

Photochromic Properties of Diarylethene Derivatives Having Benzofuran and Benzothiophene Rings Based on Regioisomers

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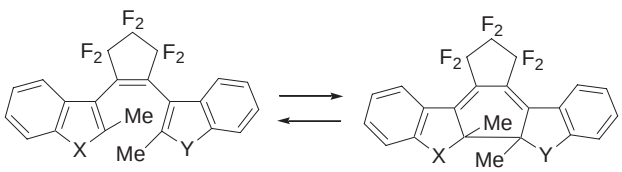
Photochromic diarylethene regioisomers having benzothiophene and benzofuran rings were synthesized and their structures were confirmed by X-ray crystallography. The photochromic properties of these diarylethenes were examined in solution as well as in the single-crystalline phase. We found that a diarylethene having 3-methylbenzofuran (FR2) ring show photochromism upon irradiation with UV light. For bis(3-methylbenzofuran) (BFR2) derivatives, the absorption band of the closed-ring isomer was longer than that of the open-ring isomer. The closed-ring isomer of the diarylethene derivatives having one 2-methylbenzofuran (FR3) ring showed a high absorption coefficient (more than 10^4 $dm^3\,mol^{-1}\,cm^{-1}$). Although the distance between two reactive carbon atoms was within 0.42 nm, some diarylethene derivatives showed no photochromic reactions in the single-crystalline phase. Diarylethene derivatives having one 2-methylbenzofuran (FR3) ring efficiently showed photochromism in the single-crystalline phase.

Photochromism has attracted considerable attention because of its potential application in photonic devices, such as optical memories and switches.[1] Among various thermally irreversible photochromic compounds, diarylethene derivatives are the most promising candidates for such application because of their fatigue resistance.[2–14] Recently, we have reported on diarylethene derivatives having benzofuran[15,16] and furan[17] rings, which also show thermally irreversible and fatigue-resistance photochromic reactions. For full-color photochromic dyes, it is crucial to develop yellow photochromic compounds that have high fatigue resistance against photoirradiation and high thermal stability at room temperature. 1,2-Bis(2,5-methylthien-3-yl)perfluorocyclopentene,[18] 1,2-bis(2-methylbenzo[*b*]-thiophen-1,1-oxide-3-yl)perfluorocyclopentene,[19] and 1-aryl-1,3-butadiene[20,21] derivatives are yellow photochromic dyes in solution. A few compounds such as 1,2-bis(3-methylthien-2-yl)perfluorocyclopentene[22] turn yellow upon irradiation with UV light in the single-crystalline phase. In particular, in the crystalline phase, the yellow developing material is useful as a pigment that show excellent fatigue resistance, because it is not oxidized in solution and its structure is optimal in the single-crystalline phase for photocyclization and photocycloreversion.[23]

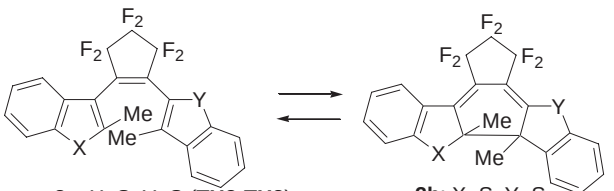
In this study, we synthesized ten diarylethene regioisomers having benzothiophene and benzofuran rings (**1a–10a**), and their photochromic performance was compared with that of their derivatives having a benzothiophene group in solution as well as in the single-crystalline phase.

Results and Discussion

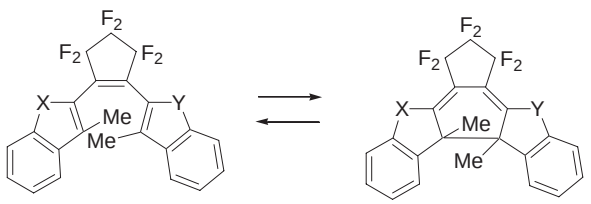
Synthesis of 1a–10a. We have synthesized the diarylethenes **1a–10a** (Scheme 1). The detailed synthetic procedures for **1a**,[12] **3a**,[13] **4a**,[15] and **7a**[14] have already been reported. **1a**,



1a: X=S, Y=S (**BTH3**) **1b**: X=S, Y=S
4a: X=O, Y=O (**BFR3**) **4b**: X=O, Y=O
7a: X=S, Y=O (**TH3-FR3**) **7b**: X=S, Y=O



2a: X=S, Y=S (**TH3-TH2**) **2b**: X=S, Y=S
5a: X=O, Y=O (**FR3-FR2**) **5b**: X=O, Y=O
8a: X=S, Y=O (**TH3-FR2**) **8b**: X=S, Y=O
9a: X=O, Y=S (**FR3-TH2**) **9b**: X=O, Y=S



3a: X=S, Y=S (**BTH2**) **3b**: X=S, Y=S
6a: X=O, Y=O (**BFR2**) **6b**: X=O, Y=O
10a: X=S, Y=O (**TH2-FR2**) **10b**: X=S, Y=O

Scheme 1.

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4a, and **7a** are basic compounds for the comparative study of regioisomers. To clarify the differences between the regioisomers, we used simple names for the structures. The bis(benzo[*b*]thiophene) derivative **1a**, which has two 2-methylbenzo[*b*]thiophen-3-yl units, is commercially available (**1a**: BTH3). The symbol "B" denotes a bis structure of benzothiophene (TH) or benzofuran (FR) ring. The number "3" denotes a position between the ring and perfluorocyclopentene moieties. The bis(benzofuran) derivative **4a**, which has two 2-methylbenzofuran-3-yl units is similar in structure to **1a** (**4a**: BFR3). The benzo[*b*]thiophene–benzofuran derivative **7a** has 2-methylbenzo[*b*]thiophen-3-yl and 2-methylbenzofuran-3-yl units (**7a**: TH3-FR3). The absorption maximum wavelength of **7b** (493 nm) was between those of **1b** (517 nm) and **4b** (469 nm) in hexane.[14]

The diarylethenes **1a–3a** are of the TH type (benzothiophene type) and have homo benzo[*b*]thiophene rings. **2a** (**2a**: TH3-TH2), which has not been reported so far, is a diarylethene in which one TH3 unit of **1a** (BTH3) is replaced by one TH2 unit. The coupling reaction of 1-(2-methylbenzo[*b*]-thiophen-3-yl)heptafluorocyclopentene having 3-methylbenzo-[*b*]thiophene gave the benzothiophene derivative **2a** in 46% yield. The diarylethene **3a** has two 3-methylbenzo[*b*]thiophen-2-yl units (BTH2), a compound in which two TH3 units of **1a** (BTH3) are replaced by two TH2 units.

