JOC Article

Chiral Helicenoid Diarylethene with Large Change in Specific Optical Rotation by Photochromism[1,2]

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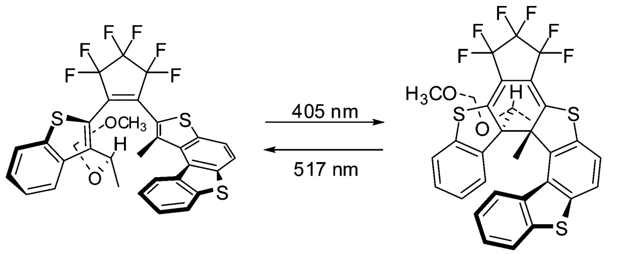
Received September 30, 2006



$[\alpha]_D$ = -69 ° (open form) $[\alpha]_D$ = -1370 ° (photostationary state)

A diarylethene possessing one [4]thiaheterohelicene and one benzothiophene, the latter with a chiral methoxymethoxyethyl group on its C-3 position, was proved to work as a switch of specific optical rotation at a wavelength at which both colored and colorless forms have no absorption in solution. The difference of the specific optical rotation was 1300° between the open form and the photostationary state. The specific optical rotation of one of the isolated optically active major colored forms was −4680°. The conversion to the colored form was 64%, and the diastereomeric excess of photocyclization was 47%.

Introduction

Diarylethenes[3] form one of the thermally irreversible photochromic families, which also include fulgides,[4] arylbutadienes,[5] and aryloxynaphthacenequinones.[6] Because of the fatigue resistivity and easy accessibility to the specially designed compounds, diarylethenes have attracted much attention as molecular-level switches.[7] We have recently reported that one stereogenic carbon atom located at the end of the peripheral of the photoreacting hexatriene moiety of a diarylethene molecule **1*O*** (open form, *O*-form) worked as the screw-bolt to fix the helical conformation of the open form by the action of the well-known allylic 1,3-strain,[8] which resulted in the generation of one diastereomer of the colored *C*-form in up to 94% de.[9]

When several aromatic rings are fused contiguously next to each other onto the spatially narrower peripheral, the resulting polyaromatic compound can no longer be planar and forms a helical structure. These compounds are called helicenes.[10] Helicenes and their closely related compounds can take two mirror-imaged helical structures: P (plus; right-handed screw)

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(1) Studies on Helicenoid Diarylethenes, Part 1.

(2) Part of this work was presented at the 21st International Conference on Photochemistry, Nara, Japan, Abstract p 155, 5A05, July, 2003.

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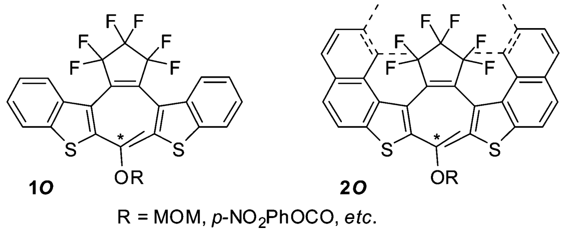


FIGURE 1. Diarylethene **1*O*** and its hypothetical extension to the helicenoid structure (**2*O***).

and M (minus; left-handed screw). When the ring number of the helicene is more than six, the interconversion between the helicities requires high temperature because of the steric crowding.[11] Helicenes are known to have large optical rotation values.[12] Therefore, if an enantiomerically pure (or at least enriched) helicenoid structure is incorporated in the diarylethene skeleton of the *C*-form by using both aromatic wings, then the helicenoid can be generated and destroyed by photoirradiation with a large change in optical rotation values.

