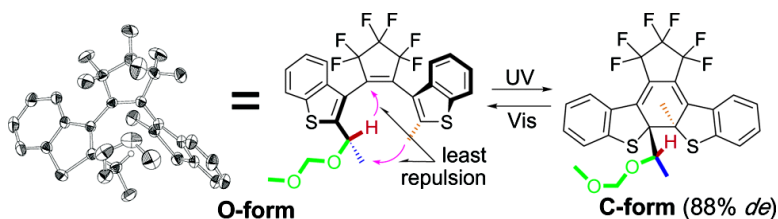


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Diastereoselective Photochromism of a Bisbenzothienylethene Governed by Steric as Well as Electronic Interactions

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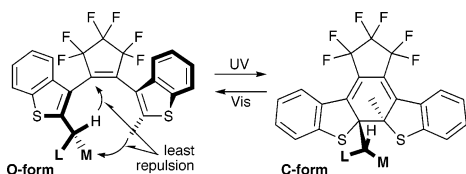
Diarylethenes are known as one of the important classes of thermally irreversible photochromic compounds.¹ The photochromic reaction of diarylethenes is, like another important class of thermally irreversible fulgides,² based on the photochemically induced conrotatory 6π -electrocyclization of the 1,3,5-hexatriene moiety, which takes a C_2 -symmetric helical structure because of the steric congestion. As a result, the photocyclization reaction produces a racemic mixture of the colored closed-form (C-form), possessing two new stereogenic carbon atoms.

If some intermolecular or intramolecular stereoregulating force works on a diarylethene molecule to make one of the enantiomeric helical structures more stable than the other, then the ratio of the stereoisomers of the C-form molecules becomes biased. If such a stereoselective photochromic reaction is possible, it can be a quite useful switch of functions for biological as well as materials sciences.² Indeed, there have been reported a number of stereoselective photochromic reactions.³ As for diarylethenes, several attempts have been reported so far. However, they were effective only at low temperature,⁴ in crystals at low conversion,⁵ or in reactions that required some additives.⁶

We here report **10**, a highly diastereoselective photochromic bisbenzothienylethene possessing only one stereogenic center in the molecule, which works efficiently at room temperature, in various solvents, with high conversion, and without any additives.

Our strategy of stereoregulation is to use allylic 1,3-strain⁷ as well as electronic repulsion between the substituents. Allylic strain has been used in various aspects of organic synthesis.⁸ When it is applied to the terminal part of the ring-closing hexatriene of a diarylethene, the smallest substituent, such as hydrogen, faces the bulky hexafluorocyclopentene that locates *cis* to the stereogenic carbon atom. Accordingly, two different substituents (medium sized M and largest L) hang down in the rather wide space as shown in Chart 1. The other benzothiophene would take the position close

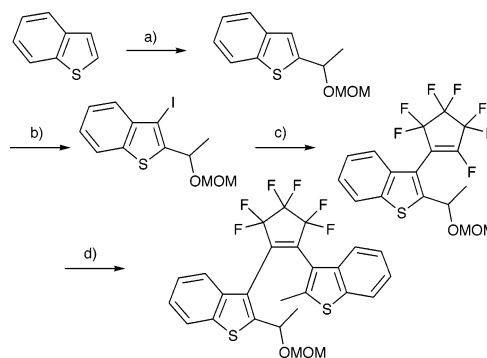
Chart 1



to M rather than close to L because of steric repulsion, resulting in the diastereomerically biased ratio of the helical conformers. If L has heteroatoms, their electronic repulsion with the sulfur atom on the second benzothiophene would make the conformer ratio more biased.

With this expectation in mind, we designed and synthesized **10** as depicted in Scheme 1, possessing a hydrogen atom, a methyl group, and a methoxymethoxyl (MOMO) group on the stereogenic carbon atom on C-2 of one of the benzothiophenes.

Scheme 1. Synthesis of Racemic **10**^a



^a (a) BuLi, CH₃CHO, 84%, then CH₃OCH₂Cl, NaH, 90%; (b) I₂, HIO₃, 38%; (c) BuLi, perfluorocyclopentene, 85%; (d) 3-lithio-2-methylbenzothiophene, 37%.

In the ¹H NMR spectrum of **10** in CDCl₃ at room temperature, four sets of doublets of the secondary methyl group of the conformational isomers (δ 0.23, 1.00, 1.45, and 1.53, in the ratio of ca. 65:15:15:5) were observed. These were generated from the combination of *anti*-parallel and parallel conformations of the hexatriene moiety and the position of the second benzothiophene group (i.e., close to M or close to L). The predominant conformational isomer showed the doublet methyl peaks at δ 0.23, suffering a strong magnetic anisotropy, suggesting that the allylic strain controlled conformation mentioned above might be the most stable.