The diarylethenes **4a–6a** are of the FR type (benzofuran type) and have homo benzofuran rings. **5a** (**5a**: FR3-FR2) is a diarylethene in which one FR3 unit of **4a** (BFR3) is replaced by one FR2 unit. The benzofuran derivative **5a** (**5a**: FR3-FR2) was also synthesized by the elimination reaction of 1-(2-methylbenzofuran-3-yl)heptafluorocyclopentene and 3-methylbenzofuran, following synthetic procedure for **2a**, to give **5a** in 35% yield. The benzofuran derivative **6a** (**6a**: BFR2) is a compound in which two FR3 units of **4a** (BFR3) are replaced by two FR2 units. It was synthesized by the coupling reaction of octafluorocyclopentene and 3-methylbenzofuran, as described for **3a**, to give **6a** in 32% yield.

7a–10a each has one benzothiophene ring and one benzofuran ring (TH-FR type). If **7a** (TH3-FR3) is basic, **8a** (TH3-FR2) and **9a** (FR3-TH2) are produced by the replacement of FR3 by FR2, and of TH3 by TH2, respectively. The coupling reaction of 1-(2-methylbenzo[*b*]thiophen-3-yl)heptafluorocyclopentene with 3-methylbenzofuran gave the diarylethene **8a** in 38% yield. **9a** (**9a**: FR3-TH2) was also synthesized by similar methods to give a 42% yield. Diarylethene **10a** (TH2-FR2) is a compound in which 2-methylbenzo[*b*]thiophene (TH3) and 2-methylbenzofuran (FR3) rings of **7a** are replaced by 3-methylbenzo[*b*]thiophene (TH2) and 3-methylbenzofuran (FR2) rings, respectively. The coupling reaction of 1-(3-methylbenzofuran-2-yl)heptafluorocyclopentene (**11**) with 3-methylbenzo[*b*]thiophene gave the diarylethene **10a** in 39% yield.

X-ray Crystallography of 2a, 5a, 6a, 8a, 9a, and 10a. To elucidate their structural differences, **2a**, **5a**, **6a**, **8a**, **9a**, and **10a** were analyzed by X-ray crystallography. Single crystals of **2a**, **5a**, **6a**, **8a**, **9a**, and **10a** were obtained by recrystallization from a mixture of hexane and diethyl ether, and their structures were determined by X-ray crystallography. Figure 1 and Table 1 show the X-ray crystallographic analysis data of single crystals of **2a**, **5a**, **6a**, **8a**, **9a**, and **10a**. The drawings indicate that **2a**, **5a**, **6a**, **8a**, **9a**, and **10a** are packed in a photoactive antiparallel conformation in the single-crystalline phase. **1a**,[25] **3a**,[13] **4a**,[15] and **7a**[14] take a photoactive antiparallel conformation in the single-crystalline phase. The photochromic performance of these derivatives is dependent on the distance between reactive carbon atoms. At a distance within 0.42 nm, the diarylethene derivatives undergo photochromism in the single-crystalline phase.[23] For **2a**, the distance between reactive carbon atoms (C1 and C16) is 0.385 nm. The distances obtained from X-ray crystallographic analysis are summarized in Table 2. For the benzothiophene derivatives **1a**, **2a**, and **3a**, the distances decreased in this order with the replacement of 2-methylbenzo[*b*]thiophene (TH3) by 3-methylbenzo[*b*]-thiophene (TH2). Except for **1a**, the distance was within 0.42 nm. For the benzofuran derivatives **4a**, **5a**, and **6a**, the distances were almost constant (0.34–0.36 nm). For the benzothiophene–benzofuran derivatives **7a**, **8a**, **9a**, and **10a**, the distance decreased with the replacement of the 2-methylbenzo[*b*]-thiophene ring (TH3) by the 3-methylbenzo[*b*]thiophene ring (TH2). However, all the compounds had distances within 0.42 nm. Details of the photochromic behavior in the single-crystalline phase are summarized in the section, "Photochromism in single-crystalline phase."

Photochromism of 1a–10a in Hexane Solution. The diarylethenes **1a–3a** are of the TH type. **1a** (BTH3)[12] and **3a** (BTH2)[13] show photochromism in solution. Figure 2a shows the photochromism of **2a** (TH3-TH2) in hexane. **2a** had an absorption maximum at 309 nm (ε, 1.03×10^4 dm^3 mol^{-1} cm^{-1}). Upon irradiation with 313 nm light, the colorless solution of **2a** turned orange, whose visible absorption band was observed at 463 nm. The absorption coefficient of **2b** at 463 nm was 9.6×10^3 dm^3 mol^{-1} cm^{-1}. The absorption maximum wavelength was between those of **1b** (517 nm) and **3b** (438 nm). The orange color was due to closed-ring isomers. The conversion from **2a** to **2b** in the photostationary state under irradiation with 313 nm light was 68%. The color disappeared upon irradiation with visible light ($\lambda > 440$ nm).

The diarylethenes **4a–6a** are of the FR type. **4a** (BFR3) shows photochromism in hexane, and the closed-ring isomer **4b** has an absorption maximum at 469 nm in hexane.[15] **5a** (FR3-FR2) showed photochromism in hexane (Figure 2b). The conversion from **5a** to **5b** in the photostationary state under irradiation with 313 nm light was 55%. The absorption coefficient of **5b** at the absorption maximum (409 nm) was 1.03×10^4 dm^3 mol^{-1} cm^{-1}. The structure of **5b** was the same as that of **2b**, except for the presence of two oxygen atoms instead of sulfur atoms. The absorption maximum of **5b** (409 nm) is shorter than that of **2b** (463 nm), and the wavelength difference between these two compounds is 54 nm.