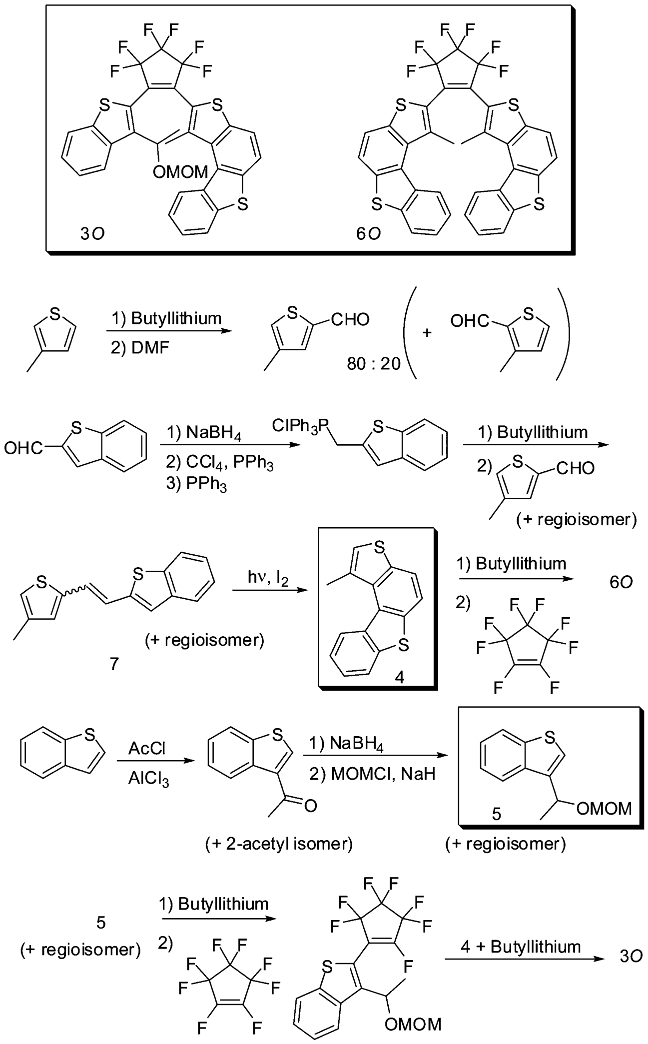
Although the introduction of a helicene-like structure into diarylethene by extending the array of the aromatic rings of **1*O*** can generate the double-helicene-like structure **2*O*** whose helicity might be controlled by the stereogenic carbon atom, it was proved that the steric repulsion between the helicene wings and the hexafluorocyclopentene ring prevented the synthetic reaction of the corresponding *O*-form (Figure 1). Therefore we decided to construct the allylic-strain-controlled chiral helicenoid structure beneath the hexafluorocyclopentene. Although racemic[13] and chiral[14] helicenoid diarylethenes have been nicely constructed by Branda and co-workers, we intended to control the helicity by only one stereogenic carbon atom. We here show the synthesis, photochromism, and optical properties of a chiral helicenoid diarylethene that shows a large change in specific optical rotation induced by photochromism.

Results and Discussion

Molecular Design. The basic structure of the compound we synthesized belongs to the diarylethenes, which form dihydrohelicene-like structures by photoirradiation. The initial diarylethene can be restored by irradiation of light of another, always longer, wavelength to the dihydrohelicene derivative. When a diarylethene has two condensed aromatic rings on the perfluorocyclopentene and each wing is not long enough to form a helicene by itself, irradiation of UV light to induce the photochemical electrocyclization may give the dihydrohelicene of which the aromatic-ring array is long enough to prohibit the change in its helicity. It is advantageous that the dihydrohelicene skeleton enhances the helicity of the whole molecular structure because the hybridization of the bond-forming carbon atoms changes from planar sp^2 to tetrahedral sp^3 by the photoreaction.

When an intramolecular regulation to determine the helical sense of the hexatriene moiety would work in the open form, UV irradiation would produce the dihydrohelicene in a stereocontrolled manner. We employed the allylic strain that successfully controlled the stereochemistry of the hexatriene moiety in **1*O*** and related compounds.[9] We therefore designed diarylethene **3*O***. As for the condensed aromatic arrays, we chose **4** and **5**, because they are too short to generate the helical structure alone, but after the photoreaction, they would cooperatively form a long-enough dihydrohelicene structure.

SCHEME 1. Structure and Synthetic Route of 3*O* and 6*O*



We also synthesized **6*O*** with two longer wings **4** possessing no stereogenic carbon atom, for the comparison of the photoreactivity.

