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Photochromism of diarylethene oxazole derivatives in a single-crystalline phase

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ABSTRACT

Four diarylethene derivatives (**3a**–**6a**) bearing an oxazole ring have been prepared in an attempt to construct a system that shows photochromism upon UV irradiation in a crystalline phase. The crystals (**3a**, **5a**, and **6a**) did not show photochromism in the crystalline phase. A pure single crystal of 1-(2-methyl-1-benzofuran-3-yl)-2-(5-methyl-2-phenyl-4-oxazolyl)perfluorocyclopentene (**4a**) shows photochromism only in a single-crystalline phase. X-ray analysis proved that **4a** packs in an anti-parallel orientation, which demonstrates photochromism in a single-crystalline phase.

1. Introduction

Various types of photochromic compounds have thus far been synthesized for possible application in optoelectronic devices [1,2]. Among these compounds diarylethene derivatives are the most promising candidates because of their fatigue resistance and thermally irreversible properties [3]. To date, reversible photochromic reactions have also led to various changes in the material characteristics, such as UV–vis absorption spectra [3], near-IR absorption spectra [4], fluorescence [5–7], oxidation/reduction potential [8,9], reflective index [10], optical rotation [11], shape of a single crystal [12], and contact angle [13].

Diarylethene derivatives have two aryl moieties, and most work has been carried out on diarylethene derivatives with thiophene or benzothiophene rings because of their excellent thermal stability and outstanding fatigue resistance. Recently, thiazole [14], phenyl [15], indene [16], benzofuran [17], pyrrole [18], and pyrazole [19] derivatives have also shown photochromism in solution. Some diarylethenes show photochromism in single-crystalline phase [20]. In general, the molecule undergoes a photocyclization reaction if it is orientated in an anti-parallel array and if the distance between two reactive carbon atoms on the aryl moiety is within 0.42 nm [20].

The oxazole derivatives 1,2-bis(5-methyl-2-phenyl-4-oxazolyl) perfluorocyclopentene (**1a**) [21] and 1,2-bis(4-methyl-3-phenyl-4-oxazoyl)perfluorocyclopentene (**2a**) [22] show photochromism in hexane. The colors of the closed-ring forms (**1b** and **2b**) are orange and pale yellow in hexane, respectively, and they are very useful materials for full-color imaging because they provide one of the three primary colors. However, the pure crystals **1a** and **2a** did not undergo photochromism in the crystalline phase [21,22]. The ORTEP drawing of the single crystal shows the molecules packed in a parallel conformation which did not give rise to photochromism in the single-crystalline phase. The mixed crystal system, composed of diarylethenes with a similar geometrical structure to **1a** and 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene, showed photochromism in the single-crystalline phase [21].

We studied mixed aryl moieties, such as benzofuran and benzothiophene rings [23], and we found that the 2-methylbenzofuran unit showed efficient photochromism in the single-crystalline phase. We suggested that two aryl moieties on the diarylethenes, such as the combination of 2-methylbenzofuran and 2-methyloxazole rings, change the orientation of the molecule from parallel to anti-parallel in a crystal. In this work, four types of hetero aryl diarylethene (**3a**–**6a**) with oxazole, benzothiophene, and benzofuran rings were synthesized to construct a photochromic system in a single-crystalline phase. The mechanism that controls the parallel and anti-parallel conformations between oxazole derivatives was considered.