Similarly to **5a**, **6a** (BFR2) shows photochromism in hexane. Figure 2c shows the photochromic reaction of **6a** in hexane. **6a** had an absorption maximum at 367 nm (ε, 1.80×10^4 dm^3 mol^{-1} cm^{-1}). Upon irradiation with 313 nm light, the pale yellow solution of **6a** turned colorless, whose absorption band was observed at 354 nm. The absorption coefficient of **6b** at 354 nm was 3.6×10^3 dm^3 mol^{-1} cm^{-1}. The absorption maximum of the closed-ring isomer **6b** (354 nm) was shorter than that of the open-ring isomer **6a** (367 nm), as observed in the

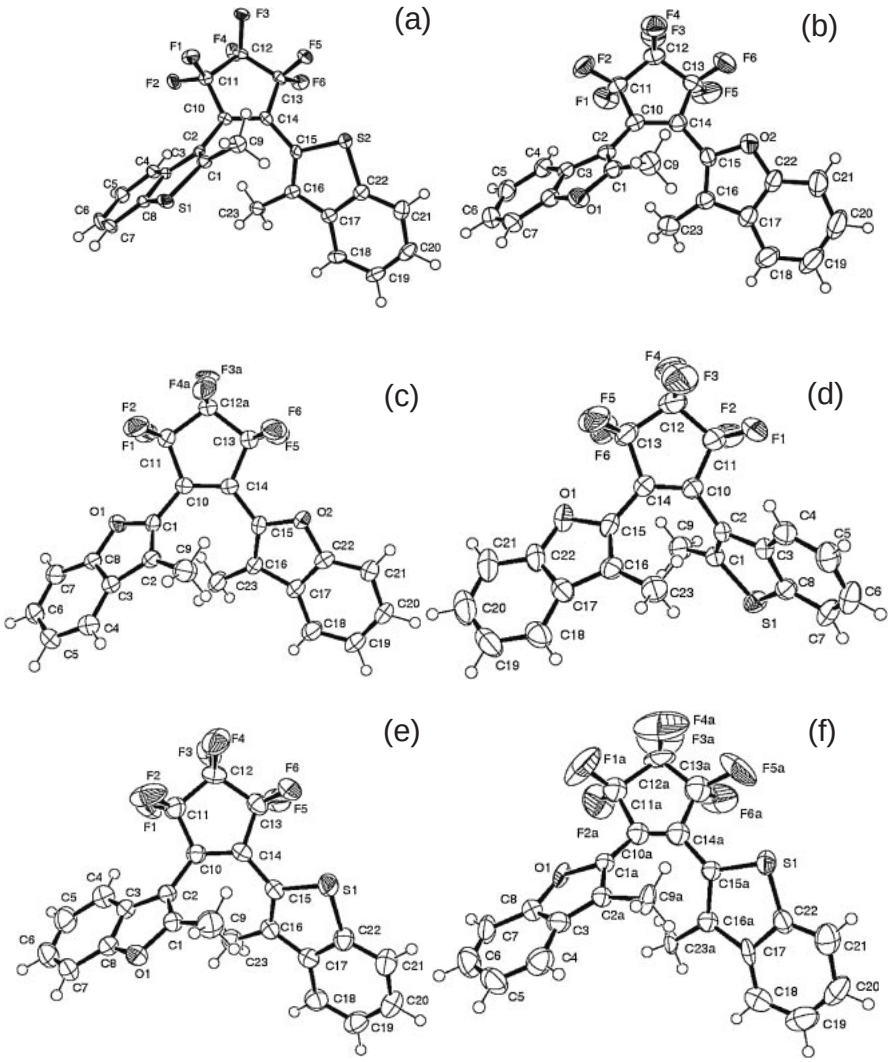

Figure 1. ORTEP drawings of (a) **2a**, (b) **5a**, (c) **6a**, (d) **8a**, (e) **9a**, and (f) **10a** showing 50% probability displacement ellipsoids.

Table 1. Crystal Data of **2a**, **5a**, **6a**, **8a**, **9a**, and **10a**

	2a	**5a**	**6a**	**8a**	**9a**	**10a**
Formula	$C_{23}H_{14}F_6S_2$	$C_{23}H_{14}F_6O_2$	$C_{23}H_{14}F_6O_2$	$C_{23}H_{14}F_6OS$	$C_{23}H_{14}F_6OS$	$C_{23}H_{14}F_6OS$
Formula weight	468.46	436.34	436.34	452.40	452.40	452.40
Temp/K	93(2)	213(2)	213(2)	243(2)	213(2)	123(2)
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	*P*2(1)/*m*	*P*2(1)/*c*	$P\bar{1}$	*P*2(1)*P*2(1)*P*2(1)	*P*2(1)/*n*	*Cc*
Unit cell dimensions						
a/Å	7.7743(19)	18.321(4)	12.159(4)	7.3625(19)	8.1880(18)	18.920(10)
b/Å	12.778(3)	6.2613(13)	12.168(3)	12.927(3)	11.900(3)	9.115(5)
c/Å	19.947(5)	18.662(4)	14.727(3)	20.956(5)	20.512(4)	11.436(6)
α/deg	90	90	74.216(4)	90	90	90
β/deg	96.081(4)	115.666(3)	74.967(4)	90	95.633(4)	92.265(8)
γ/deg	90	90	65.286(4)	90	90	90
Volume/Å^3	1970.4(8)	1929.6(7)	1878.0(7)	1994.5(9)	1989.0(7)	1970.7(19)
Z	4	4	4	4	4	4
Density (calcd)/g cm^{-3}	1.579	1.502	1.543	1.507	1.511	1.525
Goodness of fit on F^2	1.065	1.034	0.976	1.028	1.034	1.091
Final *R* indices [$I = 2\sigma(I)$]						
*R*1	0.0467	0.0475	0.0527	0.0426	0.0397	0.0586
*wR*2	0.1115	0.1208	0.1499	0.1013	0.0890	0.1620
R indices (all data)						
*R*1	0.0617	0.0711	0.0829	0.0511	0.0694	0.0802
*wR*2	0.1192	0.1332	0.1504	0.1086	0.1030	0.1845