Synthesis and Structure Determination. As shown in Scheme 1, the longer wing **4** was synthesized via photochemical oxidative ring closure of **7**, which was prepared from 3-methylthiophene and 2-formylbenzothiophene. The shorter wing **5** was synthesized from 3-acetylbenzothiophene, which was obtained as the inseparable mixture with 2-acetylbenzothiophene by Friedel−Crafts reaction of benzothiophene and acetyl chloride. The regioisomers were separated after lithiation of the mixture of 2/3-(1-methoxymethoxyethyl)benzothiophene with butyllithium followed by the reaction with octafluorocyclopentene, because the hydrogen only at C-2 (only the desired compound (**5**) possesses) could be abstracted by butyllithium to generate the carbanion. Successive introduction of **4** gave **3*O***. The ORTEP drawing of the X-ray crystallographic analysis of racemic **3*O*** is shown in Figure 2. Detailed crystallographic

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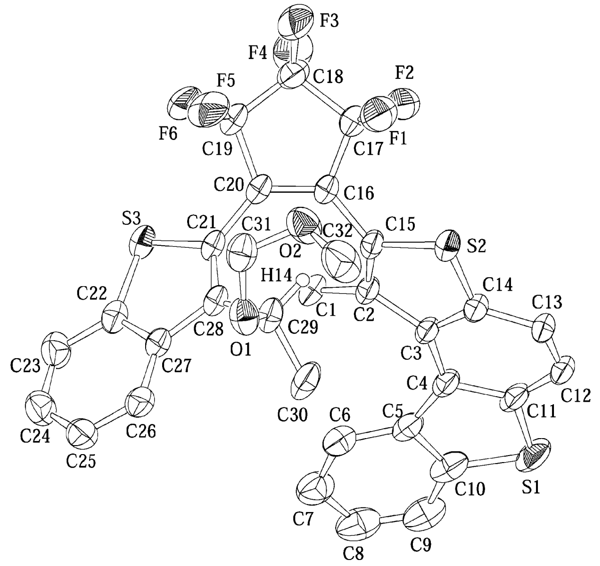

FIGURE 2. ORTEP drawing of **3*O*** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms except H(14) on the stereogenic carbon atom (C(29)) are omitted for clarity.

information is described in Supporting Information. The structure clearly shows the effect of the allylic strain. The smallest substituent (H) on the stereogenic carbon atom on C-3 of the benzothiophene comes close to the hexafluorocyclopentene ring because of the steric repulsion between the hexafluorocyclopentene and other groups (methyl and methoxymethoxyl (MOMO) groups) on the stereogenic carbon atom. Although the quadruple-ring wing is located close to the rather smaller methyl group in the crystal, it is not the only conformation in solution (vide infra).

Introduction of two molecules of **4** to octafluorocyclopentene gave **6*O***. The ORTEP drawing of **6*O***, together with the detailed crystallographic information, is shown in Supporting Information.

Unfortunately, all *C*-forms of **3** and **6**, either as the racemic mixture, diastereomeric mixture, or isolated enantiomer or diastereomer, did not give crystals suitable for X-ray crystallographic analysis.

^{1}H NMR spectra of **3*O*** and **6*O*** are shown in Supporting Information. Both spectra show that the interconversion between antiparallel and parallel conformations, the former cyclizable and the latter cyclization impossible upon photoirradiation, is so fast that only the averaged signals can be observed. The conformation issue of the related diarylethenes is discussed in the following paper.[15]

Photochromism. Irradiation of 405-nm light to a yellow solution of **6*O*** in toluene gave the red solution of the photostationary state of **6*O*** and **6*C***. The absorption spectra of **6*O***, **6*C***, and the photostationary state are shown in Figure 3. The absorption maximum wavelengths, molar absorption coefficients, and the ratio of **6*O*** and **6*C*** at the photostationary state of 405-nm light irradiation are listed in Table 1. Branda and co-workers examined the photochromic reactions of helicenoid diarylethenes **8*O*** and **9*O*** (Figure 4).[13] The diarylethene **9*O***, without the methyl groups on the ring-closing carbon atoms on the thiophene moiety, yielded the photocyclized compound, which was isolated as the fully aromatized dehydro compound **9*C*′** in good yield. On the other hand, **8*O*** with methyl groups on the ring-closing carbon atoms did not give the cyclized compound with UV light irradiation at any wavelength and at the elevated temperature. Contrary to the results for **8*O***, our compound **6*O***, with the same number of the aromatic rings as **8*O***, gave the cyclized compound. It came from the difference in the nature of the third ring counting from the ring-closing thiophene ring: six-membered benzene ring of **8*O*** and five-membered thiophene ring of **6*O***. The tight winding of the helical structure in **8*O*** caused by the six-membered ring compared with the rather loose winding of **6*O***, in view of the steric repulsion between both ends of the helicenoid, might be one of the reasons for the lack of photoreactivity of **8*O***.

