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Correlation between Steric Substituent Constants and Thermal Cycloreversion Reactivity of Diarylethene Closed-Ring Isomers

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Two kinds of diarylperfluorocyclopentenes having 5-phenyl-2-propyl-3-thienyl and 2-isobutyl-5-phenyl-3-thienyl group as the aryl groups were newly synthesized, and the thermal stability of their closed-ring isomers was investigated. The bulkiness of the substituent (R) at the reacting positions in photochromic diarylethenes plays an important role in the thermal cycloreversion reactivity of the photogenerated closed-ring isomers. The steric substituent constant was introduced to investigate the relationship between the steric hindrance of the substituent R and the thermal cycloreversion reactivity. We employed three steric substituent constants, E_s(R), $E_s{}^c$(R), and ν(R) values. We found that there is a good correlation between the $E_s{}^c$(R) value and the thermal cycloreversion reactivity. Furthermore, the E_s(CH$_2$R) value has also a good correlation with the thermal cycloreversion reactivity, while E_s(R) has no correlation. These results indicate that the steric hindrance has an effect on the thermal cycloreversion and there is no hyperconjugation of the α-hydrogen on the 2-substituent on the thiophene ring. Moreover, the activation energy was also found to be related to the steric substituent constant. These findings would give a new useful strategy to design novel diarylethenes having desired thermal stability.

Photochromism is defined as a chromatic change upon photoirradiation.[1,2] Photochromic compounds change not only colors but also geometric structures and physicochemical properties such as conductivity, dielectric constant, refractive index, and fluorescence. Therefore, photochromic compounds have been attractive for application in optoelectronic devices. Photochromic compounds can be classified into two types, T-type and P-type. T-type photochromic compounds, e.g., azobenzene and spiropyran, give rise to thermally unstable photogenerated isomers. P-type photochromic compounds, e.g., furyl fulgide and diarylethene, are thermally stable for both isomers. Therefore, P-type photochromic compounds have potential for application to optical memories and switches.

Among a number of photochromic compounds, diarylethenes with heterocyclic aryl groups are the most promising compounds for applications to optical memories and switches because of their thermal stability and fatigue resistant properties.[3] The thermal stability of the colored closed-ring isomers of diarylethenes is known to depend on the aryl groups.[3] There are at least three factors determining thermal stability: (i) aromatic stabilization energy of the aryl groups, (ii) electron-withdrawing substituents at the aryl groups, and (iii) steric hindrance of the substituents at the reactive carbons as shown in Figure 1. In the case of (i), when the aryl groups are thiophene or benzothiophene groups, the closed-ring isomers are thermally stable, while closed-ring isomers having phenyl, pyrrolyl, or indolyl groups are thermally unstable. The decrease in the thermal stability is due to the high aromatic stabilization energies of the aryl substituents.[4] In the case of (ii), when electron-withdrawing substituents are introduced at the aryl group, the closed-ring isomers become thermally unstable because the central carbon–carbon bonds in the photogenerated closed-ring isomers are weakened by the electron-withdrawing substituents.[5] In the case of (iii), the bulky substituents at the reacting positions led to thermal cycloreversion reactions of the closed-ring isomers.[6] The theoretically calculated bond length of the central carbon–carbon bond is related to the thermal stability.[7] However, the thermal cycloreversion reactivity has never been correlated by any substituent constants yet. Concerning to all three factors, a difference in enthalpy between the open- and closed-ring isomers in the ground state is the criterion for determining the thermal stability of the closed-ring isomers.[8]

Here, we have focused on the effect of steric hindrance of the substituents. Two bisphenylthienylethenes **1a** and **2a** were newly synthesized and the rate constants of the thermal cycloreversion were evaluated (Scheme 1). Although there are various substituent constants as parameters for steric hindrance, we found a good correlation between specific substituent constants and the kinetic parameters of the thermal cycloreversion. This report may provide a useful strategy to design novel diarylethenes having desired thermal stability properties.

