into T- and P-types. Azobenzene, spiropyran, and spirooxazine are well known as representative T-type photochromic compounds. Their photogenerated isomers are thermally unstable and return to the original isomer at room temperature in the dark. Therefore, they can be applied in photomodulated materials such as photochromic ophthalmic lenses [3]. In contrast, both isomers in P-type photochromic compounds such as furyl fulgide and diarylethene are thermally stable at room temperature and can revert to the original isomer only by photoirradiation. Therefore, they have potential for application to various optoelectronic devices such as optical memory, photooptical switching, displays, nonlinear optics, and photoresponsive actuators [4–9].

Although most of the diarylethene derivatives have thermal stability and fatigue resistance, their properties are changed slightly according to the substituent [4]. Among these derivatives, it is quite important to control the thermal stability of the colored closed-ring isomers by introduction of a substituent. The thermal stability of the closed-ring isomer can be determined by the following three factors: (1) aromatic stabilization energy of the aryl groups [10], (2) electron-withdrawing substituents at the aryl groups [11, 12], and (3) the steric hindrance of the substituents at the reactive carbons [13-15]. The theoretically calculated bond length between the central carbons is related to the thermal cycloreversion reactivity [16]. We have recently reported a correlation between the thermal cycloreversion reactivity of the closed-ring isomers and steric substituent constants in relation to (3) [17]. The values of three steric substituent constants, $E_s(\mathbb{R}^1)$ [18], $E_s^c(\mathbb{R}^1)$ [19], and $v(\mathbf{R}^{1})$ [20] were employed and a good correlation was obtained between the thermal cycloreversion reactivity and the $E_s^c(\mathbf{R}^1)$ value, while $E_s(\mathbf{R}^1)$ had no correlation with the reactivity. Furthermore, the $E_{\rm s}(\rm CH_2R^1)$ value also has good correlation with the reactivity. These can be applied only for alkyl groups (Scheme 1). It is difficult to predict the thermal cycloreversion reactivity for substituent groups other than alkyl groups, due to the absence of the substituent constants.

In the present work, two new diarylethenes (1a and 2a), which introduce isobutoxy and neopentoxy groups at the reactive carbons, respectively, were synthesized and their optical properties and thermal cycloreversion reactivity were examined (Scheme 2). The correlation between the thermal cycloreversion reactivity and steric hindrance of the substituents was systematically investigated for diarylethenes having alkyl and alkoxy groups at the reactive carbons.



Scheme 1 Photochromism of diarylethenes with alkyl groups



Scheme 2 Photochromism of diarylethenes with alkoxy groups

Experimental

General

Spectroscopic grade solvents were used and purified by distillation before use. ¹H NMR spectra were recorded at 300 MHz using a BRUKER AV-300 N spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Mass spectra were obtained using a JEOL JMS-700/700S mass spectrometer. Absorption spectra were obtained using a JASCO V-560 absorption spectrophotometer. High-performance liquid chromatography (HPLC) was carried out using a Hitachi L-7150/L-2400 HPLC system equipped with a KANTO CHEMICAL Mightysil Si 60 column.

Materials

1,2-Bis(2-isobutoxy-5-phenyl-3-thienyl)perfluorocyclopentene (1a) and 1,2-bis(2-neopentoxy-5-phenyl-3-thienyl)perfluorocyclopentene (2a) were synthesized according to methods similar to those in the literature [21]. The products were purified by HPLC and recrystallization.

1a: mp. 145–146 °C; ¹H NMR (300 MHz, CDCl₃, TMS) $\delta = 0.81$ (d, J = 6.8 Hz, 12H, CH₃), 1.75 (m, 2H, CH), 3.68 (d, J = 6.4 Hz, 4H, CH₂), 7.15 (s, 2H, Aromatic), 7.15–7.48 (m, 10H, Aromatic). MS (FAB) m/z = 636.1592 (M⁺). Calcd for C₃₃H₃₀F₆O₂S₂ = 636.1591.

2a: mp. 175–176 °C; ¹H NMR (300 MHz, CDCl₃, TMS) $\delta = 0.88$ (s, 18H, CH₃), 3.65 (s, 4H, CH₂), 7.07 (s, 2H, Aromatic), 7.21–7.44 (m, 10H, Aromatic). MS (FAB) m/z = 664.1906 (M⁺). Calcd for C₃₅H₃₄F₆O₂S₂ = 664.1904.

Photochromism

Photocyclization and cycloreversion quantum yields were determined in hexane as relative quantum yields using diarylethene derivatives whose quantum yields have already been determined [22]. The photocyclization and photocycloreversion reactions were followed by absorption spectra. The samples were not degassed.

