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Photochromism

A Unified Strategy for Exceptionally High Diastereoselectivity in the Photochemical Ring Closure of Chiral Diarylethenes**

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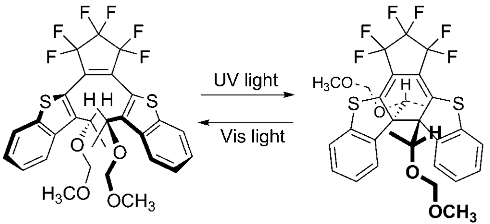
Photochromism, a photochemically induced reversible transformation of a chemical species between two states having different absorption spectra,[1] has attracted much attention. This photoinduced change is not limited to the color or absorption spectra, as the change occurs between two different molecules with different physical and chemical properties. When a photochromic compound is chiral and non-racemic,[2] its chiroptical properties such as circular dichroism spectra[3,4] and optical rotation[5–7] also change reversibly. These chiral and chiroptical differences can be used to: 1) detect the state of the system without inducing any property change,[5–7] 2) induce and control the alignment of a chiral nematic liquid crystal in a sensitive manner,[8–10] or 3) make a chiral complex[11] that may work as a chiral catalyst.[12]

Diarylethenes are one of the most promising photochromic compounds for optical and optoelectronic applications because of their high thermal and photochemical durability, as well as their synthetic feasibility, even when they are relatively complex.[13] Their photochemical reactions are based on 6π electrocyclization, which can generate a pair of enantiomers of the closed form (C form) according to the helical conformations of the hexatriene moiety of the open form (O form).[2]

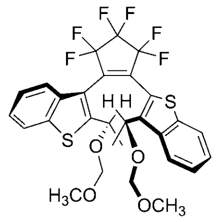
Diastereoselective ring closure of diarylethenes through photochemical reactions, which can be achieved for molecules possessing at least one chirality unit, have been reported in solution,[14] crystals,[15] amorphous solids,[16] and gels.[17] We have also developed the diastereoselective ring closure of photochromic diarylethenes in solution by applying the concept of the allylic 1,3-strain[18–21] to the hexatriene moiety, which gave 88–94 % diastereomeric excess (*de*) by using only one chiral unit to control the stereochemistry.[22–25] Herein, we report on a photochromic system that undergoes a highly diastereoselective ring closure with up to 100 % *de*.

Our new strategy is simple: use two benzothiophene rings equipped with chiral substituents, which have the same chirality on each benzothiophene ring, to control the stereochemistry. Thus, electrostatic and steric repulsion between the two 1-methoxymethoxyethyl side chains are expected. With this molecular design, it does not matter where the sulfur atom of the aromatic ring is located.[25] In addition, this methodology is applicable to any diarylethene derivative as long as the chiral unit that controls the stereochemistry can be attached to both of the carbon atoms where ring closure occurs.

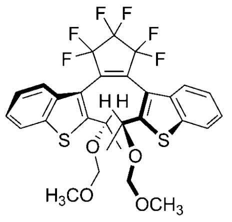
We synthesized three diarylethenes (**1**–**3**) from two chiral benzothiophene components **4** and **5**.[26] The chiral benzothiophenes were obtained by way of the enantioselective reduction of the corresponding ketones with the Corey–Bakshi–Shibata oxazaborolidine **6**[27,26] protocol and subsequent introduction of a methoxymethyl (MOM) group.[26] To avoid contamination of the diarylethenes by the *meso* isomers and enantiomers, either the chiral benzothiophenes or the final diarylethenes were purified by repeated recrystallization and/or HPLC on a chiral stationary phase.