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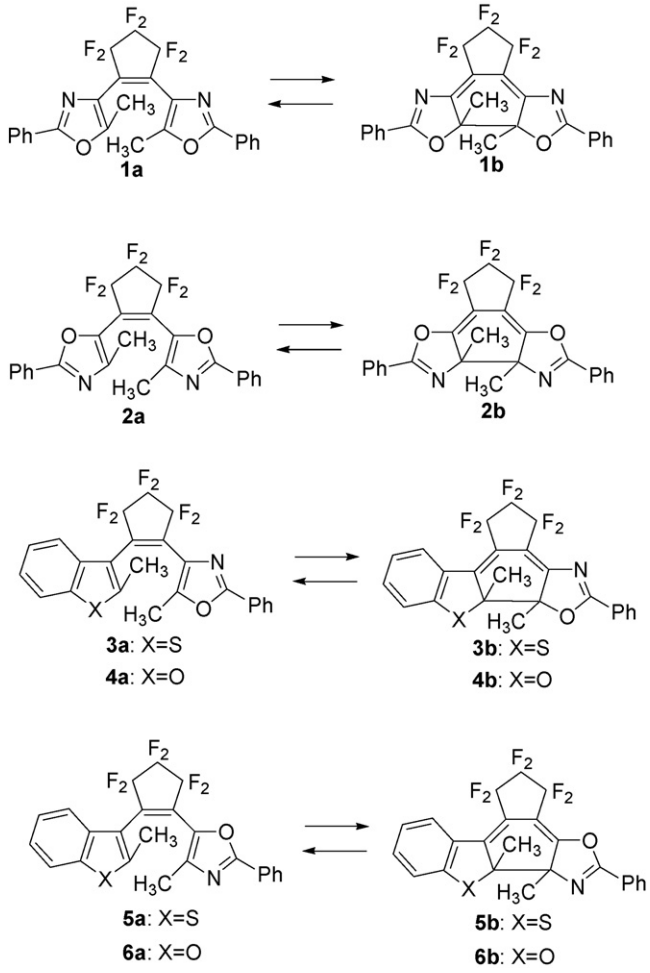

2. Experimental methods

2.1. General

The solvents used were of spectrophotometric grade and were purified by distillation before use. Absorption spectra in solution were measured with a Shimadzu UV-2500PC spectrophotometer. The cyclization and cycloreversion quantum yields were determined in comparison with the photoisomerization rate of furylfulgide in toluene as a reference. Absorption spectra in the single-crystalline phases were measured using an OPTI-POL 2POL (Nikon) polarizing microscope connected to a Hamamatsu PMA-11 detector. A mercury lamp (Ushio, 500 W) was used as the light source. Light of appropriate wavelength was isolated by passing light through a monochromator (Shimadzu SPG-120S) or L-29, Y-42, and UV-D33S filters. ^{1}H NMR spectra were recorded on a Gemini 200 spectrometer (200 MHz) with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. Mass spectra were taken with a Shimadzu GCMS-QP5050A gas chromatography–mass spectrometer. X-ray crystallography was carried out using a Bruker SMART CCD X-ray diffractometer (55 kV, 35 mA). HPLC was carried out on a Shimadzu LC-10AD liquid chromatography coupled with a Shimadzu SPD-10AV spectrophotomeric detector. A silica gel column (Wako Wakosil-5SIL) was used to analyze diarylethene isomers.

2.2. Synthesis of the diarylethene derivatives

2.2.1. 4-Bromo-5-methyl-2-phenyloxazole (**7**)

According the method of reference [24], the compound was synthesized.

7: Colorless crystal; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.42 (s, 3H), 7.42–7.46 (m, 3H), 8.00–8.03 (m, 2H). Ms (m/z) 238 (M^+). Calcd for $C_{10}H_8BrNO$: C 50.45, H 3.39, N 5.88%. Found: C 50.48, H 3.43, N 5.88%.

2.2.2. 1-(5-Methyl-2-phenyl-4-oxazolyl)-2-(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene(***3a***)

To a stirred THF solution (40 mL) containing 4-bromo-5-methyl-2-phenyloxazole (**7**) (0.5 g, 2.10 mmol), 1.44 mL of 1.6 M butyllithium hexane solution (2.31 mmol) was slowly added at −78 °C, and the solution was stirred for 15 min at −78 °C. Then 1-(2-methylbenzo[*b*]thiophen-3-yl)heptafluorocyclopentene (0.714 g, 2.10 mmol) was added slowly to the reaction mixture at −78 °C and left to stand with stirring at −78 °C and was gradually warmed to 30 °C for 12 h. The reaction mixture was poured into a concentrated sodium chloride solution and extracted with diethyl ether. The organic phase was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexane) to give 0.304 g of **3a** in 30% yield.

3a: colorless liquid; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.96 (s, 0.7H), 2.19 (s, 2.3H), 2.30 (s, 0.7H), 2.43 (s, 2.3H), 7.09–7.56 (m, 7H), 7.66–7.81 (m, 2H). Ms (m/z) 479 (M^+). Calcd for $C_{24}H_{15}F_6NOS$: C 60.12, H 3.15, N 2.92%. Found: C 60.37, H 3.13, N 2.90%.