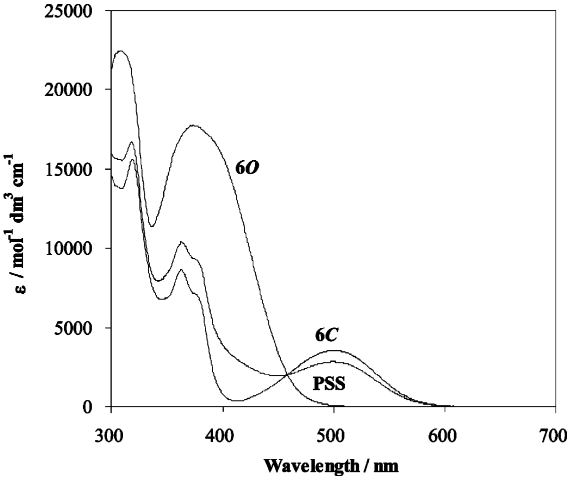

FIGURE 3. UV−vis spectra of **6*O***, **6*C*** (calculated spectrum), and the photostationary state (PSS) of 405-nm light irradiation to **6*O*** in toluene.

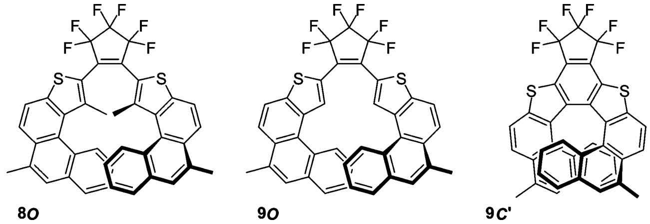

FIGURE 4. Diarylethenes **8*O*** and **9*O*** reported by Branda et al.[13]

TABLE 1. Absorption Spectral Data and 6*O*/6*C* Ratio of Photostationary State (PSS) with 405-nm Light Irradiation in Toluene

λ_{max}/nm (ϵ/mol^{-1}dm^{3}cm^{-1})		
O-form	*C*-form	**6*O***/**6*C*** at PSS
374 (17770)	501 (3550)	20/80

Next we focused on the photochromism of **3*O***. First we resolved the enantiomers of **3*O*** (**3*O*$_f$** and **3*O*$_s$**, moving more quickly (**3*O*$_f$**) and more slowly (**3*O*$_s$**) in the chiral column (Daicel Chiralpac OD−H) of HPLC).

Absorption spectral change by 405-nm light irradiation to a toluene solution of **3*O*$_f$** is shown in Figure 5. The absorption maximum at 485 nm is attributed to the formation of **3*C***. HPLC analysis proved that a major *C*-form (**3*C*$_{f/major}$**: the major *C*-form generated from **3*O*$_f$**) and a minor *C*-form (**3*C*$_{f/minor}$**: the minor *C*-form generated from **3*O*$_f$**) were formed. The ratio of the isomers **3*O*$_f$**, **3*C*$_{f/major}$**, and **3*C*$_{f/minor}$** at the photostationary

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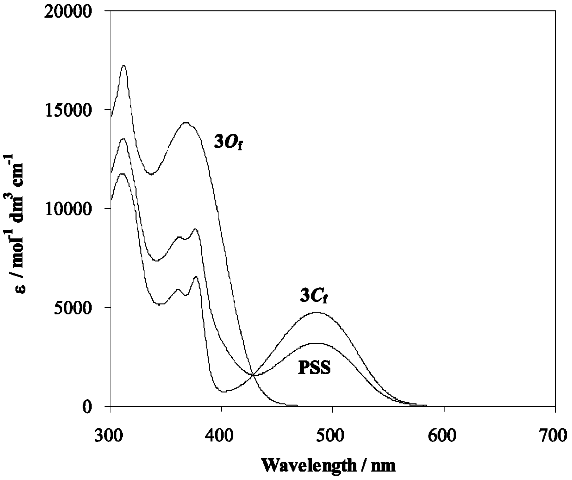