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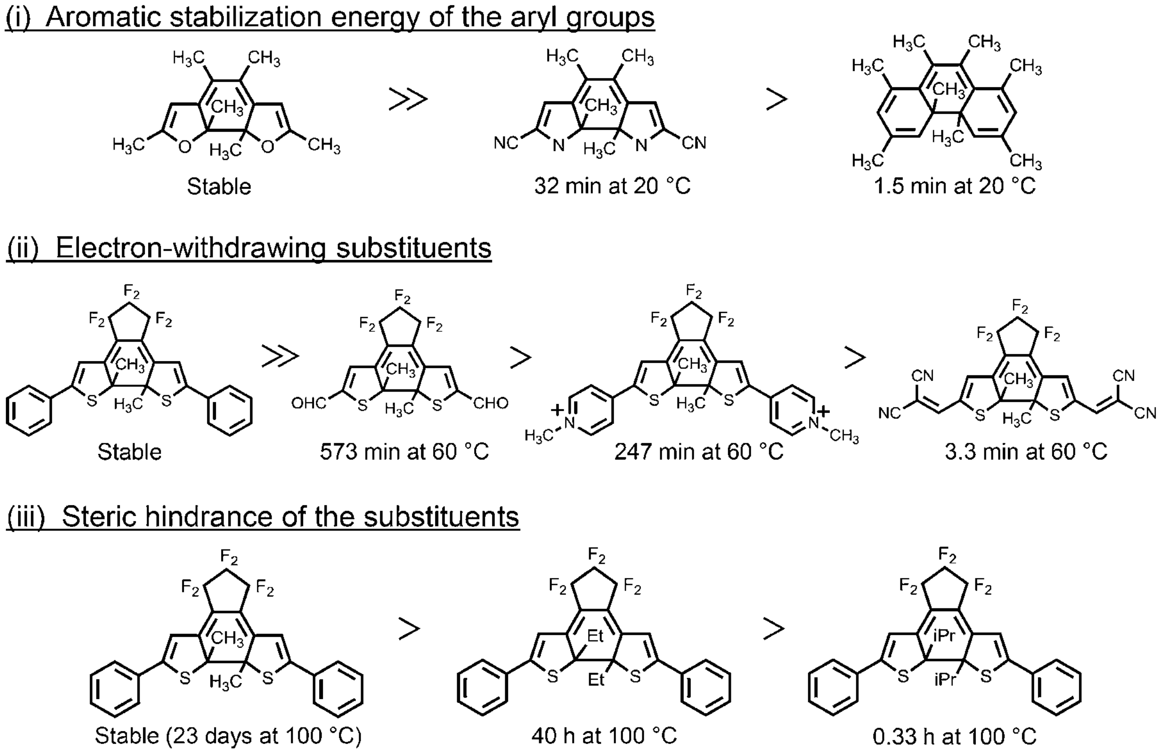
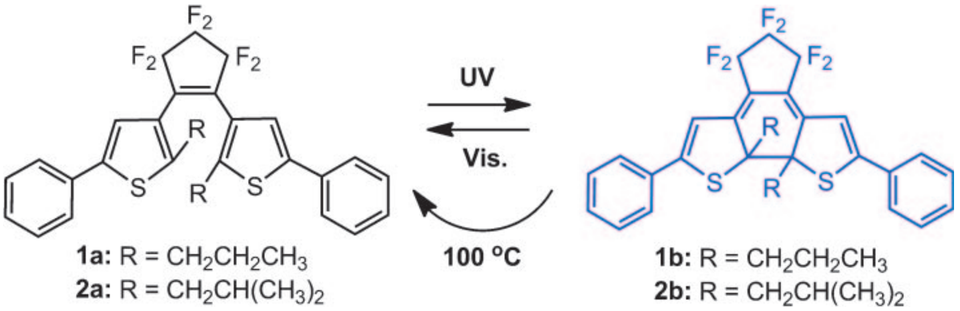


Figure 1. Thermal stability of diarylethene closed-ring isomers. The values below the molecular structures show the half-life of thermal cycloreversion.



Scheme 1. Photochromic reactions of diarylethenes synthesized in this work.

Results and Discussion

Photochromism. Figure 2 shows the absorption spectral changes of **1a** and **2a** in hexane by ultraviolet (UV) light irradiation. Diarylethenes **1a** and **2a** have absorption maxima at 288 and 286 nm, respectively. Upon irradiation with 313-nm light, the colorless hexane solution of **1a** and **2a** turned blue, in which a visible absorption maximum was observed at 603 and 615 nm for **1b** and **2b**, respectively. The blue color disappeared by irradiation with visible light ($\lambda > 460$ nm), and the absorption spectrum returned to that of the initial state.

The difference in the absorption maximum wavelength is ascribed to the difference of substituents (R) at the reactive carbon positions, while the substituents are not conjugated with the entire π-conjugation of the closed-ring isomers. Figure 3 depicts the relationship between the absorption maximum wavelength of the closed-ring isomers and the Taft's steric substituent constant (E_s(R)).[9] The diarylethenes bearing substituents with more negative E_s have the absorption maximum at longer wavelength. This correlation indicates that the steric hindrance of the substituent at the reactive carbon positions on the thiophene ring reduces the HOMO–LUMO energy gap. This means that the energy level in the ground state is destabilized by the steric hindrance of the R group. This is related to the thermal stability of the closed-ring isomers, as described later.

