Dyes and Pigments 89 (2011) 223–229

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Highly diastereoselective photochromic ring closure of bisbenzothienylethenes possessing dual fluorinated stereocontrollers

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ARTICLE INFO

Article history:
Received 30 December 2009
Received in revised form
1 March 2010
Accepted 5 March 2010
Available online 15 March 2010

Keywords:
Photochromism
Diarylethene
Diastereoselectivity
Allylic strain
Fluoroalkanoyl group
Electrocyclization

ABSTRACT

Three regioisomeric bisbenzothienylethenes equipped with two (*R*)-pentafluoropropanoyloxyethyl groups on both ends of the hexatriene moiety displayed high diastereoselectivity towards light-induced 6π-electrocyclization reactions, particularly in polar solvents. In non-polar solvents such as hexane and octafluorotoluene, however, diastereoselectivity was not very high owing to the fluorophobic or less fluorophilic interactions, respectively, between the fluoroalkanoyl side chains and the solvent molecules.

1. Introduction

Diarylethenes [1,2] are a representative group of thermally irreversible photochromic compounds based on the 6π-electrocyclization reaction between a hexatriene and cyclohexadiene (Scheme 1) [1–3]. Since transformation from the former to the latter generates two sp^3 carbon atoms, a pair of enantiomers is produced by photochemical conrotatory ring closure. If the compound has at least one intrinsic chirality within the molecule, transformation can produce a pair of diastereomers with a biased ratio when the intrinsic chirality affects the cyclization reaction to a certain extent.

In a previous paper, it was shown that diarylethenes **1**–**3** (Scheme 2), possessing two chiral substituents on the terminal carbon atoms of the hexatriene moiety, displayed extremely high diastereoselectivity – up to 100/0 diastereomer ratio (dr) – when optimal conditions such as the kind of solvent used and the reaction temperature were selected [4]. Together with previous reports concerning **4** [5] and **5** [6] (Scheme 2) in which only one stereocontroller was introduced, it was noticed that both steric and electronic repulsion between the methoxymethoxy (MOMO) groups in **1**–**3** were effective in anchoring the conformation of the colorless open form at the ground state. This finding prompted the use of electronically richer substituents than the MOMO group, in which context, it was decided to employ perfluoroalkyl groups in which each fluorine atom is densely covered with electrons so that repulsive interactions between the side chains would be large. This paper reports the improvement of the diastereoselectivity of ring closure for diarylethenes **6**–**8** (Scheme 2) imparted by using chiral substituents bearing pentafluoropropanoate esters on both ends of the hexatriene moiety, and the effects of both the solvent used and temperature on their diastereoselectivity of photochromic ring closure.

2. Results and discussion

2.1. Molecular design

Previously, we have shown that the two chiral MOMO groups (dual stereocontroller) on both ends of the hexatriene moiety within a bisbenzothienylethene molecule are extremely effective in attaining unprecedented high diastereoselectivity in photoinduced 6π-electrocyclization reactions [4]. The high selectivity thus achieved is attributable to both electronic as well as steric repulsive interactions between two MOMO groups when the molecules take a photochemically cyclizable conformation in which two MOMO groups come closer to each other (Scheme 3). Although the steric repulsion between two MOMO groups is larger than that between

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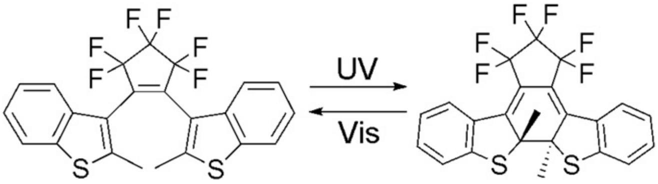
doi:10.1016/j.dyepig.2010.03.008



Scheme 1. Photochromism of bisbenzothienylethene.

two methyl groups, the electronic repulsion between the MOMO groups is expected to be much larger than that between the methyl groups.

In order to increase the diastereoselectivity, the number of heteroatoms on the side chains with large number of lone pairs should be increased. Although halogen atoms such as iodine, bromine, and chlorine are suitable from the viewpoint of both their steric as well as electronic nature, they are unstable towards photochemical or thermal treatments. For other heteroatoms such as nitrogen, sulfur, or phosphorus, it is difficult to put several atoms on the limited space of side chains. However, the fluorine atom fulfills all the requirements. A fluorine atom has three lone pairs, the largest value of electronegativity, good side chain packing allowance of several atoms, and high stability towards photochemical as well as thermal reactions. We also selected the ester functional group to connect the chiral hydroxyethyl group and the fluoroalkyl group, because it has two additional oxygen atoms which can work as the electronically repulsive functional group.

As the benzothienyl groups can be connected to the central ethene moiety either at the C2 or C3 carbon atoms, we decided to synthesize and examine the diastereoselectivity for compounds **6**–**8**, in order to see whether this strategy is common to all the bisbenzothienylethenes.