FIGURE 5. UV−vis spectra of $\mathbf{3}\boldsymbol{O}_\mathrm{f}$, $\mathbf{3}\boldsymbol{C}_\mathrm{f}$ (calculated spectrum), and the photostationary state (PSS) of 405-nm light irradiation to $\mathbf{3}\boldsymbol{O}_\mathrm{f}$ in toluene.

TABLE 2. Conversion Ratio and Diastereomeric Excess (de) Values of 3*O* in Several Solvents with the Indices of Solvent Polarity, $E_T(30)$

entry	solvent (E_T(30))	**3*O*/3*C***	de (%)
1	hexane (31.0)	37/63	32
2	toluene (33.9)	33/67	41
3	methanol (55.4)	35/65	41
4	ethyl acetate (38.1)	36/64	47

state was determined to be 33/47/20 by HPLC. The conversion ratio (*O*/*C*) was 33/67. The diastereomeric excess was 41%.

The solvent effects on the ratio of isomers were then examined. We chose three other solvents (hexane, methanol, and ethyl acetate) in addition to the toluene commonly used in our laboratory. The conversion ratios, the diastereomeric excess values, and the indices of polarity of the solvents are shown in Table 2. The best diastereomeric excess (47% de) was observed in ethyl acetate.

The reason for the lower diastereomeric excess of **3*O*** (47% de), compared with that of **1*O*** and the related compounds (88−94% de), was explained as follows. It is apparent that the allylic strain worked well to fix the conformation of the *O*-form around the stereogenic center with regard to the double bond on the benzothiophene. The diastereomeric excess is determined mainly by the ratio of the conformational isomers in which the larger right wing comes closer to either the sterically and electronically less repulsive methyl group on the stereogenic center (more stable conformation) or closer to the sterically and electronically more repulsive methoxymethoxyl group (less stable conformation). The only difference in the arrangement of the molecular structure around the hexatriene moiety between **1*O*** and **3*O*** is the position of the sulfur atom. In **1*O***, the sulfur atom on the other benzothiophene is close to the methoxymethoxyl group when it takes the unfavorable conformation. On the other hand, the corresponding sulfur atom in **3*O*** is now far from the methoxymethoxyl group even in the unfavorable conformation. Therefore the repulsion between the sulfur atom on the aromatic ring close to the perfluorocyclopentene and the oxygen atoms on the methoxymethoxyl group in **1*O*** and **3*O*** played a crucial role in determining the diastereoselectivity of the photocyclization.

In order to obtain further information about the conformation of **3*O*** in solution, ^{1}H NMR spectra of **3*O*** in different solvents were measured. We chose toluene-d_8, methanol-d_4, and cyclohexane-d_{12}, as well as the common solvent $CDCl_3$. In all solvents, only a set of signals were observed even though the existence of the antiparallel and parallel conformers as well as the combination of the chirality of the stereogenic center and the helicity of the whole molecular shape were expected. We concluded that it is because of the fast exchange of the conformers. Chemical shifts of signals of doublet and singlet methyl groups around the hexatriene array as well as the methyl signal on the MOM group (Figure 6) in different deuterated solvents are listed in Table 3.

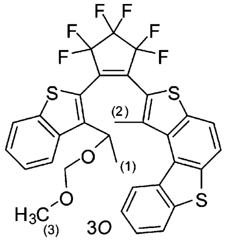

FIGURE 6. Assignment of methyl groups of ^{1}H NMR measurement in Table 3.