Thermal Cycloreversion Reaction. 1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene ($R = CH_3$) exhibits thermally irreversible photochromism.[10,11] The colored closed-ring isomer remains stable even at 100 °C. This is one of the main advantages of the diarylethene photochromic compounds. However, it has been reported that the diarylethene closed-ring isomers undergo thermal cycloreversion at temperatures above 100 °C by the introduction of the bulky substituents at the reactive positions.[6,12] For example, 1,2-bis(2-isopropyl-5-phenyl-3-thienyl)perfluorocyclopentene (R =

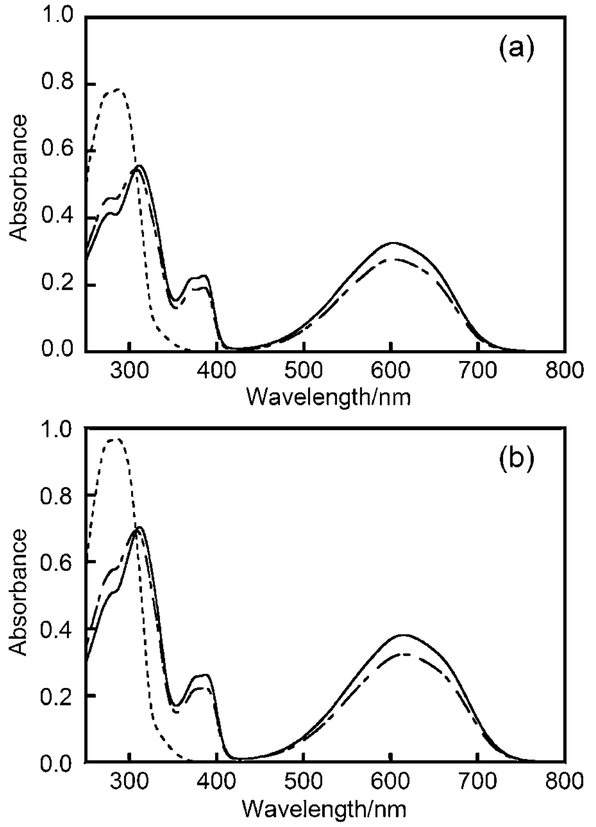


Figure 2. Absorption spectral changes of **1a** (2.2×10^{-5} mol dm^{-3}) (a) and **2a** (2.6×10^{-5} mol dm^{-3}) (b) in hexane: open-ring isomer (----), closed-ring isomer (——), the photostationary solution upon irradiation with 313-nm light (–––).

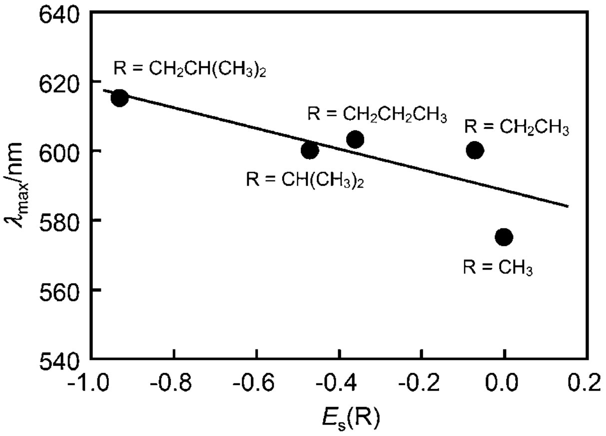


Figure 3. Relationship between the absorption maximum wavelength of the closed-ring isomers in hexane and the Taft's steric substituent constant (E_s(R)).

$CH(CH_3)_2$) shows thermally reversible photochromism.[6] The colored closed-ring isomer can return to the colorless open-ring isomer by heating above 100 °C, showing a half-life of 0.33 h at 100 °C.

The thermal cycloreversion reactivity of diarylethenes **1a** (R = $CH_2CH_2CH_3$) and **2a** (R = $CH_2CH(CH_3)_2$) with bulky substituents was examined in toluene at 80–125 °C. Figure 4 depicts the decay curves of absorbance of the colored toluene solution of **1b** and **2b**. At higher temperatures, the decay of absorbance of **1b** and **2b** was accelerated. Although the substituents R in both **1b** and **2b** are primary alkyl groups, the decay speeds of **1b** and **2b** were quite different. The decay curves of **1b** and **2b** followed first-order kinetics. The rate constants of the thermal cycloreversion of **1b** and **2b** were determined from the linear relation of the first-order kinetic plots. The half-lives for **1b** and **2b** were estimated to be 29 and 1.9 h at 100 °C, respectively. This indicates that the steric effect of the β-position in substituent R influenced the reactivity.