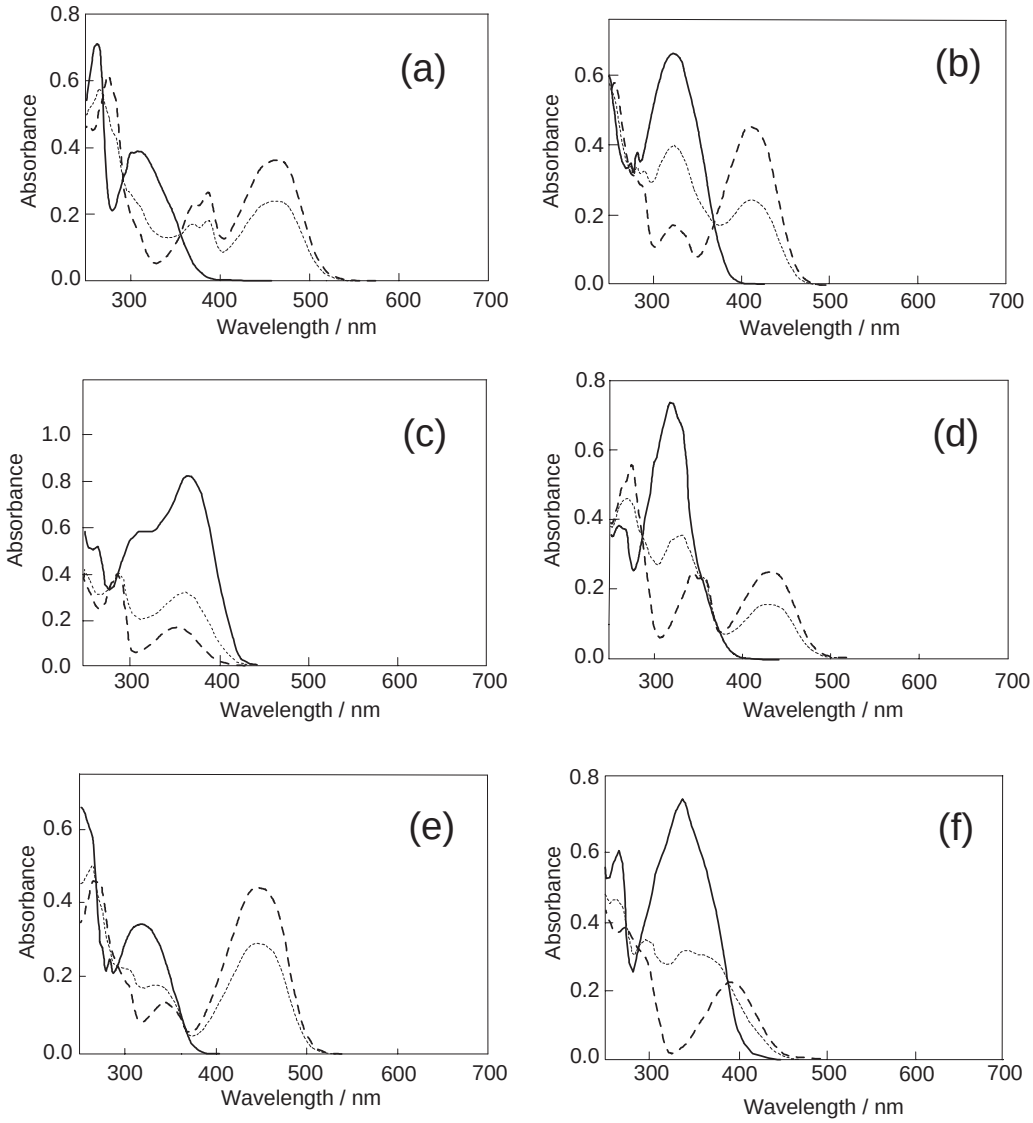

Figure 2. Absorption spectra of (a) **2** (7.0×10^{-5} mol L^{-1}), (b) **5** (4.4×10^{-5} mol L^{-1}), (c) **6** (4.8×10^{-5} mol L^{-1}), (d) **8** (3.7×10^{-5} mol L^{-1}), (e) **9** (3.3×10^{-5} mol L^{-1}), and (f) **10** (4.6×10^{-5} mol L^{-1}) in hexane solution. Solid, dashed, and dotted lines represent **a** (open form), **b** (closed-ring form), and in the photostationary state under irradiation with 313 nm light, respectively.

Table 2. Distances between Reactive Carbon Atoms for **1a–10a** Calculated by X-ray Crystallography and Photochromism Determination in Single-Crystalline Phase

	Distance/nm	Photochromic reaction in single-crystalline phase
1a	0.435	No
2a	0.385	No
3a	0.354	No
4a	0.356	Yes
5a	0.342	Yes
6a	0.361, 0.350	No
7a	0.402	Yes
8a	0.385	No
9a	0.365	Yes
10a	0.346, 0.355	No

1,2-(5-methyl-2-thienyl)perfluorocyclopentene[18] and 1,2-bis-(4-methyl-2-phenyl-5-thiazoyl)perfluorocyclopentene[25] systems. The conversion from an open-ring isomer to a closed-ring isomer was 75% under irradiation with 313 nm light. **6b** did not transform perfectly from **6b** to its original **6a** under irradiation with 285 nm light, because the absorption bands of **6a** and **6b** overlapped. The conversion was 30% under irradiation with 285 nm light. This is the first report that the diarylethenes **5a** and **6a** having 3-methylbenzofuran-2-yl (FR2) unit show photochromism in solution.