When racemic **10** was irradiated with 313-nm light in hexane at room temperature, two diastereomeric **1C** were formed. An HPLC analysis proved that the diastereomer excess (de) was 87%, with the conversion ratio to the C-form of 80%. It returned to **10** completely by 519-nm light irradiation. In other solvents such as ethyl acetate (88% de, 85% conversion) and toluene (88% de, 85% conversion), the de values were similarly high. The changes in absorption spectra during 313-nm light irradiation to give the photostationary state (pss) and during 519-nm light irradiation to the pss solution in hexane are available as Supporting Information.

Optical resolution of **1C** was successfully done with an HPLC equipped with Daicel OD-H column. Although all trials to obtain the single crystals of **1C** were unsuccessful because of its rather amorphous-like nature, crystals suitable for X-ray crystallographic analysis of enantiomerically pure **10** were obtained after visible-light irradiation to one of the resolved enantiomer of **1C**. Its ORTEP drawing is shown in Figure 1.⁹

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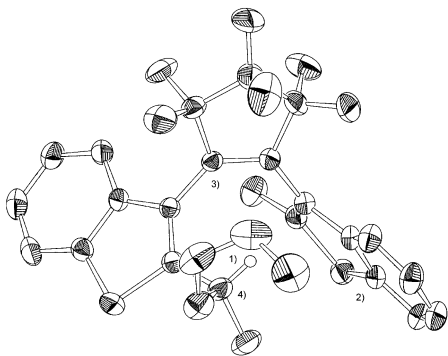
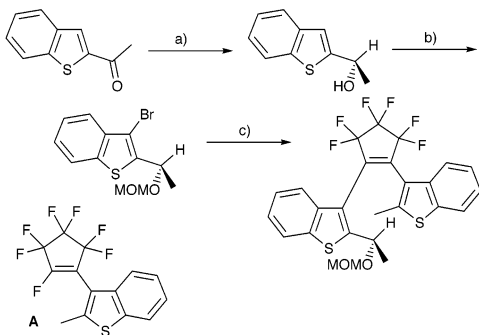


Figure 1. ORTEP drawing of (*S*)-**10** (30% probability). Numbers shown in the figure correspond to the explanations in the text below.

The crystal structure of **10** revealed that (1) the allylic strain is nicely working around the relevant double bond on the benzothiophene, so that the hydrogen atom on the stereogenic center is facing the perfluorocyclopentene ring; (2) the second benzothiophene resides close to the methyl group; (3) the hexatriene moiety takes the *s-cis-cis-s-cis* (i.e., *anti-parallel*) conformation so that the photochemical ring closure can occur easily; (4) the absolute configuration of the stereogenic center of this enantiomer was determined to be *S* by the Flack parameter⁹ (0.1(1)) of the X-ray analysis.

To avoid the optical resolution during the synthesis, we tried to synthesize optically enriched **10** by the enantioselective reduction of a ketone to generate the asymmetric center. We employed (*S*)-2-methyl-CBS-oxazaborolidine reduction¹⁰ of 2-acetylbenzothiophene, which is known to give the *R* configuration from aromatic alkyl ketones. The reduction gave (*R*)-2-hydroxyethylbenzothiophene in 100% yield and 96.5% ee (by HPLC) for 800–900 mg of starting ketone (Scheme 2). Completion of the synthesis gave (*R*)-**10** (vide infra).

Scheme 2. Synthesis of (*R*)-**10**^a



^a (a) (*S*)-2-Methyl-CBS-oxazaborolidine, THF, $-23\text{ }^{\circ}\text{C}$, 100%, 96.5% ee; (b) Br_2 , methyloxirane, THF, then, $\text{CH}_3\text{OCH}_2\text{Cl}$, NaH, THF, 87%; (c) BuLi, THF, then **A**, 61%.

If the change in optical rotation at the wavelength outside the absorption of both isomers is large, then we can detect the state of the photochromic system without inducing the photoreaction.^{3a} The change in specific optical rotation values by photochromic reactions is examined for (*S*)-**10** in hexane at 820 nm, where both isomers have no absorbance. It was -144° for the open form, whereas it was -50° at pss. As the O-form may take the helical structure, the value is larger than that of the planar C-form possessing three asymmetric carbon atoms. As the diarylethene prepared from the CBS-oxazaborolidine route showed $+137^{\circ}$ for the O-form and $+48^{\circ}$ for pss, it was proved that it is the enantiomer of the resolved **1**.

In conclusion, we have succeeded to obtain a highly diastereoselective photochromic diarylethene system only by introducing one asymmetric center, employing the steric as well as the electronic interactions. The synthesis includes enantioselective preparation of **10**. By photoirradiation, a change in optical rotation at 820 nm, where neither **10** nor **1C** absorbs light, was observed repeatedly.

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Supporting Information Available: Crystallographic data of (*S*)-**10**, change in absorption spectra during photoreactions, and experimental details of the synthesis of **10** with characterization data. This material is available free of charge via Internet at <http://pubs.acs.org>.

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