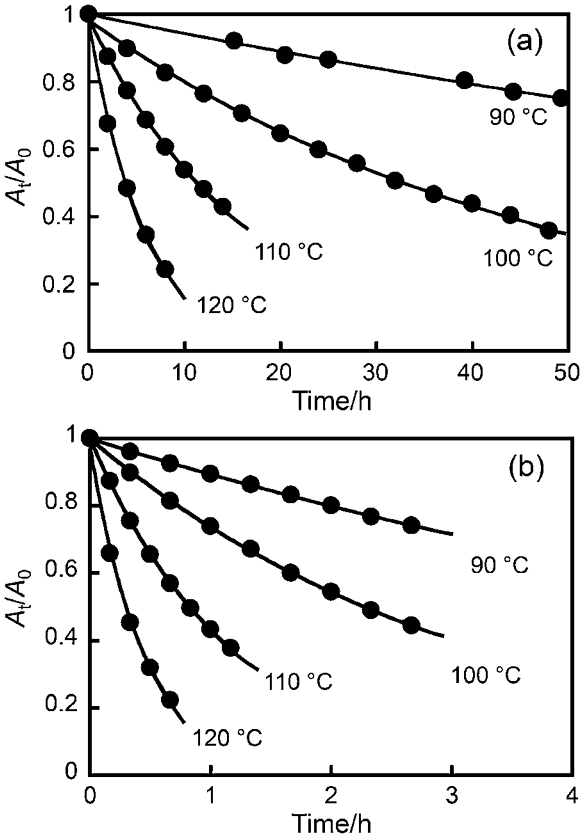


Figure 4. Decay curves for the thermal cycloreversion of **1b** (a) and **2b** (b) in toluene.

The temperature dependence of the rate constants (k) is plotted in Figure 5. The activation energy (E_a) and frequency factor (A) of the reaction were also determined from the linear relation. The obtained values are summarized in Table 1 with the data of other diarylethenes which have already been reported. With increasingly bulky substituents, the rate constant tends to increase and the activation energy tends to decrease. This clearly indicates that the difference in the reactivity can be ascribed to the steric hindrance of the substituent at the reactive carbon positions.

Correlation between Substituent Constant and Thermal Stability. The Taft's steric substituent constant (E_s(R)) is a typical steric substituent constant. It concerns the rate of hydrolysis of $RCOOCH_2CH_3$. In some cases, the steric effect can be interpreted using this constant.[16] The hydrolysis is affected by hyperconjugation of the α-hydrogens of R in the ester. The hyperconjugation effect can be removed according to

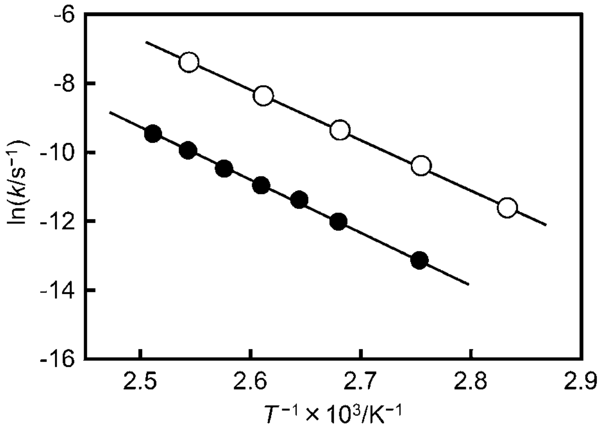


Figure 5. Temperature dependence on the rate constant of the thermal cycloreversion of **1b** (●) and **2b** (○).

Table 1. Kinetic Parameters for the Thermal Cycloreversion of Diarylethene Closed-Ring Isomers

R	k/s^{-1} a) at 100 °C	$t_{1/2}$/h$^{a)}$ at 100 °C	E_a /kJ mol^{-1}	A/s^{-1}	Ref.
CH_3	3.5×10^{-7}	550	139	1.0×10^{13}	11
CH_2CH_3	4.8×10^{-6}	40	128	4.0×10^{12}	13
$CH_2CH_2CH_3$	6.7×10^{-6}	29	125	2.1×10^{12}	This work
$CH_2CH(CH_3)_2$	1.0×10^{-4}	1.9	120	6.5×10^{12}	This work
$CH(CH_3)_2$	5.8×10^{-4}	0.33	118	1.9×10^{13}	6
OCH_3	1.4×10^{-6}	140	137	2.1×10^{13}	14
OCH_2CH_3	4.8×10^{-6}	40	129	5.5×10^{12}	14
$OCH(CH_3)_2$	3.3×10^{-5}	5.8	123	5.5×10^{12}	14
O(cyclo-C_6H_{11})	7.0×10^{-5}	2.8	120	4.4×10^{12}	14
$OC(CH_3)_3$	8.3×10^{-2}	0.0023	91.7	5.7×10^{11}	15

a) Recalculated from the E_a and A values.