2.2.3. 1-(5-Methyl-2-phenyl-4-oxazolyl)-2-(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene(***4a***)

The reaction of 4-bromo-5-methyl-2-phenyloxazole (**7**) (0.5 g, 2.10 mmol) and 1-(2-methyl-1-benzofuran-3-yl)heptafluorocyclopentene (0.68 g, 2.10 mmol) was carried out using by the same procedure as that for compound **3a**. The crude product was purified by column chromatography to give 0.292 g of **4a** in 30% yield.

4a: colorless crystals, mp. 116–117 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.10 (s, 3H), 2.32 (s, 3H), 7.19–7.47 (m, 7H), 7.79–7.84 (m, 2H). Ms (m/z) 463 (M^+). Calcd for $C_{24}H_{15}F_6NO_2$: C 62.21, H 3.26, N 3.02%. Found: C 62.28, H 3.32, N 3.12%.

2.2.4. 1-(4-Methyl-2-phenyl-5-oxazolyl)-2-(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene(***5a***)

The reaction of 5-bromo-4-methyl-2-phenyloxazole [24] (0.500 g, 2.10 mmol) and 1-(2-methylbenzo[*b*]thiophen-3-yl) heptafluorocyclopentene (0.714 g, 2.10 mmol) was carried out using the same procedure as that for compound **3a**. The crude product was purified by column chromatography to give 0.282 g of **5a** in 28% yield.

5a: colorless crystals, mp. 135–136 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.37 (s, 3H), 2.45 (s, 3H), 7.22–7.45 (m, 7H), 7.83–7.88 (m, 2H). Ms (m/z) 479 (M^+). Calcd for $C_{24}H_{15}F_6NOS$: C 60.12, H 3.15, N 2.92%. Found: C 60.07, H 3.14, N 2.91%.

2.2.5. 1-(4-Methyl-2-phenyl-5-oxazolyl)-2-(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene(***6a***)

The reaction of 5-bromo-4-methyl-2-phenyloxazole [24] (0.500 g, 2.10 mmol) and 1-(2-methyl-1-benzofuran-3-yl)heptafluorocyclopentene (0.680 g, 2.10 mmol) was carried out using the same procedure as that for compound **3a**. The crude product was purified by column chromatography to give 0.319 g of **6a** in 33% yield.

6a: colorless crystals, mp. 86–87 °C (dec.); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.24 (s, 3H), 2.38 (s, 3H), 7.16–7.55 (m, 9H). Ms (m/z) 463 (M^+). Calcd for $C_{24}H_{15}F_6NO_2$: C 62.21, H 3.26, N 3.02%. Found: C 62.18, H 3.27, N 3.07%.