2.2. Synthesis

Optically pure (*R*)-1-methoxymethoxyethyl-substituted 1,2-bisbenzothienylethenes **1**–**3** were synthesized according to methods we have already reported [4]. Cleavage of two MOM groups to produce the corresponding alcohols **9**–**11** followed by their esterification with 2,2,3,3,3-pentafluoropropanoic acid using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and DMAP in dichloromethane afforded the corresponding diesters **6**–**8** (Scheme 4). Their structures were fully characterized by ^{1}H NMR, IR, MS, and UV–Vis spectra, and their purity was examined by HPLC.

2.3. Photochromic reactions

2.3.1. Photochromic reactions followed by UV–Vis spectra

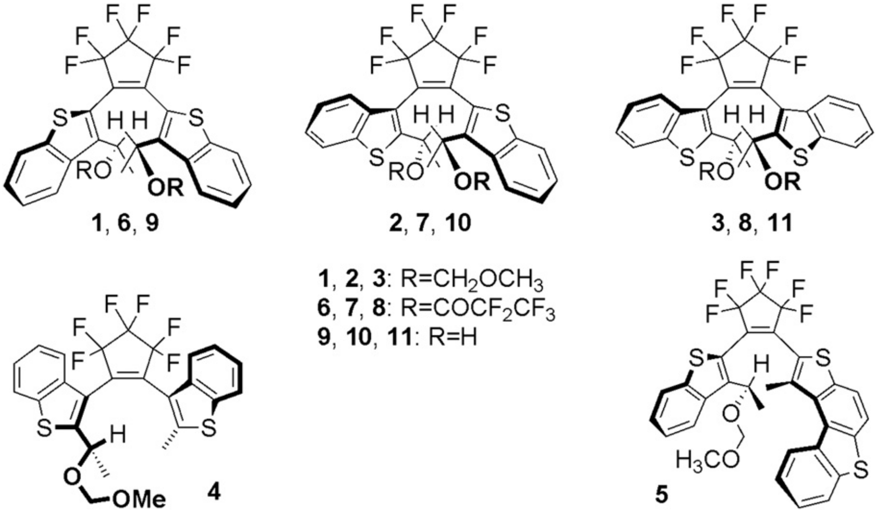
Photochromic reactions of the fluorinated diarylethenes **6**–**8** were first carried out in acetonitrile. They showed changes in their UV–Vis spectra upon UV-light irradiation (366 nm for **6** and 313 nm for **7** and **8**) for the ring closing reactions and visible light irradiation (436 nm for **6**, 483 nm for **7**, and 512 nm for **8**) for the ring opening reactions. Changes in their spectra in acetonitrile are shown in Fig. 1 and the absorption spectral features are shown in Table 1, together with the quantum yields of the photochromic reactions.

2.3.2. HPLC detection of diastereomers

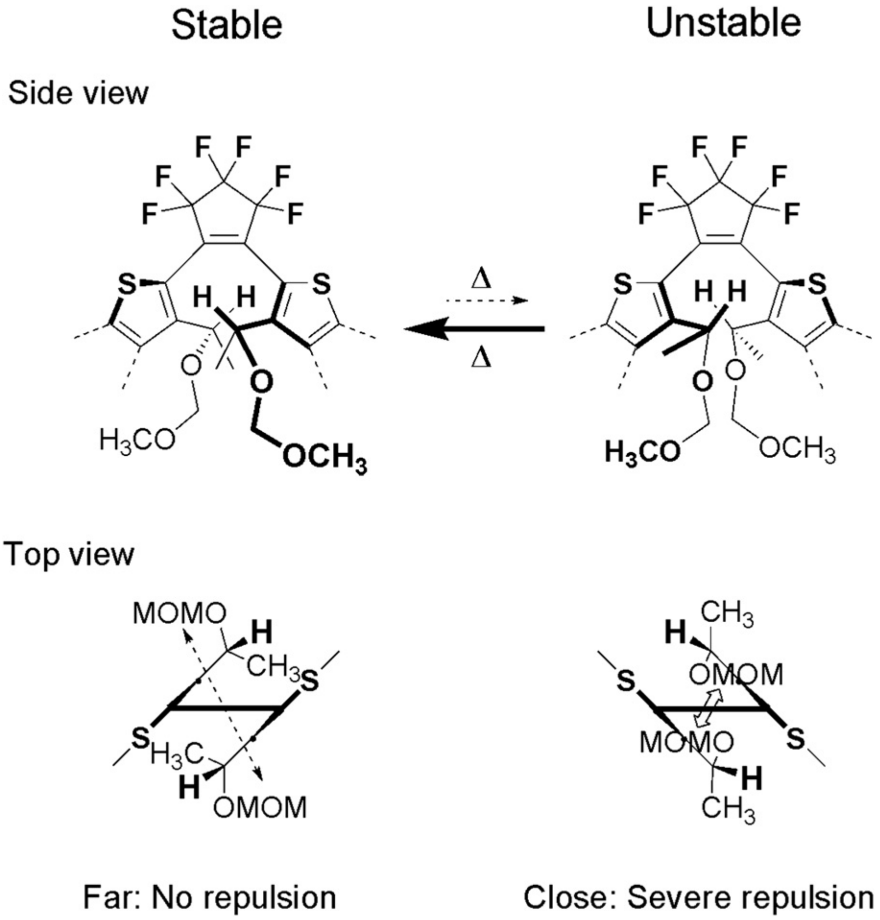
The photochromic reactions at room temperature in various solvents were examined by HPLC equipped with a column packed with a chiral adsorbent (Daicel® CHIRALCEL OD-3). Before UV irradiation, only the colorless open form (O-form) was detected for all of the diarylethenes. Upon UV irradiation, two new peaks appeared when detected at the isosbestic point in the UV region. When the detection of HPLC was carried out at the visible region, peaks corresponding to two diastereomers of the colored closed form (C-form) were observed in a highly biased ratio. Irradiation of visible light to the resultant photostationary state (PSS) solution restored the initial O-form peaks. The HPLC chromatograms of **6**–**8** in acetonitrile are shown in Fig. 2.