TABLE 3. ^{1}H NMR (300 MHz) Signals of Methyl Groups of 3*O* in Different Solvents

deuterated solvent (diastereomer excess)	chemical shift of methyl protons/δ (coupling data) secondary methyl (1)	aromatic methyl (2)	MOM methyl (3)
cyclohexane-d_{12} (32% de^a)	0.946 (d, 6.6 Hz)	2.62 (s)	3.10 (s)
toluene-d_8 (41% de)	0.919 (d, 6.6 Hz)	2.49 (s)	2.97 (s)
$CDCl_3$^{b} (−)	0.949 (d, 6.6 Hz)	2.65 (s)	3.22 (s)
CD_3OD (41% de)	0.878 (d, 6.8 Hz)	2.58 (s)	3.15 (s)

[a] Data in hexane. [b] 270 MHz.

In all cases, the conformational isomers were not observed. This means that all possible conformational isomers exchange rapidly in solution at room temperature. In toluene and in methahol, the diastereomeric excess is higher than in hexane. The chemical shifts of the doublet methyl group in methanol and in toluene are located in the higher magnet field compared with that in cyclohexane. It may be the result of close proximity of the right side wing to the secondary methyl group when **3*O*** takes the stable cyclization-possible conformation, which will increase the diastereoselectivity. The same tendency can be seen for the aromatic methyl group. The chemical shifts in toluene and in methanol are at a higher field than that in cyclohexane. The shielding effect of the magnetic field by the aromatic rings worked more strongly to the methyl group in toluene and in methanol than in cyclohexane. To the contrary, no such influence was observed for the methyl group on the MOM group because the MOM group suffers the solvent effect strongly as it is located outside of the molecule.

Change in Specific Optical Rotation. We resolved the enantiomers of **6*C*** by HPLC. The optical rotation of one of the enantiomers of **6*C*** ($\mathbf{6}\boldsymbol{C}_\mathrm{f}$; faster-moving enantiomer on Daicel Chiralpac OD-H with 1 v/v % 2-propanol in hexane as the eluent) in toluene was −4510° at 633 nm and −1170° at 820 nm. Although $\mathbf{6}\boldsymbol{C}_\mathrm{f}$ is chiral, it will generate the non-chiral **6*O*** when it is irradiated with visible light because its *O*-form exists as a mixture of racemic conformers. Although the change in optical rotation may be repeated when the resolved **6*C*** is

TABLE 4. Specific Optical Rotation Values of 3O_f and PSS in Several Solvents

entry	solvent	de (%)	$[\alpha]_D$ (deg) 3O_f	$[\alpha]_D$ (deg) PSS
1	hexane	32	−64	−804
2	toluene	41	−74	−1320
3	methanol	41	−66	−1170
4	ethyl acetate	47	−69	−1370

introduced to a rigid matrix such as a high-T_g polymer film, the helical chirality is loose and unreliable when the compound experiences the hot ground state just after the photochemical isomerization. In order to repeat the change in optical rotation by photoirradiation securely, an enantiomerically pure (or highly biased) chiral compound with a rigid chirality such as the optically resolved **3*O*** is required.

We resolved **3*O*** into enantiomers in a manner similar to the resolution of **6*C***, and observed the change in specific optical rotation values by the photochromic reaction of **3O_f**. The results are listed in Table 4. As expected, the largest difference in optical rotation values (PSS −1370°, **3O_f** −69°, difference 1300°) at 589 nm (sodium D-line) was recorded in ethyl acetate. The difference of specific optical rotation outside the absorption band between *O*-form and PSS is comparable to the data of Branda et al.[14] Although we can observe the change in optical rotation values between the *O*-form and the photostationary state (PSS), the optical rotation value of the resolved **3*C*** is scientifically interesting. Thus, we separated **3$C_{f/major}$** from the PSS mixture. Unfortunately, as **3$C_{f/minor}$** was not completely separated from **3O_f** by the preparative scale HPLC, the specific optical rotation of only **3$C_{f/major}$** was measured. The specific optical rotation of **3$C_{f/major}$** at 589 nm was −4680° in ethyl acetate. This result shows that the magnitude of specific optical rotation of **3$C_{f/major}$** is larger than that of **6C_f**, though the number of the rings of **3$C_{f/major}$** is smaller.