a method by Hancock et al.,[17] which is defined as $E_s{}^c$(R) with the following equation:

$$E_s{}^c(\mathrm{R}) = E_s(\mathrm{R}) + 0.306(N - 3) \quad (1)$$

where N is the number of hydrogen atoms on the α-carbon of substituent R. On the other hand, the ν(R) value also corresponds to the steric-effect substituent constant determined from van der Waals radii for the substituent as defined by Charton.[18] The values of each substituent constant are summarized in Table 2. The $E_s(CH_3)$ value is normalized to zero.

Figures 6a–6d show the relationship between each substituent constant and the rate constant of the thermal cycloreversion. The E_s(R) value does not exhibit a good correlation with the rate constant, as shown in Figure 6a. On the other hand, $E_s{}^c$(R) correlates well with the rate constant with an r-factor of 0.933, as shown in Figure 6b. These results indicate that the reactivity is affected by only the steric hindrance of the substituents at the reactive carbon positions and not affected by the hyperconjugation of the α-hydrogens in the substituent R.

The E_s(R) and $E_s{}^c$(R) values are applicable when the substituent is an alkyl group. When the substituent is an alkoxy group, the correlation between the E_s(R) or $E_s{}^c$(R) values and the thermal cycloreversion reactivity are not useful.

Table 2. Steric Substituent Constants, E_s(R), $E_s{}^c$(R), $E_s(CH_2R)$, and ν(R)$^{a)}$

R	E_s(R)	$E_s{}^c$(R)	$E_s(CH_2R)$	ν(R)
CH_3	0	0	−0.07	0.52
CH_2CH_3	−0.07	−0.38	−0.36	0.56
$CH_2CH_2CH_3$	−0.36	−0.67	−0.39	0.68
$CH_2CH(CH_3)_2$	−0.93	−1.24	−0.51	0.98
$CH(CH_3)_2$	−0.47	−1.08	−0.93	0.76
OCH_3	0.69$^{b)}$	—	−0.19	0.36
OCH_2CH_3	—	—	−0.37	0.48
$OCH(CH_3)_2$	—	—	—	0.75

a) Ref. 9. b) Ref. 19.

Here, $E_s(CH_2R)$ is discussed. The $E_s(CH_2R)$ value can support various types of substituents. Figure 6c shows the relationship between the $E_s(CH_2R)$ value and the rate constant. The $E_s(CH_2R)$ value had a good correlation even if the substituent is alkyl or alkoxy group with an r-factor of 0.964, which means that neither the hyperconjugation of the α-hydrogens nor the polarity of the substituent affect the thermal cycloreversion reactivity. The ν(R) value also applies to various types of substituents. Figure 6d shows the relationship between the ν(R) value and the rate constant of the thermal cycloreversion. The ν(R) value did not show a satisfactory level of correlation with the rate constant, with an r-factor of only 0.772.

Correlation between Substituent Constant and Activation Energy. The activation energy is an important factor for determining the thermal cycloreversion reactivity. Figures 7a–7d show the relationship between each substituent constant and the activation energy of the cycloreversion. The E_s(R) value does not exhibit a good correlation with the activation energy, as shown in Figure 7a. On the other hand, the $E_s{}^c$(R) value had a good correlation with an r-factor of 0.954, as shown in Figure 7b. These results are consistent with the relationships between the E_s(R) or $E_s{}^c$(R) values and the thermal cycloreversion reactivity.

As described above, the E_s(R) and $E_s{}^c$(R) values do not apply to alkoxy groups. Figures 7c and 7d show the relationship between the $E_s(CH_2R)$ value or ν(R) value and the activation energy of the thermal cycloreversion. The $E_s(CH_2R)$ value shows satisfactory even if the substituent is an alkyl or alkoxy group showing an r-factor of 0.901, whereas the ν(R) did not with an r-factor of 0.833. These results are also similar to the relationships between the $E_s(CH_2R)$ or ν(R) values and the thermal cycloreversion reactivity.