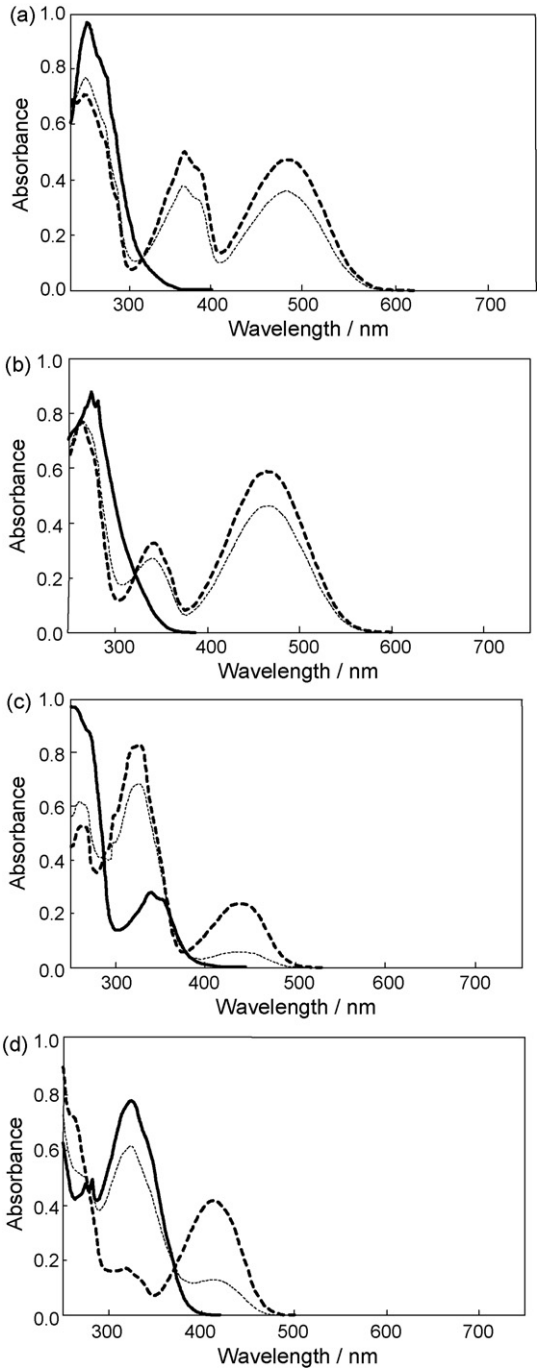

Fig. 1. Absorption spectra of (a) **3** (4.4×10^{-5} mol/L), (b) **4** (4.0×10^{-5} mol/L), (c) **5** (1.4×10^{-5} mol/L), and (d) **6** (4.6×10^{-5} mol/L) in hexane. Solid, dashed, and dotted lines represent **a** (open form), **b** (closed-ring form), and the photostationary state under irradiation with 313 nm light.

Table 1
Absorption characteristics and photochromic reactivities of diarylethene derivatives **2**–**6** in hexane.

Compound	ε/10^4 dm^3 mol^{-1} cm^{-1}		Quantum yield	
	a	**b**	Cyclization	Cycloreversion
2[a]	1.70 (373 nm)	0.24 (353nm)	0.10 (373 nm)	0.33 (252 nm)
3	2.15 (267 nm)	1.05 (482 nm)	0.19 (313 nm)	0.08 (482 nm)
4	2.19 (275 nm)	1.47 (463 nm)	0.27 (313 nm)	0.11 (463 nm)
5	1.97 (325 nm)	0.57 (440 nm)	0.04 (313 nm)	0.49 (440 nm)
6	1.70 (324 nm)	0.91 (411 nm)	0.08 (313 nm)	0.49 (411 nm)

[a] Reference [22] data.

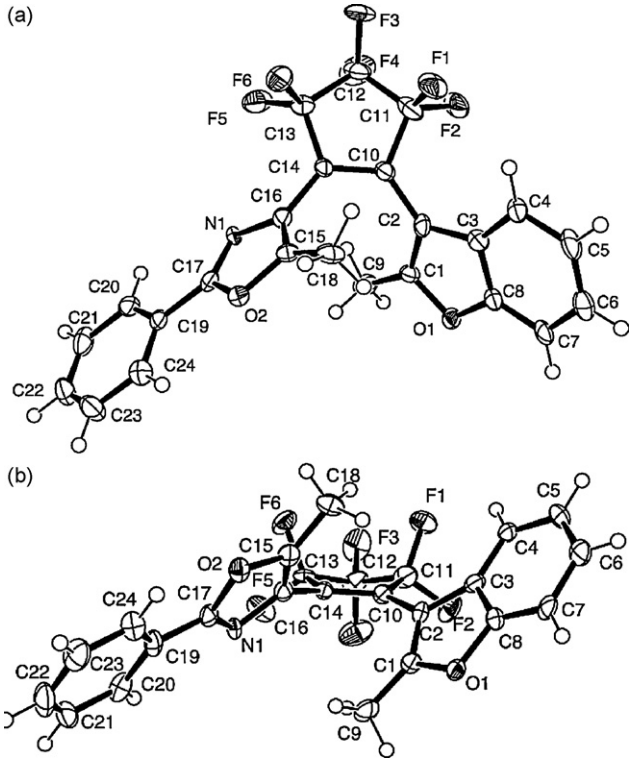

Fig. 2. ORTEP drawings of **4a** showing 50% probability displacement ellipsoids: (a) top view and (b) side view.