7a–10a are of TH-FR type. **7a** (TH3-FR3) and **7b** have absorption maxima in hexane at 281 and 493 nm, respectively.[14]

Figure 2d shows the photochromic reaction of **8** (TH3-FR2) in hexane. Upon irradiation with 313 nm light, the colorless solution of **8a** turned yellow, whose visible absorption band was observed at 430 nm. The absorption coefficient of **8b** at 430 nm was 0.66×10^4 dm^3 mol^{-1} cm^{-1}. The conversion from **8a** to **8b** in the photostationary state under irradiation with

Table 3. Absorption Maxima and Coefficients of Open- and Closed-Ring Forms of **1–10** and Quantum Yields of Cyclization and Cycloreversion Reactions in Hexane Solution

Compound	$\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1}		Quantum yield		Conversion
	a	**b**	Cyclization	Cycloreversion	
1	1.4 (258 nm)	0.91 (517 nm)	0.35 (313 nm)	0.35 (517 nm)	47% (313 nm)
2	1.03 (309 nm)	0.96 (463 nm)	0.38 (313 nm)	0.51 (436 nm)	68% (313 nm)
3	1.37 (325 nm)	0.65 (438 nm)	0.46 (313 nm)	0.47 (436 nm)	63% (313 nm)
4	1.00 (274 nm)	1.44 (469 nm)	0.38 (313 nm)	0.35 (469 nm)	48% (313 nm)
5	1.52 (322 nm)	1.03 (409 nm)	0.18 (313 nm)	0.59 (405 nm)	55% (313 nm)
6	1.80 (367 nm)	0.36 (354 nm)	0.18 (313 nm)	0.58 (313 nm)	75% (313 nm) 30% (285 nm)
7	1.13 (281 nm)	1.53 (493 nm)	0.32 (313 nm)	0.25 (493 nm)	47% (313 nm)
8	2.00 (317 nm)	0.66 (430 nm)	0.11 (313 nm)	0.55 (436 nm)	56% (313 nm)
9	1.04 (317 nm)	1.33 (445 nm)	0.37 (313 nm)	0.51 (436 nm)	67% (313 nm)
10	1.62 (338 nm)	0.48 (393 nm)	0.25 (313 nm)	0.55 (313 nm)	73% (313 nm)

313 nm light was 56%. The color disappeared after irradiation with visible light ($\lambda > 420$ nm).

Similarly to **8**, **9** (FR3-TH2) shows photochromism in hexane (Figure 2e). The conversion from **9a** to **9b** in the photostationary state under irradiation with 313 nm light was 67%. The absorption coefficient of **9b** at 445 nm was 1.33×10^4 dm^3 mol^{-1} cm^{-1}. The molar absorption coefficient of **9b** is twofold that of **8b**.

Theoretical calculations of the absorption bands of the closed-ring isomers **8b** and **8b** were carried out with Gaussian 03.[26,27] The calculated wavelengths of **8b** were 441.90 nm ($f = 0.1282$) and 356.14 nm ($f = 0.1004$), and those of **9b** were 452.10 nm ($f = 0.2338$) and 347.17 nm ($f = 0.0428$). The absorption wavelengths correlated well with the experimental wavelengths.

Figure 2f shows the photochromic reaction of **10** (TH2-FR2) in hexane. The absorption coefficient of **10b** at 393 nm was 0.48×10^4 dm^3 mol^{-1} cm^{-1}. The conversion from an open-ring isomer to a closed-ring isomer was 73%. The low conversion upon irradiation with 313 nm light was due to the high molar coefficiency of the open-ring isomer compared with that of the closed-ring isomer at 313 nm.

Table 3 shows a summary of the absorption maxima and the absorption coefficients of the open- and closed-ring isomers of **1–10** in hexane. The cyclization and cycloreversion quantum yields were measured and are also included in Table 3. The benzothiophene derivative **1b** showed an absorption maximum at 517 nm in hexane. The absorption maximum showed hypsochromic shifts of as much as 54 nm for **2b** and 79 nm for **3b**.

The benzofuran derivative **4b** showed an absorption maximum at 469 nm in hexane. The absorption maxima of **5b** and **6b** shifted to shorter wavelengths, that is, 409 and 354 nm, respectively.

The cyclization quantum yields of **2** (0.38) and **3** (0.46), which had a 3-methylbenzo[*b*]thiophen-2-yl (TH2) group, increased compared with that of **1** (0.35) in hexane. The benzothiophene diarylethenes having a 3-methylbenzo[*b*]thiophen-2-yl (TH2) group also led to an increase in cycloreversion quantum yield.

The cyclization quantum yields of **5** and **6** (0.18 and 0.18, respectively) were low compared with that of **4** (0.38). Those of the diarylethenes having a 3-methylbenzofuran-2-yl (FR2) were also low. On the other hand, the cycloreversion quantum yields of **5** and **6** were very high (0.58 and 0.59).

7b showed an absorption maximum at 493 nm in hexane.[14] The absorption maxima of the colored isomers shifted to shorter wavelengths after introducing the 3-methylbenzo[*b*]thiophen-2-yl (TH2) or the 3-methylbenzofuran-2-yl (FR2) group. The absorption maximum of **8b** (430 nm) is 63 nm shorter than that of **7b** (493 nm) upon replacement of the 2-methylbenzofuran-3-yl (FR3) group by the 3-methylbenzofuran-2-yl group (FR2). The absorption maximum of **9b** (445 nm) is 48 nm shorter than that of **7b** upon replacement of the 2-methylbenzo[*b*]thiophen-3-yl (TH3) group by the 3-methylbenzo[*b*]thiophen-2-yl (TH2) group. **10b** showed an absorption maximum at 393 nm. This wavelength indicates a hypsochromatic shift of as much as 100 nm compared with that for

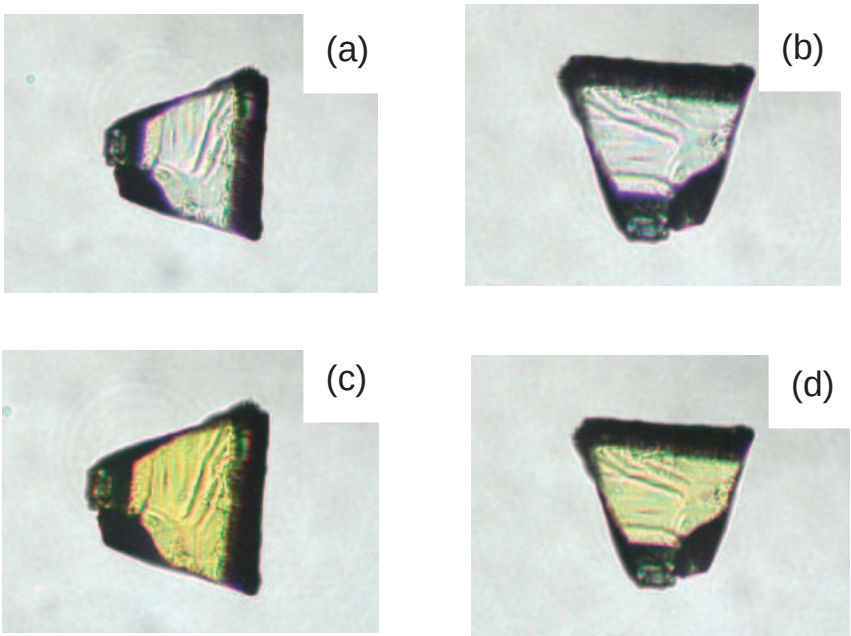

Figure 3. Photographs of single crystal **3a** under polarized light before (a, $\theta = 0°$; b, $\theta = 90°$) and after (c, $\theta = 0°$; d, $\theta = 90°$) irradiation with 365 nm light. θ is the rotation angle of the crystal.