We examined the diastereoselectivity of photochemical ring closing reactions in several solvents with different polarity. The results together with the solvent polarity values E_T^N [7] are shown in Table 2.

In ethyl acetate at room temperature, the diastereomer ratio of **1**, **2**, and **3** possessing two (*R*)-methoxymethoxyethyl groups are 99/1, 99/1, 97.5/2.5, respectively. Although the selectivity of **6** and **7** possessing two (*R*)-pentafluoropropanoyloxyethyl groups are slightly lower than the structurally corresponding **1** and **2**, that for **8**, which belongs to the well-investigated 1,2-bis(3-benzothienyl) ethene, is superior to the corresponding compound **3**. Thus, the concept of a dual stereocontroller works to achieve no less than 99/1 selectivity at room temperature when the optimal type of solvent and substituents are selected.



Scheme 2. Chiral diarylethenes appearing in this article.



Scheme 3. Origin of high diastereoselectivity exemplified by diarylethene **1**.

2.4. Solvent effects on diastereoselectivity

There are several remarkable features we can extract from Table 2.

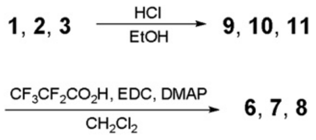
(i) The diastereoselectivity of ring closure in polar solvents are higher than that in less polar solvents.
(ii) The diastereoselectivity of **6** in hexane and octafluorotoluene are particularly low, and that of **7** in these solvents are relatively low. In contrast, that of **8** is always excellent.
(iii) The diastereoselectivity increases in the order of **6** < **7** < **8**.

The first two features can be interpreted by the nature of the perfluoroalkyl substituents. As we expected, the electron-rich substituents interacted with the polar solvent molecules more strongly than with the non-polar solvents. Thus, the more stable conformation of the O-form, in which the fluorinated substituents extend themselves towards the outside of the molecule to interact with the solvent molecules, becomes yet more stable in polar solvents.

Contrarily, in less polar solvents, positive interactions to further stabilize the stable conformer do not work effectively so that the stabilization afforded by the intramolecular interactions between the two fluorinated side chains becomes comparable. This tendency is the most clearly apparent for **6**, with two C2 connections of the benzothienyl groups to the perfluorocyclopentene, and can be observed to a certain extent for **7**, with one C2 connection. However, this tendency is not so prominent for **8**, with no C2 connection to the central ethene moiety. As we previously observed, diarylethene **5** with two C2 connections to the central ethene showed low diastereoselectivity due to the small electronic repulsion between the oxygen atoms on the side chain and the sulfur atom on the other side [6]. In **6**, repulsion between the sulfur atoms and the side chain fluorine atoms does not occur so that the fluorine-containing side chains come inside the molecule to avoid fluorophobic solvents [8] such as hexane. As for **7**, because there is repulsion between the fluorine atoms and the sulfur atom on one side, its selectivity in hexane is lower than **8** in which the repulsion is twice as strong.

Although this tendency is not outstanding in polar solvents, it can still be detected so that the diastereoselectivity is generally higher for **8**, as described in feature (iii) of the system. Although the electronic repulsion between the fluorine atoms and sulfur atom was an additional interaction, it was decisive in making the diastereoselectivity high, particularly in less polar solvents.

A surprising observation we made was that the diastereoselectivity of these diarylethenes in octafluorotoluene was not very high. As the fluorocarbon compounds are known to be fluorophilic rather than fluorophobic [9], the side chains were expected to be pulled out of the molecule so that the diastereoselectivity would be high. However, the results were opposite of our



Scheme 4. Synthetic scheme of diarylethenes **6**–**8**.