3. Results and discussion

3.1. Synthesis of diarylethenes *3a*–*6a*

Diarylethenes **3a** and **5a** were prepared from 1-(2-methylbenzo[*b*]thiophen-3-yl)heptafluorocyclopentene in a one-step coupling reaction with 4-bromo-5-methyl-2-phenyloxazole and 5-bromo-4-methyl-2-phenyloxazole, respectively. Similarly, diarylethenes **4a** and **6a** were prepared from 1-(2-methyl-1-benzofuran-3-yl)heptafluorocyclopentene in a one-step coupling reaction with 4-bromo-5-methyl-2-phenyloxazole and 5-bromo-4-methyl-2-phenyloxazole, respectively. Their structures were confirmed by ^{1}H NMR, mass spectrometry, and elemental analysis. Diarylethenes **4a**–**6a** were confirmed by X-ray crystallography.

3.2. Photochromic properties in hexane solution

First, we examined photochromic properties in hexane. Fig. 1(a) shows the absorption spectra of **3a** in hexane upon irradiation with 313 nm light. **3a** and **3b** have absorption maxima at 267 nm (ε, 2.15×10^4 M^{-1} cm^{-1}) and 482 nm (ε, 1.05×10^4 M^{-1} cm^{-1}), respectively. The conversion from **3a** to **3b** in the photostationary state under irradiation with 313 nm light was 85%.

Fig. 1(b) shows changes in the absorption spectrum of **4a** in hexane upon irradiation with 313 nm light. **4a** and **4b** have absorption maxima at 275 nm (ε, 2.19×10^4 M^{-1} cm^{-1}) and 463 nm (ε, 1.47×10^4 M^{-1} cm^{-1}), respectively. The closed-ring diarylethene, 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene, has an absorption maximum at 469 nm (ε, 1.44×10^3 M^{-1} cm^{-1}) [17]. Upon changing from the 5-methyl-2-phenyloxazole ring to the 2-methyl-1-benzofuran ring, the absorption band of the closed-ring isomer shifted to a slightly shorter wavelength. **4b** was a vivid yellow color in hexane with high molar absorptivity at the maximum. The conversion value from **4a** to **4b** is very high (89%

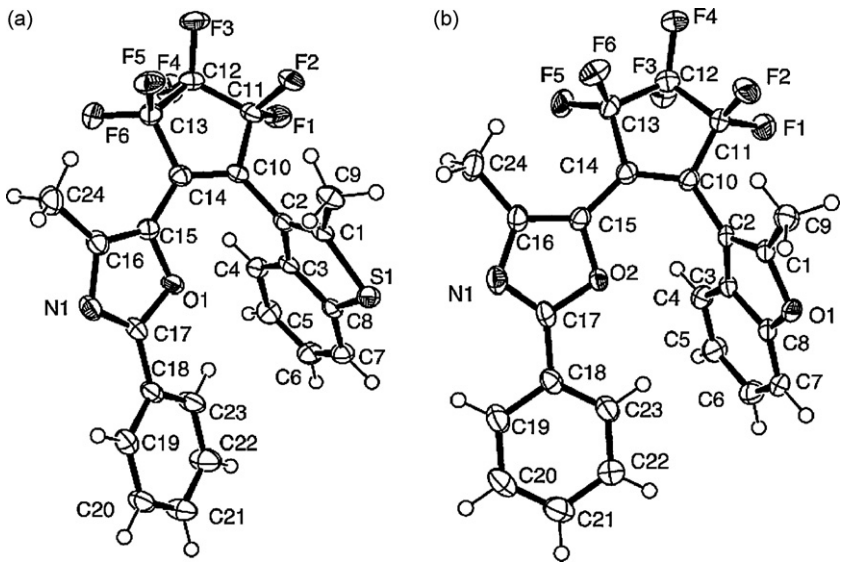

Fig. 3. ORTEP drawings of (a) **5a** and (b) **6a** showing 50% probability displacement ellipsoids.

under irradiation with 313 nm light) because of the introduction of the 5-methyl-2-phenyloxazole ring.