7b (493 nm). The closed-ring isomers of the diarylethene derivatives having one 2-methylbenzofuran (FR3) ring (**4a**, **5a**, **7a**, and **9a**) showed high molar absorption coefficients ($>10^4$ dm^3 mol^{-1} cm^{-1}). The closed-ring isomers of the derivatives having 3-methylbenzo[*b*]thiophene (TH2) and 3-methylbenzofuran (FR2) rings showed low molar absorption coefficients (**3b**: 0.65×10^4 dm^3 mol^{-1} cm^{-1}, **6b**: 0.36×10^4 dm^3 mol^{-1} cm^{-1}, and **10b**: 0.48×10^4 dm^3 mol^{-1} cm^{-1}).

The cyclization quantum yield of **8**, which had the 3-methylbenzofuran-2-yl (FR2) group, decreased (0.11). The cyclization quantum yield of **9**, which had the 3-methylbenzo[*b*]thiophen-2-yl (TH2) group, increased (0.37). The cyclization quantum yield of **10** was between (0.25) those of **8** and **9**. The cycloreversion quantum yields of **8**–**10** (0.51–0.55) were higher than that of **7** (0.25). In summary, the diarylethenes having TH2 or FR2 structures had high their cycloreversion quantum yields (about 0.5), and the high cycloreversion quantum yields led to the low-efficiency cyclization conversion upon UV light irradiation.

Photochromism in Single-Crystalline Phase. Some diarylethene derivatives show photochromic reaction in the single-crystalline phase.[23] An antiparallel conformation and a distance shorter than 0.42 nm are necessary conditions for photochromism in the single-crystalline phase. The X-ray crystallography of **1a**–**10a** revealed regioisomer structures and the distances between reactive carbon atoms. **1a**–**10a** were packed in an anti-parallel conformation.

1a shows no photochromism in the crystal phase, because its distance between two reactive carbon atoms is 0.435 nm. The benzothiophene derivatives **2a** and **3a** have distances as short as 0.385 and 0.354 nm, respectively. Although these distances are within 0.42 nm, these compounds show no photochromism in the crystalline phase under irradiation with 365 nm. It has been reported that single crystals of 1,2-bis(3-ethylbenzo[*b*]thiophen-2-yl)perfluorocyclopentene show no photochromism in the single-crystalline phase, in spite of the distance is 0.393 nm.[28] Crystals of the diarylethenes show no fluorescence in the single-crystalline phase upon irradiation with 313 nm light and 366 nm light. The energy received upon light irradiation may be deactivated by a nonradiative process in the crystalline phase.

However, the benzofuran derivatives **4a** and **5a** show photochromism in the single-crystalline phase. Figure 3 shows photographs of the single-crystal photochromism of **5a** observed under polarized light. The crystal surface is the (010) face. Before photoirradiation, the crystal was colorless (Figures 3a and 3b). Upon irradiation with 365 nm light, the crystal became yellow at a certain angle (Figure 3c). When the crystal was rotated by 90°, it became pale yellow. The yellow color reappeared at 180°. The clear dichroism indicates that the photochromic reaction proceeds in the crystal lattice. Upon irradiation with 420 nm light, the crystal became colorless.

Figure 4 shows the polarized absorption spectra of UV-irradiated single crystals of **5** at (a) 0 and (b) 90°, and polar plots of absorbance at 400 nm. The absorption maximum of the colored crystals of **5b** is 400 nm. The absorption band of the colored isomer showed a hypsochromic shift in comparison with the spectrum in hexane. The compounds **4a** and **5a** having 2-methylbenzofuran (FR3) rings efficiently underwent photochromism in the single-crystalline phase.

The above law in the crystalline phase is applicable to the TH-FR system (**7a**–**10a**). The diarylethenes **7a** and **9a**, which have the 2-methylbenzofuran (FR3) ring, show the efficient photochromic reactions in the single-crystalline phase. Figure 5a shows the polarized absorption spectra of **9** after irradiation with 365 nm light under a polarized microscope. Figure 5b shows a polar absorbance plot of **9** at 450 nm. The observed crystal surface is the (010) face, which is a well-developed face. Upon irradiation with 365 nm light, the crystal became orange at a certain angle. When the crystal was rotated

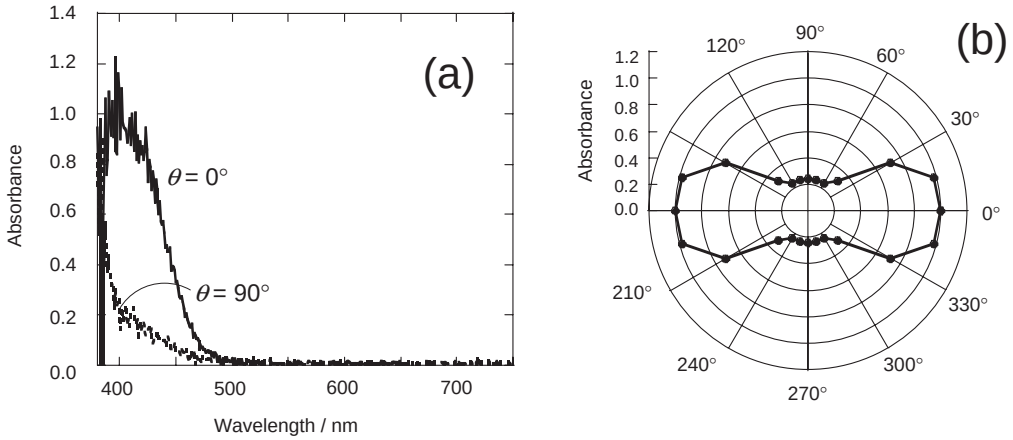

Figure 4. (a) Polarized absorption spectra and (b) polar plots at 400 nm of colored crystal of **5**.