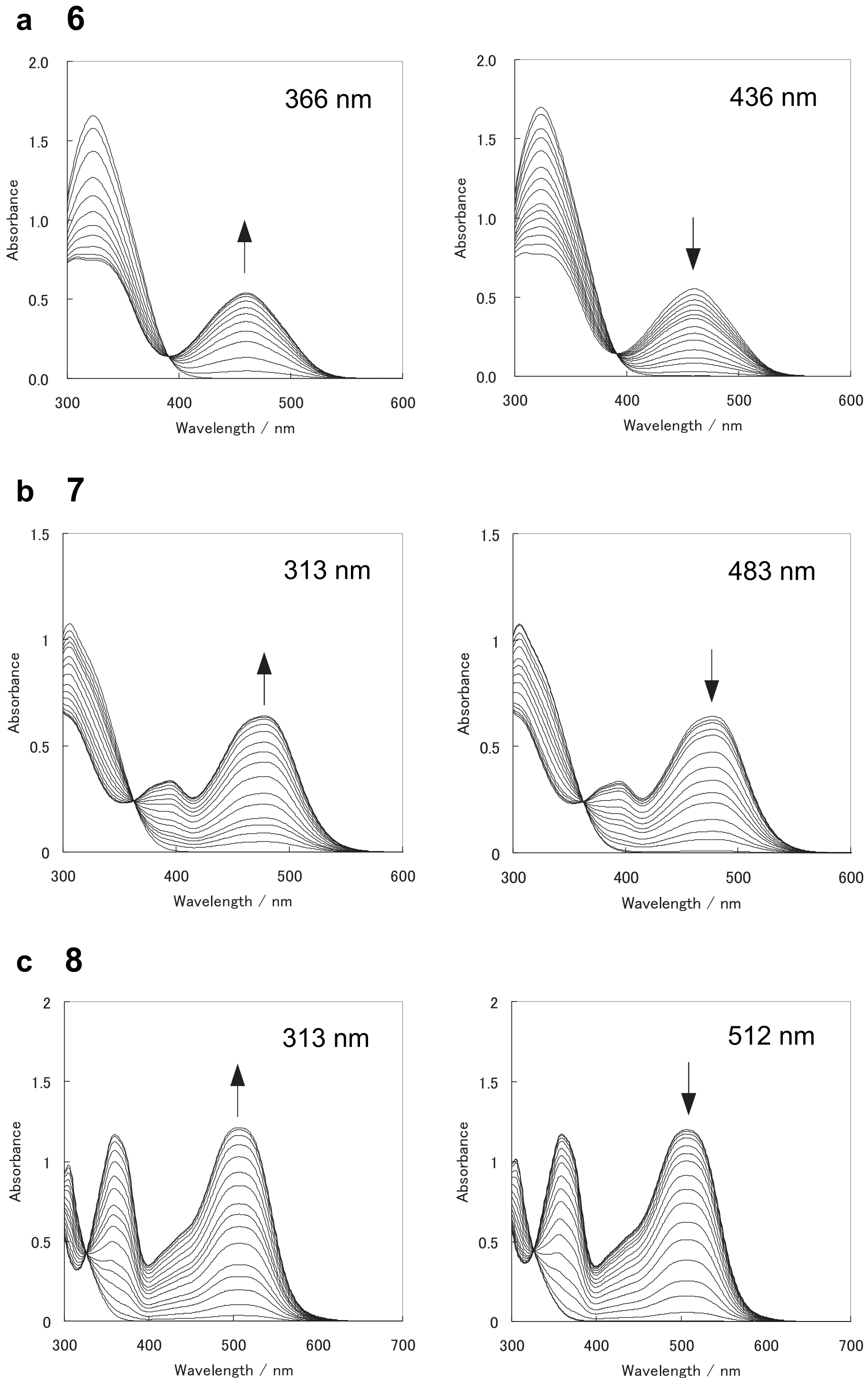


Fig. 1. Absorption spectral changes of diarylethenes **6**, **7**, and **8** by photoirradiation in acetonitrile at room temperature. (a) **6** with 366 nm and 436 nm lights. (b) **7** with 313 nm and 483 nm lights. (c) **8** with 313 nm and 512 nm lights.

expectations. This is because the interaction between octafluorotoluene and the fluorinated side chain is comparable to that between the side chains working intramolecularly.

Thus, although it is not a quantitative consideration, the diastereomer ratio of ca. 75/25 in hexane and octafluorotoluene for **6** suggests that the non-attracting interactions between the solvent and the side chains and that between the side chains are comparable, and that this ratio is a result generated only by the steric effect. As the diastereoselectivity of **7** was almost 93/7 for both solvents, this can be the result of an additional electronic repulsion working between the fluorine atoms and a sulfur atom.

*2.5. Temperature effect on diastereoselectivity of ring closure of **8***

In the previous paper, we observed that **3** showed curious behavior when the temperature of photoirradiation was changed [4]. At r.t., the diastereomer ratio was 97.5/2.5 in ethyl acetate. When the irradiation temperature was cooled down to −70 °C,

Table 1
Spectroscopic data, quantum yields, and conversion ratio of **6**, **7**, and **8** in acetonitrile.

	λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})[a]		Quantum yield			CR/%[g]
	O-form	C-form	Φ_{OC}(UV)	Φ_{CO}(UV)	Φ_{CO}(Vis)	
6	323 (13600)	460 (7280)	0.16[b]	0.81[b]	0.79[d]	62
7	306 (11500)	478 (9310)	0.23[c]	0.25[c]	0.14[e]	74
8	305 (7390)	507 (9660)	0.35[c]	0.26[c]	0.06[f]	94

[a] Unit for M: mol dm^{-3}.
[b] 366 nm.
[c] 313 nm.
[d] 436 nm.
[e] 483 nm.
[f] 512 nm.
[g] Conversion ratio to the C-form at the photostationary state.