In the case of **5a** which has a 4-methyl-2-phenyloxazole ring and 2-methylbenzo[*b*]thiophene rings, the absorption spectrum was markedly changed. Fig. 1(c) shows the change in the absorption spectrum of **5** in hexane upon irradiation with 313 nm light. **5a** and **5b** have absorption maxima at 275 nm and 440 nm, respectively. The conversion of **5a** to **5b** in the photostationary state under irradiation with 313 nm light was 22%.

Fig. 1(d) shows the change in the absorption spectrum of **6**, which has 4-methyl-2-phenyloxazole and 2-methyl-1-benzofuran rings, in hexane upon irradiation with 313 nm light. **6a** and **6b** have absorption maxima at 324 nm and 411 nm, respectively. The conversion from **6a** to **6b** in the photostationary state under irradiation with 313 nm light was 35%.

Table 1 summarizes the absorption maxima and absorption coefficients of open- and closed-ring isomers in hexane. The quantum yields for cyclization and cycloreversion were also measured and are included in Table 1. In hexane, the absorption maximum of the closed-ring isomer **1b** was 462 nm, and the maximum of the closed-ring isomer **2b** was 353 nm. The absorption maxima of the closed-ring isomer changed as a function of the position of the point of attachment of the perfluorocyclopentene. In the case of **3b**–**6b**, the absorption maxima have wavelengths between those of **1b** and **2b**.

The quantum yields for cyclization and cycloreversion were also dependent on the substitution position. In the case of benzothiophene derivatives **3** and **5**, the cyclization quantum yield was decreased from 0.19 (**3**) to 0.04 (**5**) by changing the ring from 5-methyl-2-phenyloxazole to 4-methyl-2-phenyloxazole. The cycloreversion quantum yield was increased from 0.08 (**3**) to 0.49 (**5**) by changing the ring from 5-methyl-2-phenyloxazole to 4-methyl-2-phenyloxazole. The quantum yields for cyclization and cycloreversion control the conversion rates upon irradiation with 313 nm light. The same results in terms of the substitution effects and quantum yields were observed for benzofuran derivatives **4** and **6**, as shown in Table 1.

Table 2
Crystal data for **4a**, **5a**, and **6a**.

	4a	**5a**	**6a**
Formula	$C_{24}H_{15}F_6NO_2$	$C_{24}H_{15}F_6NOS$	$C_{24}H_{15}F_6NO_2$
Formula weight	463.37	479.43	463.37
Temperature/K	103(2)	123(2)	123(2)
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	Pna2(1)	P-1	P-1
Unit cell dimensions			
a/Å	19.948(6)	9.686(3)	9.271 (3)
b/Å	14.952(5)	9.781(3)	9.457(3)
c/Å	6.774(2)	12.571(4)	13.108(4)
α/°	90	97.756(5)	110.549(4)
β/°	90	107.336(5)	99.493(4)
γ/°	90	109.216(5)	104.591(4)
Volume/Å^3	2020.5(11)	1037.0(6)	999.9(5)
Z	4	2	2
Density (calcd)/(g/cm^3)	1.523	1.535	1.539
Goodness-of-fit on F^2	1.125	1.067	1.049
Final *R* indices[$I/2\sigma(I)$]			
*R*1	0.0670	0.0530	0.0572
*wR*2	0.1679	0.1405	0.1538
R indices (all data)			
*R*1	0.0712	0.0578	0.0600
*wR*2	0.1705	0.1455	0.1582

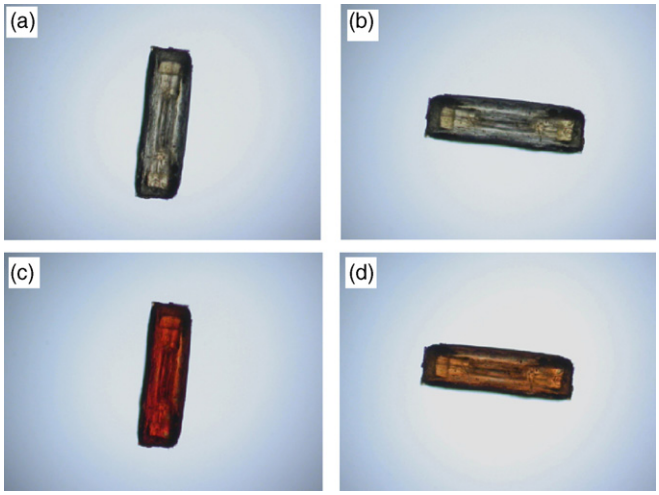

Fig. 4. Photographs of a single crystal of **4a** under polarized light before ((a) $\theta = 0°$; (b) $\theta = 90°$) and after ((c) $\theta = 0°$; (d) $\theta = 90°$) irradiation with 365 nm light. θ is the rotation angle of the crystal.