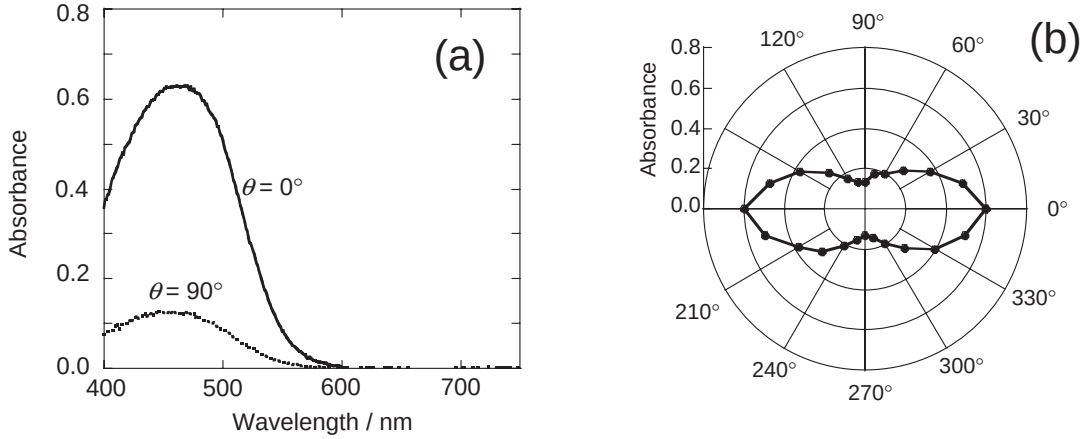

Figure 5. (a) Polarized absorption spectra and (b) polar plots at 450 nm of colored crystal of **9**.

by 90°, it became pale orange. The orange color reappeared at 180°. A clear dichroism was observed by rotating the single crystal. These results support the finding that the photochromism of **9** occurs in the single-crystalline phase.

On the other hand, **8a** and **10a**, which have no 2-methylbenzofuran (FR3) ring, show no photochromism in the single-crystalline phase under the microscope. Although the distance between the reactive carbon atoms are within 0.42 nm, for example, for **2a**, **3a**, **6a**, **8a**, and **10a**, no photochromic reaction occurred in the single-crystalline phase. We found that the diarylethenes **4a**, **5a**, **7a**, and **9a** having 2-methylbenzofuran (FR3) ring show photochromism in the single-crystalline phase.

Conclusion

We have synthesized diarylethene regioisomers (**1a**–**10a**) having benzothiophene and benzofuran heteroaryl groups, and examined their structure by X-ray crystallography. Their photochromic properties were examined in solution as well as in the single-crystalline phase. All the compounds showed photochromism in hexane, especially the diarylethenes **5a**, **6a**, **8a**, and **10a** having a 3-methylbenzofuran-2-yl (FR2) unit. For **6**, that has two 3-methylbenzofuran-2-yl) units (BFR2), its closed-ring isomer **6b** (367 nm) had a shorter absorption maximum than its of the open-ring isomer **6a** (354 nm). The closed-ring isomer of the diarylethene derivatives having one 2-methylbenzofuran (FR3) ring (**4a**, **5a**, **7a**, and **9a**) showed a high molar absorption coefficient ($>10^4$ dm^3 mol^{-1} cm^{-1}) at the absorption maximum wavelength in hexane. For example, **9b** had a molar absorption coefficient (ε: 1.33×10^4 dm^3 mol^{-1} cm^{-1}) twofold that of **8b** (ε: 0.66×10^4 dm^3 mol^{-1} cm^{-1}). The cyclization/cycloreversion quantum yields varied depending on the presence of benzothiophene and benzofuran rings. In particular, the cyclization quantum yield of **8** (0.11) is threefold that of **9** (0.37).

Although the distance between two reactive carbons was within 0.42 nm, diarylethenes that have no 2-methylbenzofuran (FR3) ring such as **2a**, **3a**, **6a**, **8a**, and **10a** showed no photochromic reactions in the single-crystalline phase. The diarylethene derivatives having one 2-methylbenzofuran (FR3) ring (**4a**, **5a**, **7a**, and **9a**) efficiently showed photochromism in the single-crystalline phase.

Experimental

General. The solvents used were of spectrophotometric grade and were purified by distillation before use. Absorption spectra in solution were measured with a Hitachi UV-3500 spectrophotometer. Absorption spectra in the single-crystalline phases were measured using an OPTI-POL 2POL polarizing microscope connected to a Hamamatsu PMA-11 detector. Mercury lamp (Ushio, 500 W) and mercury-xenon lamp (Moritex, 200 W) were used as the light source. Light of appropriate wavelength was iso-

lated by passing light through a monochromator (JOBIN YVON H-10 UV) or band pass (L-42 and Y-44) filters. ^{1}H NMR was recorded on a Gemini 200 spectrometer (200 MHz) with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. X-ray crystallography was carried out using a Bruker SMART CCD X-ray diffractometer.

1-(2-Methylbenzo[*b*]thiophen-3-yl)-2-(3-methylbenzo[*b*]thiophen-2-yl)perfluorocyclopentene (2a). To a stirred THF solution (40 mL) containing 3-methylbenzo[*b*]thiophene (0.50 g, 3.4 mmol) was slowly added 2.3 mL of 1.6 M *n*-BuLi hexane solution (3.7 mmol) at −78 °C, and the solution was stirred for 15 min at −78 °C. Then, 1-(2-methylbenzo[*b*]thiophen-3-yl)heptafluorocyclopentene (1.1 g, 3.4 mmol) was added slowly to the reaction mixture at −78 °C, and left to stand with stirring at −78 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 0.722 g of **2a** in 46% yield.