Conclusion

In conclusion, 5-phenyl-2-propyl-3-thienyl (**1a**) and 2-isobutyl-5-phenyl-3-thienyl (**2a**) photochromic diarylethenes were synthesized, and the thermal cycloreversion reactivity of their closed-ring isomers was discussed in the context of other diarylethenes which have already been reported. The rate constant of thermal cycloreversion of compounds with an alkyl group at the reactive carbon positions was found to be related to the specific steric substituent constant, $E_s{}^c$(R). In order to take into account both alkyl and alkoxy groups, the $E_s(CH_2R)$ and ν(R) values were discussed. $E_s(CH_2R)$ showed a satisfactory level of correlation with the rate constant. These results

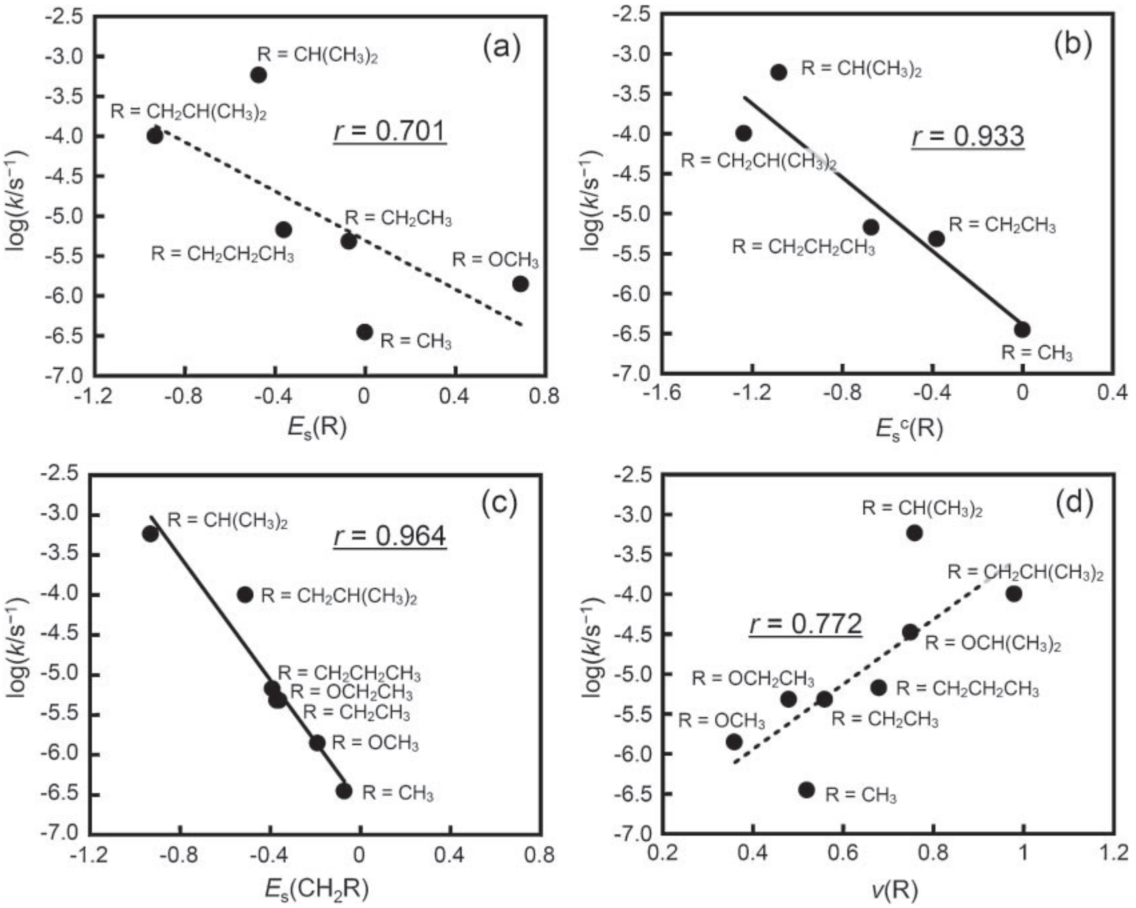


Figure 6. Relationship between the logarithm of k at 100 °C and the steric substituent constants, E_s(R) (a), E_s^c(R) (b), E_s(CH_2R) (c), and v(R) (d). The r value shows the Pearson correlation coefficient.

indicate that the reactivity was only affected by steric hindrance of the substituents at the reactive carbon positions. The activation energy also correlated with the steric substituent constants. This work may be useful for the design of diarylethene molecules having desired thermal stability.

Experimental

General. Solvents used were spectroscopic grade and purified by distillation before use. ^{1}H NMR spectra were recorded with a Bruker AV-300N spectrometer (300 MHz). Tetramethylsilane was used as an internal standard. Mass spectra were taken with a JEOL JMS-700/700S mass spectrometer. UV–visible absorption spectra were measured with a JASCO V-560 absorption spectrophotometer. The heating of the sample for the thermal cycloreversion was carried out using a constant temperature chamber ESPEC ST-110. The sample in an optical quartz cell was degassed and sealed off under vacuum. High-performance liquid chromatography (HPLC) was carried out using a HITACHI HPLC system equipped with a Kanto Chemical Mightysil Si 60 column.