Table 2
Solvent effect on the diastereoselectivity of photocyclization of **6**, **7**, and **8** at the photostationary state of UV irradiation.[a]

Solvent	E_T^N	**6** (2,2)	**7** (2,3)	**8** (3,3)
Hexane	0.009	75.2/24.8	92.5/7.5	98.4/1.6
Octafluorotoluene	(0.108)[b]	75.4/24.6	93.5/6.5	98.7/1.3
THF	0.207	98.5/1.5	98.2/1.8	99.2/0.8
Ethyl Acetate	0.228	97.9/2.1	98.2/1.8	99.5/0.5
Acetonitrile	0.460	98.8/1.2	98.9/1.1	99.7/0.3

[a] 366 nm light for **6**, 313 nm light for **7** and **8**.
[b] Value of hexafluorobenzene.

it became 94.5/5.5. In contrast, when the reaction temperature was raised to 67 °C, the ratio became as high as 99/1. This is not in good agreement with the widely accepted view of chemists: When the population (ratio) of the conformers of the O-form directly corresponds to the ratio of the diastereomers of the C-form, the diastereomer ratio of the C-form becomes higher as the temperature is lowered. This is due to the increase in the ratio of the more stable conformer of the O-form when the ratio of O-form conformers is governed by the Boltzmann distribution. Since the reason why this reversal phenomenon occurs is presently under investigation, we are interested in the temperature dependence of the diastereoselectivity upon photoirradiation of **8**. The results carried out in ethyl acetate are shown in Table 3.

It is obvious that **8** showed normal behavior in variable temperature experiments. The diastereomer ratio of the C-form becomes higher when the temperature was lowered. In order to clarify the nature of these phenomena, the ^{1}H NMR behaviors of **3** and **8** at different temperatures are now under investigation.

3. Experimental

3.1. General

Chemical reactions were carried out under a dry nitrogen atmosphere. Dichloromethane was freshly distilled from calcium hydride immediately before use. All other solvents were used as received. All flash column chromatography were carried out on 230–400 mesh silica gel using ethyl acetate and hexane as eluent. Analytical thin-layer chromatography was performed on the precoated 0.25-mm thick silica gel TLC plates.

^{1}H NMR spectra were recorded in deuteriochloroform ($CDCl_3$) with a 300 MHz spectrometer. *J* values are expressed in Hz and quoted chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Infrared spectra (IR) were recorded on an FT-IR spectrometer equipped ATR. Low- and high-resolution mass spectra were measured by the electron impact and fast atom bombardment mass spectrometry using a Mass spectrometer. Ultraviolet and visible spectra were recorded on a UV/Vis spectrophotometer. Melting points were measured using hot stage microscope, and those were uncorrected.

The syntheses of **1*O***, **2*O***, and **3*O*** were described elsewhere [4].

Photochemical reactions were all carried out in a 10-mm path length quartz cell. Photoirradiation with 313-nm light was carried out using a 500-W high-pressure mercury lamp, separated by filters (a 5 cm water filter, a UV-D35 glass filter, a 5-cm aqueous $NiSO_4$ $6H_2O$ solution, a 1-cm aqueous K_2CrO_4 solution, and a 1-cm aqueous potassium diphthalate solution). Photoirradiation with 366-nm light was carried out with a 500-W high-pressure mercury lamp, separated by filters (a 5-cm water filter, a 5-cm aqueous $CuSO_4$ $5H_2O$ solution, a UV-35 glass filter, a UV-D35 glass filter, and a UV-D36A glass filter). Photoirradiation with 436-nm light was carried out with a 500-W high-pressure mercury lamp, separated by filters (a 5-cm water filter, a V-40 glass filter, a Y-43 glass filter, and a V-44 glass filter). Photoirradiation with 483-nm light was carried out with a 500-W xenon lamp, separated by filters (a 5-cm water filter, a 5-cm toluene filter, an IRA-25S glass filter, a Y-47 glass