2a: colorless crystals; mp 173–174 °C; ^{1}H NMR (200 MHz): δ 2.06 (s, 3H), 2.36 (s, 3H), 7.26–7.40 (m, 4H), 7.56–7.61 (m, 2H), 7.70–7.75 (m, 2H). Ms (EI) *m*/*z*: [M$^+$] 468. Anal. Calcd for $C_{23}H_{14}F_6S_2$: C, 58.97; H, 3.01%. Found: C, 58.96; H, 3.00%. CCDC deposition number: 662654. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

1-(3-Methylbenzofuran-2-yl)-2-(2-methylbenzofuran-3-yl)perfluorocyclopentene (5a). The coupling reaction of 3-methylbenzofuran (0.50 g, 3.8 mmol), 1.6 M *n*-BuLi (2.6 mL, 4.2 mmol), and 1-(2-methylbenzofuran-3-yl)heptafluorocyclopentene (1.23 g, 3.8 mmol) was performed as described for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.578 g of **5a** in 35% yield.

5a: colorless crystals; mp 110–111 °C; ^{1}H NMR (200 MHz): δ 1.87 (s, 3H), 2.21 (s, 3H), 7.14–7.48 (m, 8H). Ms (EI) *m*/*z*: [M$^+$] 436. Anal. Calcd for $C_{23}H_{14}F_6O_2$: C, 63.31; H, 3.23%. Found: C, 63.19; H, 3.22%. CCDC deposition number: 662653.

1,2-Bis(3-methylbenzofuran-2-yl)perfluorocyclopentene (6a). The coupling reaction of 3-methylbenzofuran (0.50 g, 3.8 mmol), 1.6 M *n*-BuLi (2.6 mL, 4.2 mmol), and octafluorocyclopentene (0.24 mL, 1.8 mmol) was performed as described for **3a**.[13] The crude product was purified by column chromatography on silica gel (hexane) to give 0.263 g of **6a** in 32% yield.

6a: pale yellow crystals; mp 129–130 °C; ^{1}H NMR (200 MHz) δ 1.91 (s, 6H), 7.09–7.57 (m, 8H). Ms (EI) *m*/*z*: [M$^+$] 436. Anal. Calcd for $C_{23}H_{14}F_6O_2$: C, 63.31; H, 3.23%. Found: C, 63.22; H, 3.23%. CCDC deposition number: 662652.

1-(3-Methylbenzofuran-2-yl)-2-(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene (8a). The coupling reaction of 3-methylbenzofuran (0.50 g, 3.8 mmol), 1.6 M *n*-BuLi (2.6 mL, 4.2 mmol), and 1-(2-methylbenzo[*b*]thiophen-3-yl)heptafluorocyclopentene (1.23 g, 3.8 mmol) was performed as described for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.647 g of **8a** in 38% yield.

8a: colorless crystals; mp 117–118 °C; ^{1}H NMR (200 MHz) δ 1.98 (s, 3H), 2.37 (s, 3H), 7.14–7.51 (m, 7H), 7.74–7.78 (m, 1H). Ms (EI) *m*/*z*: [M$^+$] 452. Anal. Calcd for $C_{23}H_{14}F_6OS$: C, 61.06; H, 3.12%. Found: C, 61.03; H, 3.08%. CCDC deposition number: 638173.

1-(2-Methylbenzofuran-3-yl)-2-(3-methylbenzo[*b*]thiophen-2-yl)perfluorocyclopentene (9a). The coupling reaction of 3-methylbenzo[*b*]thiophene (1.0 g, 6.7 mmol), 1.6 M *n*-BuLi (4.6 mL, 7.4 mmol), and 1-(2-methylbenzofuran-3-yl)heptafluorocyclopentene (2.2 g, 6.7 mmol) was performed as described for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 1.28 g of **9a** in 42% yield.

9a: colorless crystals; mp 122–123 °C; ^{1}H NMR (200 MHz) δ 1.91 (s, 3H), 2.11 (s, 3H), 7.16–7.60 (m, 6H), 7.79–7.84 (m, 2H). Ms (EI) *m*/*z*: [M$^+$] 452. Anal. Calcd for $C_{23}H_{14}F_6OS$: C, 61.06; H, 3.12%. Found: C, 61.00; H, 3.06%. CCDC deposition number: 638172.

1-(3-Methylbenzofuran-2-yl)heptafluorocyclopentene (11). To a stirred THF solution (20 mL) containing 3-methylbenzofuran (1.0 g, 7.6 mmol) was slowly added 5.2 mL of 1.6 M *n*-BuLi hexane solution (8.3 mmol) at −78 °C, and the solution was stirred for 15 min at −78 °C. Then, the solution was slowly added dropwise to a mixture of octafluorocyclopentene (2.0 mL, 15 mmol) and THF (20 mL) at −78 °C, and left to stand with stirring at −78 to 30 °C for 12 h. The reaction mixture was poured into 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 1.37 g of **11** in 59% yield.

11: colorless liquid; ^{1}H NMR (200 MHz) δ 2.44 (s, 3H), 7.31–7.35 (m, 1H), 7.43–7.47 (m, 1H), 7.52–7.54 (m, 1H), 7.61–7.63 (m, 1H). HRMS *m*/*z*: [M$^+$] 324.0374. Calcd for $C_{14}H_7F_7O$ 324.0385.

1-(3-Methylbenzofuran-2-yl)-2-(3-methylbenzo[*b*]thiophen-2-yl)perfluorocyclopentene (10a). The coupling reaction of 3-methylbenzo[*b*]thiophene (0.5 g, 3.4 mmol), 1.6 M *n*-BuLi (2.2 mL, 3.5 mmol), and **11** (1.1 g, 3.4 mmol) was performed as described for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.594 g of **10a** in 39% yield.

10a: pale yellow crystals; mp 167–168 °C; ^{1}H NMR (200 MHz) δ 1.84 (s, 3H), 1.91 (s, 3H), 7.22–7.27 (m, 2H), 7.36–7.48 (m, 4H), 7.66–7.68 (m, 1H), 7.86–7.88 (m, 1H). Ms (EI) *m*/*z*: [M$^+$] 452. Anal. Calcd for $C_{23}H_{14}F_6OS$: C, 61.06; H, 3.12%. Found: C, 61.02; H, 3.10%. CCDC deposition number: 638174.

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