Comparison of the optical rotation values of different compounds is difficult because (i) specific optical rotation value is not directly linked to the rotatory power per mole (or per molecule) because the normalization is done by the mass-based concentration of the solution, and (ii) specific optical rotation value is larger when the measuring wavelength is closer to the absorption band of the compound. In addition, as for the photochromic compounds, the measuring wavelength should be outside of the absorption band in order not to change the photochromic state. This problem is quite serious because the absorption maximum of the colored form is usually in the visible region, and the default wavelength to measure optical rotation is 589 nm (sodium D-line). In spite of these difficulties, we would compare the optical rotatory power by the molar optical rotation value $[\Phi]_\lambda$, at the wavelength close to but outside of the longest absorption band. The molar optical rotation is correlated to the specific optical rotation values $[\alpha]_\lambda$ by the equation

$$[\Phi]_\lambda = [\alpha]_\lambda \times \mathrm{MW}/100$$

where MW is the molecular weight and λ is the measuring wavelength. The molar optical rotation value of **3$C_{f/major}$** are −30380° in ethyl acetate at 589 nm and −30700° in toluene at 633 nm, respectively. While the value of **3$C_{f/major}$** was measured at a wavelength just a little longer than where the absorption band reached the baseline, that for **6C_f** was measured a little far from the absorption band. This should be the reason why the effect of the ring number (7 for **3$C_{f/major}$** and 9 for **6C_f**) is not so large.

Conclusion

Two helicenoid diarylethenes, **3*O*** with a stereogenic center and **6*O*** without a chiral unit, were synthesized. Photochromic ring closure of **6*O*** afforded racemic **6*C***, which was resolved into enantiomers. The optical rotation value of the resolved **6*C*** was 4510° at 633 nm. On the other hand, **3*O*** generated a pair of diastereomers. Its largest diastereomeric excess was observed in ethyl acetate (47% de), which showed, after optical resolution of its *O*-form, a large change in specific optical rotation at a wavelength where both *O*- and *C*-forms have no absorption (1300° at 589 nm). Thus, the photochromic **3*O***/**3*C*** system was proved to work as a switch of the optical rotation, which can be detected without inducing photochromic reaction. The fact that the diastereomeric excess of **3*O*** was not as high as that of **1*O*** and the analogs (88−94% de) was attributed to the lack of the electronic repulsion between the oxygen atoms of methoxymethoxyl group and the sulfur atom in the heteroaromatic rings. Efforts to restore the electronic repulsive nature to attain high diastereoselectivity are described in the following paper.[15]

Experimental Section

Details of synthesis, purification, optical resolution, and structure identification including measurement of optical rotation and X-ray crystallographic analysis of compounds are described in Supporting Information.

Photochemical reactions at 405 nm in solvents, such as ethyl acetate (1.50×10^{-4} M), were carried out in a 10 mm path length quartz cell, using a 500 W high-pressure mercury lamp that was separated by filters (5-cm water filter, UV-35 and V-44 glass filters, and a KL-40 interference glass filter). Photochemical reactions at 517 nm were carried out using a 500 W xenon lamp that was separated by filters (IRA-25S and Y-52 glass filters and a KL-50 interference glass filter). During the photoreaction, solutions in the cell were stirred continuously.

Change in component concentration as a function of irradiation time during photoreaction was followed by a high-pressure liquid chromatography using as eluent a mixture of ethyl acetate and hexane for the silica gel column and a mixture of 2-propanol and hexane for the chiral column.

Acknowledgment. The authors thank Dr. Yoshitaka Yamaguchi for X-ray crystallographic analyses of diarylethenes and Zeon Corp. for the generous gift of octafluorocyclopentene. This work was supported by a Grant-in-Aid for Scientific Research (A) (no. 16205025) and a Grant-in-Aid for Scientific Research on Priority Area (404) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors thank the Analytical Instrument Center of Yokohama National University for the use of ^{1}H NMR and MS facilities.

Supporting Information Available: Experimental details of synthetic procedures, ^{1}H NMR spectra, ORTEP drawing of **6*O***, characterization data of all new compounds, experimental details of X-ray crystallographic analysis, crystallographic data of **3*O*** and **6*O***, and CIF files of **3*O*** and **6*O***. This material is available free of charge via the Internet at http://pubs.acs.org.

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