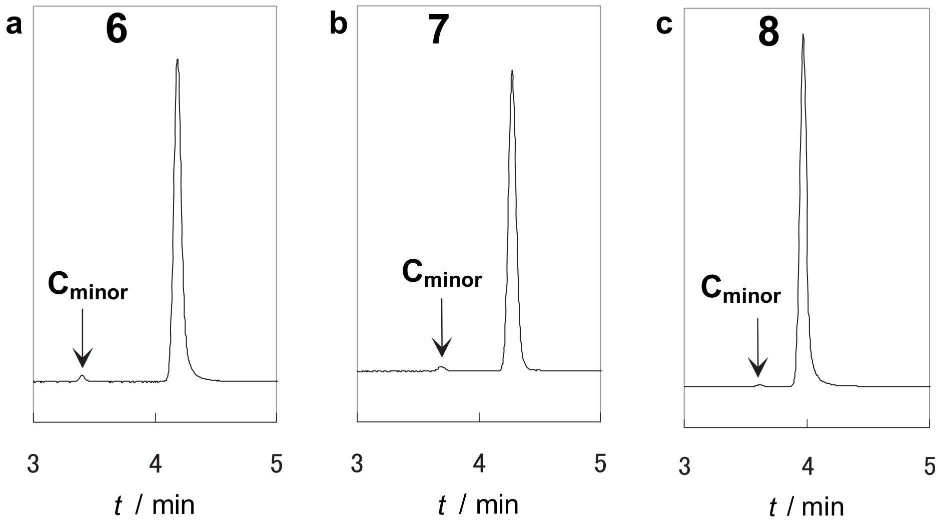


Fig. 2. HPLC chromatograms of diarylethenes **6**, **7**, and **8** at the photostationary state of UV irradiation in acetonitrile at room temperature. (a) **6** with 366 nm light; (b) **7** with 313 nm light; (c) **8** with 313 nm light. Column: Daicel Chiralcel OD-3, Solvent: 10% 2-propanol/hexane. Detection: at the λ_{max} wavelengths of their C-forms.

Table 3
Temperature effect of diastereoselectivity of ring closure of **8**.

Temperature	Diastereomer ratio	CR/%[a]
66 °C	96.2/3.8	91.9
R.t.	99.5/0.5	95.7
−73 °C	99.6/0.4	99.5

[a] Conversion ratio to the C-form at the photostationary state.

filter, and a KL-47 interference glass filter). Photoirraidation with 512-nm light was carried out with a 500-W xenon lamp, separated by filters (a 5-cm water filter, a Pyrex glass filter, an IRA-25S glass filter, a Y-47 glass filter, and a KL-50 interference glass filter). During the photoreaction, solutions in the cell were stirred continuously.

High-performance liquid chromatography equipped with a UV/Vis detector and a chiral column (Daicel chiralcel OD-3, 4.6 mm diameter × 250 mm) was used to determine the conversion ratios and the diastereomer excess values of diarylethenes.

3.2. Synthesis of diarylethenes

3.2.1. 1,2-bis-{(R)-3-(1-hydroxyethyl)-2-benzo[b]thienyl}hexafluorocyclopentene (**9**)

A solution of 1,2-bis-{(*R*)-3-(1-methoxymethoxyethyl)-2-benzo[b]thienyl}hexafluorocyclopentene (**1**) (269.8 mg, 0.417 mmol, 1.0 eq) and aqueous 3 mol dm^{-3} HCl (3.0 mL) in ethanol (20 mL) was refluxed for 6 h. After the solution was stirred at room temperature overnight, the reaction was quenched by adding aqueous $NaHCO_3$, and the resultant mixture was extracted with AcOEt three times. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography on silica gel using AcOEt/hexane (15%) as the eluent, to give 220.1 mg (0.417 mmol) of compound **9** as a viscous pale yellow liquid in 100% yield.

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ/ppm 1.45 (d, *J*/Hz = 6.6, 6H), 2.08 (s, 2H), 5.07 (q, *J*/Hz = 6.4, 2H), 7.32–7.41 (m, 4H), 7.78–7.84 (m, 2H), 8.00–8.07 (m, 2H).

IR (neat) ν/cm^{-1} 3332, 2982, 1339, 1066, 757.

LRMS (EI, 70 eV) m/z, 528 (M$^+$), 484, 467, 419.

Found: m/z 528.0677. Calcd for $C_{25}H_{18}F_6O_2S_2$: M, 528.0652.

3.2.2. 1,2-bis-{(R)-3-(1-pentafluoropropanoyloxyethyl)-2-benzo[b]thienyl}hexafluorocyclopentene (**6O**)

To a solution of 1,2-bis-{(*R*)-3-(1-hydroxyethyl)-2-benzo[b]thienyl}hexafluorocyclopentene (**9**) (195.5 mg, 0.370 mmol, 1.0 eq) and 4-dimethylaminopyridine (47.8 mg, 0.391 mmol, 1.1 eq) in anhydrous CH_2Cl_2 (15 mL) was added pentafluoropropanoic acid (0.260 mL, 2.47 mmol, 6.7 eq) at 0 °C under a nitrogen atmosphere, and the solution was stirred for 1 h. To the solution was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (218.6 mg, 1.14 mmol, 3.1 eq), and the solution was stirred overnight with gradual warming up to room temperature. The reaction was quenched by adding water, and the resultant mixture was extracted with $CHCl_3$ three times. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography on silica gel using AcOEt/hexane (5%) as the eluent, to give 214.2 mg (0.261 mmol) of compound **6O** as a white solid in 71% yield.

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ/ppm 1.21 (d, *J*/Hz = 6.8, 6H), 6.14 (q, *J*/Hz = 6.8, 2H), 7.38–7.48 (m, 4H), 7.83 (dd, *J*/Hz = 7.3, 1.9, 2H), 7.99 (dd, *J*/Hz = 7.0, 2.1, 2H).

Mp 139–141 °C.

IR (neat) ν/cm^{-1} 1785, 1337, 1068, 615.

LRMS (FAB) m/z, 820 (M$^+$), 657, 493, 451.

Found: m/z 820.0206. Calcd for $C_{25}H_{18}F_6O_2S_2$: M, 820.0234.