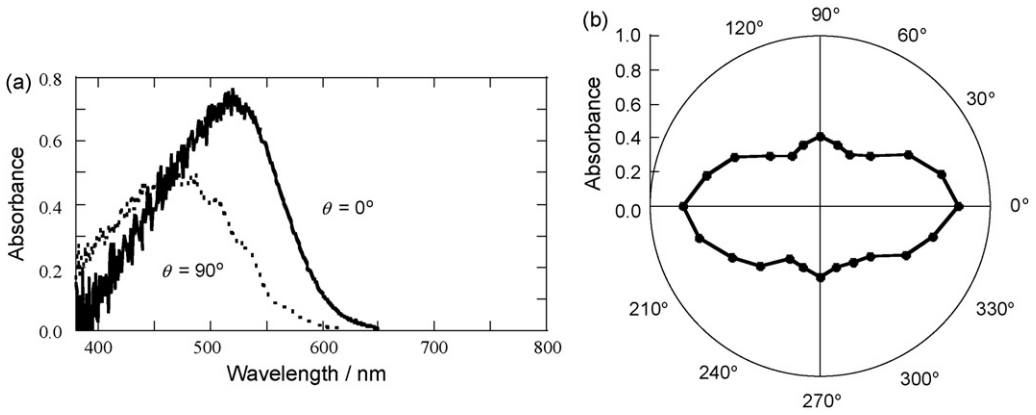

Fig. 5. Polarized absorption spectra of the colored crystal of **4a**: (a) direction of the polarizer and, (b) polarized absorption spectra.

3.3. X-ray crystallographic analysis

Single crystals of **4a**–**6a** were obtained by recrystallization from the solution of diethyl ether and hexane. **3a** was obtained as micro crystals (re-crystallization solvent: hexane), which did not analyze by X-ray crystallography (<0.01 mm in size), and **3a** was obtained not a single crystal but amorphous solid by re-crystallization from diethyl ether. X-ray crystallographic data was analyzed for single crystals **4a**–**6a** (Table 2). Fig. 2 shows the X-ray crystallographic data for a single crystal of **4a** [25]. The drawing indicates that **4a** is packed in the photoactive anti-parallel conformation in the crystal, but the distance between the reactive carbon atoms is 0.345 nm. The distance is sufficiently short for the molecules to undergo the photochromic reaction in the crystalline phase.

Fig. 3 shows the X-ray crystallographic data for single crystals of **5a** and **6a**. Diarylethenes **5a** and **6a** are packed in parallel conformations. The structures for **5a** and **6a** are similar to those for **1a** [21] and **2a** [22]. These single crystals do not show photochromism in the single-crystalline phase. A similar structure, which has thiazole units, 1,2-bis(5-methyl-2-phenyl-4-thiazoyl)perfluorocyclopentene, shows photochromism in the crystal [21].

The difference between the oxazole and thiazole rings controls the formation of photoactive anti-parallel and photoinactive parallel conformations. Therefore, we examined the distances between all the atoms in the ORTEP drawings. There is no hydrogen bond distance in the drawings for **4a**–**6a**.

For the photoinactive oxazole derivative, however, the dihedral angle between aryl rings (benzofuran, benzothiophene, oxazole) and the perfluorocyclopentene moiety was small. In the case of **5a** and **6a**, the dihedral angles (C2–C10–C14–C15) were −6.4° and 0.7°, respectively. In the case of **4a**, the dihedral angle (C2–C10–C14–C16) was 15.1°. The small values for **5a** and **6a** indicate strong methyl repulsion between aryl rings.