Materials. 3,5-Dibromo-2-propylthiophene: Bromine (9.7 mL, 0.19 mol) was added slowly into a flask containing 2-propylthiophene (10 g, 0.079 mol), acetic acid (180 mL), and water (9 mL). The reaction mixture was stirred overnight at room temperature. The mixture was neutralized and extracted with ether. The ether extract was dried over $MgSO_4$, filtrated, and evaporated. The residue was purified by silica gel column chromatography using hexane as the eluent. The product was obtained as a colorless oil of 15 g (67% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, $J = 7.3$ Hz, 3H), 0.99–2.70 (m, 4H), 6.85 (s, 1H).

3-Bromo-5-phenyl-2-propylthiophene: To 250 mL of dry ether containing 3,5-dibromo-2-propylthiophene (15 g, 0.053 mol) was added 35 mL of 15% *n*-BuLi hexane solution (0.056 mol) at −78 °C under argon atmosphere, and the solution was stirred for 1 h at that temperature. Tri-*n*-butylborate (21 mL, 0.078 mol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 2 h at that temperature and then overnight at room temperature. The reaction mixture was concentrated by evaporator. To the residue were added THF (200 mL), 20 wt % Na_2CO_3(aq) (70 mL), iodobenzene (10 g, 0.049 mol), and [$Pd(PPh_3)_4$] (0.72 g, 0.62 mmol). After the mixture was refluxed for 5 h at 70 °C, it was neutralized with HCl(aq) and extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane as the eluent to give 9.8 g of the product in 66% yield as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (t, $J = 7.6$ Hz, 3H), 1.72 (dt, $J = 7.6$, 7.3 Hz, 2H), 2.77 (t, $J = 7.3$ Hz, 2H), 7.11 (s, 1H), 7.2–7.5 (m, 5H).

1,2-Bis(5-phenyl-2-propyl-3-thienyl)perfluorocyclopentene (1a): To 25 mL of dry THF solution containing 3-bromo-