3.2.3. 1-{(R)-2-(1-hydroxyethyl)-3-benzo[b]thienyl}-2-{(R)-3-(1-hydroxyethyl)-2-benzo[b]thienyl}hexafluorocyclopentene (**10**)

A solution of 1-{(*R*)-2-(1-methoxymethoxyethyl)-3-benzo[b]thienyl}-2-{(*R*)-3-(1-methoxymethoxyethyl)-2-benzo[b]thienyl}hexafluorocyclopentene (**2**) (464.4 mg, 0.753 mmol, 1.0 eq) and aqueous 3 mol dm^{-3} HCl (3.0 mL) in ethanol (22 mL) was refluxed for 5 h. After the solution was stirred at room temperature overnight, the reaction was quenched by adding aqueous $NaHCO_3$, and the resultant mixture was extracted with AcOEt three times. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography on silica gel using AcOEt/hexane (20%) as the eluent, to give 320.5 mg (0.606 mmol) of compound **10** as a viscous pale yellow liquid in 81% yield.

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ/ppm 0.99 (d, *J*/Hz = 6.6, 3H (minor conformer)), 1.35 (d, *J*/Hz = 6.4, 3H (minor conformer)), 1.54 (d, *J*/Hz = 6.8, 3H (major conformer)), 1.60 (d, *J*/Hz = 6.6, 3H (major conformer)), 1.67 (d, *J*/Hz = 2.1, 1H (major conformer)), 1.96 (d, *J*/Hz = 2.8, 1H (minor conformer)), 2.34 (d, *J*/Hz = 3.4, 1H (minor conformer)), 2.46 (d, *J*/Hz = 3.0, 1H (major conformer)), 4.97 (dq, *J*/Hz = 6.6, 3.0, 2H (minor conformer)), 5.03–5.21 (m, 2H (major conformer)), 7.30–8.12 (m, 8H (major conformer, minor conformer)).

IR (neat) ν/cm^{-1} 3370, 2980, 1339, 1066, 758.

LRMS (EI, 70 eV) m/z, 528 (M$^+$), 484, 467, 419.

Found: m/z 528.0682. Calcd for $C_{25}H_{18}F_6O_2S_2$: M, 528.0652.

3.2.4. 1-{(R)-2-(1-pentafluoropropanoyloxyethyl)-3-benzo[b]thienyl}-2-{(R)-3-(1-pentafluoropropanoyloxyethyl)-2-benzo[b]thienyl}hexafluorocyclopentene (**7O**)

To a solution of 1-{(*R*)-2-(1-hydroxyethyl)-3-benzo[b]thienyl}-2-{(*R*)-3-(1-hydroxyethyl)-2-benzo[b]thienyl}hexafluorocyclopentene (**10**) (261.8 mg, 0.495 mmol, 1.0 eq) and 4-dimethylaminopyridine (60.5 mg, 0.495 mmol, 1.0 eq) in anhydrous CH_2Cl_2 (15 mL) was added pentafluoropropanoic acid (0.40 mL, 3.81 mmol, 7.7 eq) at 0 °C under a nitrogen atmosphere, and the solution was stirred for 1 h. To the solution was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (328.0 mg, 1.71 mmol, 3.5 eq), and the solution was stirred overnight with gradual warming up to room temperature. The reaction was quenched by adding water, and the resultant mixture was extracted with $CHCl_3$ three times. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography on silica gel using AcOEt/hexane (5%) as the eluent, to give 280.6 mg (0.342 mmol) of compound **7O** as a white solid in 69% yield.

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ/ppm 0.67 (d, *J*/Hz = 4.9, 3H (major conformer)), 1.11 (d, *J*/Hz = 6.4, 3H (minor conformer)), 1.54 (d, *J*/Hz = 6.8, 3H (major conformer)), 1.60 (d, *J*/Hz = 6.6, 3H (major conformer)), 1.67 (d, *J*/Hz = 2.1, 1H (major conformer)), 1.96 (d, *J*/Hz = 2.8, 1H (minor conformer)), 2.34 (d, *J*/Hz = 3.4, 1H (minor conformer)), 2.46 (d, *J*/Hz = 3.0, 1H (major conformer)), 4.97 (dq, *J*/Hz = 6.6, 3.0, 2H (minor conformer)), 5.03–5.21 (m, 2H (major conformer)), 7.30–8.12 (m, aromatic 8H (major conformer, minor conformer)).

Mp 146–147 °C.

IR (neat) ν/cm^{-1} 2988, 1777, 1069, 614.

LRMS (FAB) m/z, 820 (M$^+$), 674, 657, 493, 451.

Found: m/z 820.0206. Calcd for $C_{25}H_{18}F_6O_2S_2$: M, 820.0234.

3.2.5. 1,2-bis-{(R)-2-(1-hydroxyethyl)-3-benzo[b]thienyl}hexafluorocyclopentene (**11**)

A solution of 1,2-bis-{(*R*)-2-(1-methoxymethoxyethyl)-3-benzo[b]thienyl}hexafluorocyclopentene (**3**) (556.9 mg, 0.903 mmol, 1.0 eq) and aqueous 3 mol dm^{-3} HCl (1.5 mL) in ethanol (20 mL) was refluxed for 14 h. After the solution was stirred at room temperature overnight, the reaction was quenched by adding aqueous $NaHCO_3$, and the resultant mixture was extracted with ethyl acetate three times. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography on silica gel using AcOEt/hexane (8%) as the eluent, to give 305.4 mg (0.578 mmol) of compound **11** as a white solid in 64% yield.