At the same time, the result indicates that π-conjugation effect between the aryl ring and the perfluorocyclopentene moiety induces a parallel conformation. The strength of π-conjugation is reflected by the bond distance between oxazole rings and the perfluorocyclopentene moiety. In compounds **5a** the distances between the carbon atoms (C14–C15) are 0.1435 nm, and in compound **6a** the distance between the atoms (C14–C15) are 0.1453 nm. For diarylethene **5a** and **6a**, one oxazole ring and the perfluorocyclopentene moiety are almost coplanar. However, for diarylethene **4a** the distance between two atoms (C14–C16) is 0.1478 nm. The slightly long distance between oxazole rings and the perfluorocyclopenthene moiety represents a weak π-conjugation effect.

In the case of **2a**, which has 3-methyl oxazole units, the distances are 0.1442 and 0.1447 nm, and the perfluorocyclopentene moiety and oxazole ring are almost coplanar, at a distance of 0.1442 nm. In the case of **1a**, which has 2-methyl oxazole units, the distances are 0.1457 and 0.1478 nm, and the perfluorocyclopentene moiety and the oxazole ring are almost coplanar, at a distance of 0.1457 nm.

As a result, the characteristics that control the parallel and anti-parallel conformations are methyl repulsion and the degree of extension of π-conjugation which involves one oxazole ring and a perfluorocyclopentene moiety.

3.4. Photochromic reaction in the single-crystalline phase

Although the benzothiophene derivative **3** does not display photochromism in the crystalline phase upon irradiation with 365 nm light, the benzofuran derivatives of **4** undergoes photochromism upon irradiation with 365 nm light in the single-crystalline phase. Upon irradiation with 365 nm light under a polarized microscope, the single crystals turned brown, and the brown color disappeared when the crystals were irradiated with visible light ($\lambda > 400$ nm).

The changes in absorption spectra for a single crystal of crystal **4a** were observed under polarized light. Fig. 4 shows photographs of the color changes. Fig. 4(a) and (b) show the crystal before UV irradiation, were it is pale yellow. Upon irradiation with 356 nm light, the crystal turned brown (Fig. 4(c)). When the crystal was rotated as much as 90°, the color of the crystal changed to orange (Fig. 4(d)).

Fig. 5(a) shows the polarized absorption spectra of the colored crystal. By rotating the crystal sample under polarized light, the absorption intensity ratio at 520 nm changed. The change in the color from orange to brown by rotating the crystal sample indicates that the closed-ring isomer is regularly orientated in the crystal.

Fig. 5(b) shows the polarized absorption spectra at 520 nm. The absorption anisotropy indicates the direction of the electronic transition moment of the closed-ring form in the crystal. These results confirm that a photoreaction takes place in the crystal.

Although the cyclization quantum and cycloreversion yields of **3** are almost same the same as those of **4**, **3** does not show photochromism in the crystalline phase. The quantum yields did not affect the photochromism in the crystalline phase. The results may indicate that the compound **3** tends to form photoinactive parallel conformation or anti-parallel conformation which the distance between reactive carbon atoms is longer than 0.42 nm [20].

The compounds **5a** and **6a** did not show any photochromism in the single-crystalline phase. Photochromic reactivity is strongly dependent on molecular structure. X-ray crystallographic analysis of the crystals of **5a** and **6a** revealed that the molecules were packed in a photo-inactive parallel conformation in their single crystals.

4. Conclusions

We have synthesized diarylethene derivatives **3a**–**6a** with one oxazole ring. All the derivatives displayed photochromism upon alternating irradiation with UV and visible light in hexane. The oxazole derivatives **3**, **5**, and **6** did not show photochromism in the single-crystalline phase. X-ray crystallography of these compounds revealed that the usual oxazole derivatives have a photo inactive parallel conformation. However, diarylethene **4** was found to undergo photochromism in the single-crystalline phase, and the ORTEP drawing shows the photoactive anti-parallel conformation. The characteristics of oxazole derivatives that control the parallel and anti-parallel conformations are the methyl repulsion between two aryl rings and the extension of π-conjugation which involves one oxazole ring and the perfluorocyclopentene moiety. The color change of the 365-nm-light irradiated crystal from orange to brown caused by rotating the sample was observed under polarized light.

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[25] CCDC 721873, 721874, and 721875 (compounds **4a**, **5a**, and **6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.