Thermal cycloreversion reaction

The thermal cycloreversion reaction of the diarylethene closed-ring isomer was carried out in toluene as follows. The diarylethene open-ring isomer was put in an optical quartz cell degassed and sealed under vacuum. The solution in the cell was irradiated with 313 nm light to give the closed-ring isomer. The photoirradiation was carried out using a 200-W mercury-xenon lamp (MORITEX MUV-202) as the light source. Monochromic light was obtained by passing the light through a monochromator (Jobin–Yvon H10 UV). The cell was placed in a constant temperature chamber (ESPEC ST-110) during the thermal cycloreversion reaction. The reaction yields were periodically determined by absorption spectroscopic measurement.

Results and discussion

Photochromism

Figure 1a shows the absorption spectral change of diarylethene 1a in hexane upon irradiation with 313-nm light. The colorless solution of 1a has an absorption maximum wavelength (λ_{max}) at 311 nm. Upon irradiation with ultraviolet (UV) light, the solution became blue with λ_{max} at 627 nm. The blue color is due to the closed-ring isomer 1b, and is thermally stable at room temperature. The blue-colored solution gradually reverted to the initial colorless solution upon irradiation with visible light ($\lambda > 500$ nm), which indicates that 1a exhibits photochromism in hexane. Diarylethene 2a also exhibited a similar photochromic reaction in hexane (Fig. 1b).

Table 1 shows the optical properties of diarylethenes with alkoxy groups at the reactive carbons. The cyclization quantum yields of **1a** and **2a** were 0.41 and 0.22, respectively; that for **1a** was almost the same as those of other diarylethenes [21], whereas that for **2a** was slightly smaller than those of other diarylethenes. The steric hindrance of the substituent on the β -carbon of the alkoxy group may affect the photocyclization reaction. Diarylethene has two stable conformations in the open-ring isomer, antiparallel and parallel, and the photocyclization reaction can proceed from only the antiparallel conformation [23]. Therefore, the photocyclization quantum yield depends on the content of each conformation. The content of the antiparallel conformation in **2a** may be lower than that in **1a** due to the steric hindrance.

Both of the photocycloreversion quantum yields of **1b** and **2b** were estimated to be 2.2×10^{-4} . The cycloreversion quantum yields were lower than that of diarylethene having methyl groups at the reactive carbons (R¹=CH₃) by a factor of 10^2 . The decrease in the cycloreversion quantum yield is attributed to the activation energy barrier for the cycloreversion process in the singlet excited state [24]. Diarylethenes with the alkoxy groups have a much higher energy barrier in the excited state. When the bulkiness of the alkoxy groups increases, the cycloreversion quantum yield is slightly increased, and this is considered to be ascribable to the molecular strain of the closed-ring isomers by the bulky substituents.



Fig. 1 Absorption spectral change of $1 (1.30 \times 10^{-5} \text{ M})$ (a) and $2 (1.25 \times 10^{-5} \text{ M})$ (b) in hexane upon irradiation with 313-nm light: Open-ring isomer (*dashed line*), the photostationary state under irradiation with 313-nm light (*dotted line*), closed-ring isomer (*solid line*)

Thermal cycloreversion reaction

Diarylethenes having methyl groups at the reactive carbons exhibit thermally irreversible photochromism, which means that diarylethenes have an excellent advantage as P-type photochromic compounds [4]. However, diarylethenes with bulky substituents introduced at the reactive carbons undergo the thermal cycloreversion reaction [21].

The thermal cycloreversion reactivities of the closed-ring isomers **1b** and **2b** were examined in toluene at 90–130 °C. Figure 2 shows that the decay curves for absorbance at λ_{max} in the closed-ring isomers at various temperatures; the decay curves follow first-order kinetics. The rate constant (*k*) of the cycloreversion reaction can be determined from the slope of the first-order kinetic plots. The half-lifetimes of **1b** and **2b** were estimated to be 33 and 23 h at 100 °C, respectively, and the temperature dependence of *k* is plotted in Fig. 3. The slope and intercept of the linear plots represent the activation energy (*E*_a) and frequency factor (*A*), respectively, which were determined to be 130 and 128 kJ mol⁻¹, and 7.7 × 10¹² and 5.6 × 10¹² s⁻¹ for **1b** and **2b**, respectively. Table 2 shows the kinetic parameters for the thermal cycloreversion reaction of diarylethenes with various alkoxy groups introduced at the reactive carbons. The thermal cycloreversion reactivity was dependent on the substituents and increased in the following order: OCH₃ < OCH₂CH₃ < OCH₂C(CH₃)₃ < OCH(CH₃)₂ < OC(CH₃)₃.