^1H NMR (300 MHz, $CDCl_3$, TMS) δ/ppm 0.66 (d, *J*/Hz = 6.3, 6H (minor conformer)), 1.08 (d, *J*/Hz = 3.0, 2H (major conformer)), 1.52 (d, *J*/Hz = 6.4, 6H (major conformer)), 1.95 (d, *J*/Hz = 3.0, 2H (minor conformer)), 4.91 (dq, *J*/Hz = 6.2, 3.0, 2H (minor conformer)), 5.05 (dq, *J*/Hz = 6.2, 2.9, 2H (major conformer)), 7.12–7.80 (m, aromatic 8H (major conformer, minor conformer)).

Mp 151–154 °C.

IR (neat) ν/cm^{-1} 3430, 2970, 1707, 1362, 1065, 755.

LRMS (EI, 70 eV) m/z, 528 (M^+), 510 ($M\text{-}H_2O^+$), 490, 467, 447.

Found: m/z 528.0614. Calcd for $C_{25}H_{18}F_6O_2S_2$: M, 528.0652.

3.2.6. 1,2-Bis-{(R)-2-(1-pentafluoropropanoyloxyethyl)-3-benzo[b]thienyl}hexafluorocyclopentene (**8O**)

To a solution of 1,2-Bis-{(*R*)-2-(1-hydroxyethyl)-3-benzo[b]thienyl}hexafluorocyclopentene (**11**) (205.6 mg, 0.389 mmol, 1.0 eq) and 4-dimethylaminopyridine (45.3 mg, 0.371 mmol, 0.95 eq) in anhydrous CH_2Cl_2 (15 mL) was added pentafluoropropanoic acid (0.25 mL, 2.38 mmol, 6.1 eq) at 0 °C under a nitrogen atmosphere, and the solution was stirred for 1 h. To the solution was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (225.4 mg, 1.18 mmol, 3.1 eq), and the solution was stirred overnight with gradual warming up to room temperature. The reaction was quenched by adding water, and the resultant mixture was extracted with $CHCl_3$ three times. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography on silica gel using AcOEt/hexane (5%) as the eluent, to give 274.3 mg (0.335 mmol) of compound **8O** as a viscous liquid in 86% yield.

^1H NMR (300 MHz, $CDCl_3$, TMS) δ/ppm 0.57 (d, *J*/Hz = 6.6, 6H (major conformer)), 1.70 (d, *J*/Hz = 6.2, 6H (minor conformer)), 6.14 (q, *J*/Hz = 6.3, 2H (major conformer)), 7.51 (td, *J*/Hz = 7.7, 1.1, 2H (major conformer)), 7.62 (td, *J*/Hz = 7.7, 1.1, 2H (major conformer)), 7.86 (d, *J*/Hz = 7.9, 2H (major conformer)), 8.06 (d, *J*/Hz = 7.2, 2H (major conformer)).

IR (neat) ν/cm^{-1} 3000, 1766, 1715, 755.

LRMS (FAB) m/z, 820 (M^+), 657, 493, 451.

Found: m/z 820.0270. Calcd for $C_{25}H_{18}F_6O_2S_2$: M, 820.0234.

4. Conclusions

Three regioisomeric bisbenzothienylethenes **6O**, **7O**, and **8O** with dual stereocontrollers, (*R*)-pentafluoropropanoyloxyethyl groups, on both ends of the hexatriene moiety showed high diastereoselectivity for light-induced 6π-electrocyclization reactions, particularly in polar solvents. In ethyl acetate, the diastereoselectivity of **8** is superior to the previously reported methoxymethoxyethyl-possessing **3**. In non-polar solvents such as hexane and octafluorotoluene, the diastereoselectivity was not very high due to the fluorophobic or less fluorophilic interactions, respectively, between the fluoroalkanoyl side chains and solvent molecules. This tendency was prominent for **6O** and to some extent for **7O**. This can be explained as follows: The repulsive interaction between the fluoroalkanoyl groups on the side chains and the sulfur atoms on the benzothienyl groups is negligible for **6O** and not so intense for **7O**. In contrast to **3O** with two methoxymethoxyethyl groups on both ends of the hexatriene moiety of the 1,2-bis(3-benzothienyl)ethene structure, **8O**, having the same molecular skeleton, showed an increase in diastereoselectivity when the temperature of photoirradiation was lowered.

The compounds described here generate, to some extent, the minor diastereomeric C-form so that the diastereoselection is incomplete. Efforts towards the development of a photochromic compound showing complete diastereoselection at any temperature in any kind of solvent is now underway and will be reported in due course.

Acknowledgment

The authors are grateful to Dr. Tomoko Yajima, Department of Chemistry, Ochanomizu University, for measuring the high-resolution mass spectra. This work was supported by a Grant-in-Aid for Scientific Research in Priority Areas “New Frontiers in Photochromism (No. 471)” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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