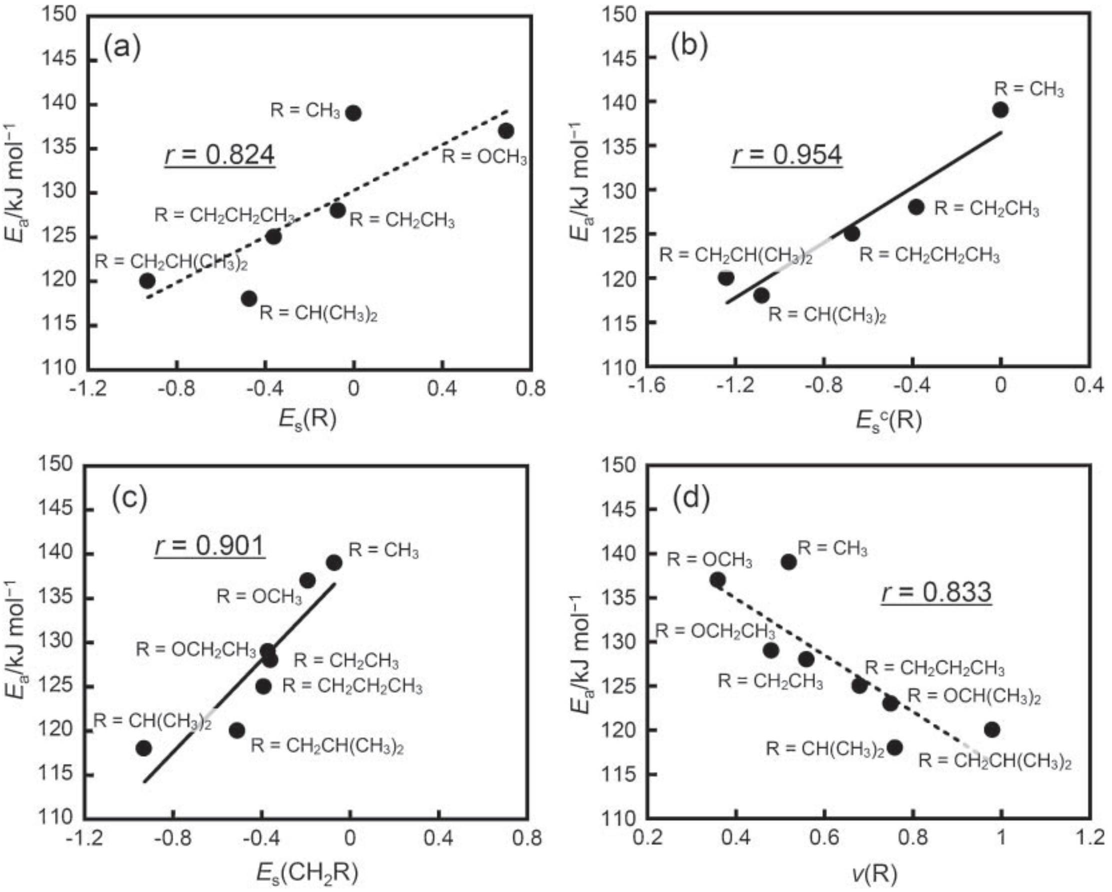


Figure 7. Relationship between the activation energy of the thermal cycloreversion and the steric substituent constants, E_s(R) (a), E_s^c(R) (b), E_s(CH_2R) (c), and ν(R) (d). The r value shows the Pearson correlation coefficient.

5-phenyl-2-propylthiophene (2.5 g, 8.9 mmol) was added 6.5 mL of 15% n-BuLi hexane solution (10 mmol) at −78 °C under argon atmosphere, and the solution was stirred for 2 h at that temperature. Octafluorocyclopentene (0.8 mL, 6.0 mmol, Nippon Zeon) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 3 h at that temperature. The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent and by recrystallization from hexane to give 1.2 g of **1a** in 47% yield as a colorless crystal; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.77 (t, $J = 7.4$ Hz, 6H), 1.35 (dt, $J = 7.4$, 7.7 Hz, 4H), 2.27 (t, $J = 7.7$ Hz, 4H), 7.2–7.6 (m, 12H); MS m/z (M^+): 576. Anal. Calcd for $C_{31}H_{26}F_6S_2$: C, 64.57; H, 4.54%. Found: C, 64.46; H, 4.52%.

3,5-Dibromo-2-isobutylthiophene: Bromine (2.0 mL, 0.039 mol) was added slowly into a flask containing 2-isobutylthiophene (2.8 g, 0.020 mol), acetic acid (40 mL), and water (3 mL). The reaction mixture was stirred overnight at room temperature. The mixture was neutralized and extracted with ether. The ether extract was dried over $MgSO_4$, filtered, and evaporated. The product was collected by distillation under reduced pressure (60–70 °C/1.2 kPa) as a colorless oil of 4.1 g (69% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (d, $J = 6.6$ Hz, 6H), 1.8–2.0 (m, 1H), 2.60 (d, $J = 7.2$ Hz, 2H), 6.86 (s, 1H).

3-Bromo-2-isobutyl-5-phenylthiophene: To 60 mL of dry ether containing 3,5-dibromo-2-isobutylthiophene (4.0 g, 0.013 mol) was added 9.0 mL of 15% n-BuLi hexane solution (0.014 mol) at −78 °C under argon atmosphere, and the solution was stirred for 1 h at that temperature. Tri-n-butylborate (5.0 mL, 0.019 mol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 3 h at that temperature and then overnight at room temperature. The reaction mixture was concentrated by evaporator. To the residue were added THF (50 mL), 20 wt% Na_2CO_3(aq) (20 mL), iodobenzene (3.3 g, 0.016 mol), and [$Pd(PPh_3)_4$] (0.18 g, 0.16 mmol). After the mixture was refluxed for 8 h at 80 °C, it was neutralized with HCl(aq) and extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane as the eluent to give 2.3 g of the product in 60% yield: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (d, $J = 6.8$ Hz, 6H), 1.8–2.0 (m, 1H), 2.66 (d, $J = 7.2$ Hz, 2H), 7.10 (s, 1H), 7.2–7.5 (m, 5H).

1,2-Bis(2-isobutyl-5-phenyl-3-thienyl)perfluorocyclopentene (2a): To 25 mL of dry THF solution containing 3-bromo-2-isobutyl-5-phenylthiophene (2.3 g, 7.8 mmol) was added 5.5 mL of 15% n-BuLi hexane solution (8.8 mmol) at −78 °C under argon atmosphere, and the solution was stirred for 2 h at that temperature. Octafluorocyclopentene (0.5 mL, 3.7 mmol, Nippon Zeon) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 8 h at that temperature.

The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent and by recrystallization from hexane to give 0.95 g of **2a** in 40% yield as a colorless crystal; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (d, $J = 6.6$ Hz, 12H), 1.6–1.8 (m, 2H), 2.13 (d, $J = 7.4$ Hz, 4H), 7.2–7.6 (m, 12H); MS m/z (M^+): 604. Anal. Calcd for $C_{33}H_{30}F_6S_2$: C, 65.54; H, 5.00%. Found: C, 65.58; H, 5.09%.

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