Correlation between thermal cycloreversion reactivity and steric substituent constants

The Taft's steric substituent constant $[E_s(R)]$ [18] was adopted to quantitatively evaluate the size of the alkoxy groups at the reactive carbons. The constant represents the rate of hydrolysis of RCOOCH₂CH₃, and in some cases the steric effect can be interpreted using this constant. Hydrolysis is affected by hyperconjugation of the α -hydrogens of substituent R in the ester. The hyperconjugation

R ²	Open-ring is	omer	Closed-ring is	somer	Quantum yield ^a		Ref.
	$\lambda_{ m max}/ m nm$	$\epsilon/M^{-1} \mathrm{~cm}^{-1}$	$\lambda_{ m max}/ m nm$	$\epsilon/M^{-1}~{ m cm}^{-1}$	$\Phi_{o ightarrow c}$	$\Phi_{c o 0}$	
CH ₃	309	33,000	625	15,000	0.44 (313 nm)	$1.7 \times 10^{-5} (625 \text{ nm})$	21
CH ₂ CH ₃	310	33,000	625	13,000	0.48 (313 nm)	$2.5 \times 10^{-4} \ (625 \ \mathrm{nm})$	21
CH ₂ CH(CH ₃) ₂	311	38,700	627	13,500	0.41 (313 nm)	$2.2 \times 10^{-4} \ (635 \ {\rm nm})$	This work
CH ₂ C(CH ₃) ₃	310	36,800	628	14,500	0.22 (313 nm)	$2.2 \times 10^{-4} \ (635 \ {\rm nm})$	This work
CH(CH ₃) ₂	312	32,000	635	13,000	0.46 (313 nm)	$6.6 \times 10^{-4} \ (635 \ {\rm nm})$	21
^a The values in pai	rentheses indicate	irradiation wavelength					

Table 1 Optical properties of diarylethenes having alkoxy groups



Fig. 2 Thermal bleaching curves of 1b (a) and 2b (b) in toluene



Fig. 3 Temperature dependence of the rate constants in thermal cycloreversion reaction of 1b (a) and 2b (b) in toluene

 Table 2
 Rate constants, half-lifetimes, and Arrhenius parameters of thermal cycloreversion reactions of diarylethenes having alkoxy groups

R^2	k/s^{-1} at 100 °C	$t_{1/2}/h$ at 100 °C	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	A/s^{-1}	$\lambda_{\rm max}/{\rm nm}$	Ref.
CH ₃	1.4×10^{-6}	140	137	2.1×10^{12}	625	21
CH ₂ CH ₃	4.8×10^{-6}	40	129	5.5×10^{12}	625	21
CH ₂ CH(CH ₃) ₂	5.8×10^{-6}	33	130	7.7×10^{12}	627	This work
CH ₂ C(CH ₃) ₃	8.4×10^{-6}	23	128	5.6×10^{12}	628	This work
CH(CH ₃) ₂	3.3×10^{-5}	5.8	123	5.5×10^{12}	635	21
C(CH ₃) ₃	8.2×10^{-2}	0.0024	92	5.7×10^{11}	656	25

effect can be removed according to a method by Hancock et al. [19], as defined by $E_s^c(\mathbf{R})$ in the following equation:

$$E_{\rm s}^{\rm c}({\rm R}) = E_{\rm s}({\rm R}) + 0.306(N-3) \tag{1}$$

where *N* is the number of hydrogen atoms of the α -carbon of substituent R. We recently evaluated the thermal cycloreversion reactivity of diarylethenes with alkyl groups (R¹) at the reactive carbons using $E_s(R^1)$ and $E_s^c(R^1)$ [17]. Consequently, the

steric effect of the thermal cycloreversion reaction could not be exactly evaluated using the $E_s(\mathbf{R}^1)$ value, because it involves factors of both steric and hyperconjugation effects. Therefore, in order to except the hyperconjugation effect, the $E_s(\mathbf{CH}_2\mathbf{R}^1)$ and $E_s^c(\mathbf{R}^1)$ values were applied to give a good correlation; however, most of the steric substituent constants for alkoxy groups were absent.

Here, we applied the steric substituent constants for \mathbb{R}^2 in the alkoxy group (OR²) to correlate the relationship between the steric substituent constant and the thermal cycloreversion reactivity. For example, the steric substituent constant of methyl group is employed when the substituent is a methoxy group. Table 3 shows the steric substituent constants and Fig. 4 indicates the relationship between the steric substituent constants and logarithm k at 100 °C or E_a in the thermal cycloreversion reaction. When the $E_s(\mathbb{R}^2)$ value was used as the substituent constant, the Pearson correlation coefficient (*r* factor) was estimated to be 0.557 and 0.571 for log(*k*) and E_a , respectively. This indicates that $E_s(\mathbb{R}^2)$ was not correlated with the thermal cycloreversion reactivity. However, when the $E_s^c(\mathbb{R}^2)$ value was used, the *r* factor was increased to 0.745 and 0.760 for log(*k*) and E_a , respectively. Much better correlation was given by the relationship between $E_s(CH_2\mathbb{R}^2)$ and the thermal cycloreversion reactivity.

Universal correlation for diarylethenes with alkyl and alkoxy groups

To generalize the correlation between the steric effect and thermal cycloreversion reactivity of diarylethenes with alkyl and alkoxy groups, we discuss a novel method for evaluation of diarylethenes with bulky substituents at the reactive carbons. $E_s^c(CH_2R^2)$ was applied as the steric substituent constant for the alkoxy group (OR²), due to the absence of $E_s^c(OR^2)$, where CH_2R^2 corresponds to the substituent with CH₂ instead of oxygen in substituent OR². For example, when the substituent is a methoxy group, the steric substituent constant E_s^c is applied for ethyl groups. In a similar way, this can be evaluated as alkyl groups instead of alkoxy groups for diarylethenes having alkyl and alkoxy substituents.

Figure 5 shows that there is a very good correlation between the thermal cycloreversion reactivity and the steric substituent constant $E_s^c(CH_2R^2)$; the plots for alkyl (R¹) and alkoxy (OR²) groups are fitted in the same straight line. These results show that oxygen atoms in alkoxy groups function as spacer without an

R	$E_{\rm s}({ m R})$	$E_{\rm s}^{\rm c}({ m R})$	$E_{\rm s}({\rm CH_2R})$
CH ₃	0	0	-0.07
CH ₂ CH ₃	-0.07	-0.38	-0.36
CH(CH ₃) ₂	-0.47	-1.08	-0.93
CH ₂ CH(CH ₃) ₂	-0.93	-1.24	-0.51
CH ₂ C(CH ₃) ₃	-1.74	-2.05	-0.34
C(CH ₃) ₃	-1.54	-2.46	-1.74

Table 3 Steric substituent constants, $E_s(R)$, $E_s^c(R)$ and $E_s(CH_2R)$

The $E_s(\mathbf{R})$ and $E_s(\mathbf{CH}_2\mathbf{R})$ values were cited from ref. [26]. The $E_s^c(\mathbf{R})$ values were calculated according to Eq. (1)



Fig. 4 Relationship between substituent constants $(E_s(\mathbb{R}^2) (\mathbf{a}, \mathbf{b}), E_s^c(\mathbb{R}^2) (\mathbf{c}, \mathbf{d}), E_s(\mathbb{CH}_2\mathbb{R}^2)$ (**e**, **f**) and log(k) (**a**, **c**, **e**) or activation energy (E_a) (**b**, **d**, **f**)

electron-withdrawing inductive influence and an electron-donor influence with conjugation.

Conclusion

Diarylethenes **1a** and **2a**, with isobutoxy and neopentoxy substituents introduced at the reactive carbons, were synthesized and evaluated with respect to thermal cycloreversion reactivity. These compounds exhibited thermal cycloreversion reactions similar to diarylethenes with bulky substituents introduced at the reactive carbons. The half-lifetimes of **1a** and **2a** at 100 °C were determined to be 33 and



Fig. 5 Relationship between $E_s^c(\mathbb{R}^1)$ (open circle) or $E_s^c(CH_2\mathbb{R}^2)$ (filled circle) and $\log(k)$ (a) and activation energy (E_a) (b)

23 h, respectively. The thermal cycloreversion reactivities of diarylethenes with alkoxy substituents at the reactive carbons were quantitatively evaluated using the Taft steric substituent constants, $E_s(R^2)$, $E_s^c(R^2)$, and $E_s(CH_2R^2)$. There was a good correlation between the thermal cycloreversion reactivity and $E_s(CH_2R^2)$. The $E_s^c(CH_2R^2)$ steric substituent constant was used for diarylethenes with alkoxy groups to generalize the thermal cycloreversion reactivity. There was a good correlation between the thermal cycloreversion reactivity. There was a good correlation between the thermal cycloreversion reactivity and $E_s^c(CH_2R^2)$ or $E_s^c(R^1)$. The oxygen atoms in alkoxy groups were found to function like a spacer without influences due to the electron-withdrawing inductive effect and the electron-donor effect in conjugation.

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