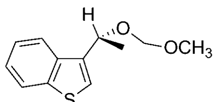
1O **1C**



2O



3O



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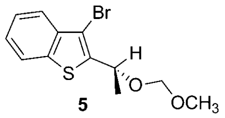

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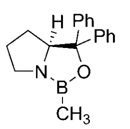

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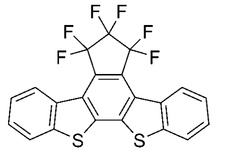

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Photochemical reactions were carried out in ethyl acetate with 366 nm (**1O**) or 313 nm (**2O**, **3O**) light for the ring closure, and 437 nm (**1C**), 483 nm (**2C**), or 515 nm (**3C**) light for the ring opening. These diarylethene derivatives showed excellent photochromism. The changes in the absorption spectra of **1** in ethyl acetate upon irradiation with UV light and visible light are shown in Figure 1. Spectroscopic data, quantum yields, and conversion ratios at the photostationary state (pss) of UV irradiation in ethyl acetate at room temperature are summarized in Table 1.

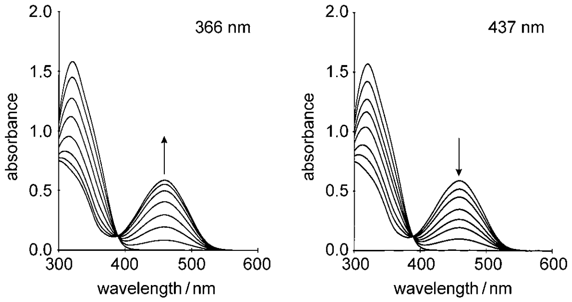

Figure 1. Absorption spectra of **1** by photoirradiation at 366 nm and 437 nm in ethyl acetate.

Table 1: Spectroscopic and photoreaction data for **1–3** in ethyl acetate.

Cpd.	λ_{max} [nm] (ε_{max})[a] O form	C form	Quantum yield[b] Φ_{OC}(UV)	Φ_{CO}(UV)	Φ_{CO}(Vis)	CR [%][c]
1	320 (15600)	459 (7180)	0.14	0.53	0.53	81
2	303 (12400)	477 (8940)	0.25	0.15	0.13	83
3	302 (7500)	519 (8690)	0.48	0.038	0.019	94

[a] Units for ε_{max}: $cm^{-1} mol^{-1} dm^3$. [b] **1**: 366 nm and 437 nm; **2**: 313 nm and 483 nm; **3**: 313 nm and 512 nm. [c] Conversion ratio to the C form at the photostationary state.

The *de* values for the ring-closing reaction at their pss were then examined using HPLC on a chiral stationary phase. The results are shown in Figure 2 and Table 2. It is apparent that the dual-stereocontroller system worked very well. However, there are still variances to be discussed. For **1** and **2** with at least one C3-substituted C2-hexafluorocyclopentene-connected benzothiophene unit the *de* values are higher than that of **3**, which has no such benzothiophene ring. Compound **3** showed only 95% *de*, although it was expected to show the highest *de* value because of the strong electronic repulsion between the oxygen atoms on the side arms and the sulfur atom, in addition to the repulsion between the side arms—though it is still higher than our previous values (88–94% *de*).[22–25]

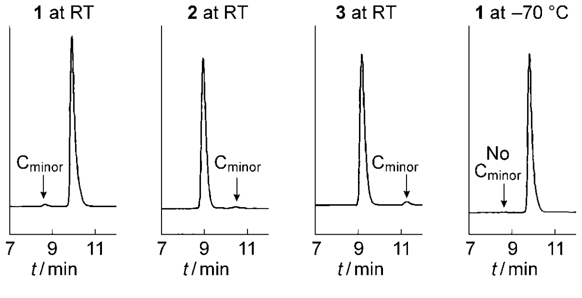

Figure 2. Liquid chromatography traces of diarylethenes **1–3** at room temperature and **1** at −70 °C in ethyl acetate recorded at λ_{max} of each C form at the photostationary state.[26]

Table 2: Diastereoselectivity of diarylethenes **1–3**.

Cpd.	Diastereomeric excess [%] (CR to the C form) ethyl acetate RT	 −70 °C	 67 °C	 hexane RT
1	98 (81)	**100** (50)	–	94 (82)
2	98 (83)	**99** (89)	–	96 (81)
3	95 (94)	89 (97)	**98** (56)	92 (94)

Next we examined the solvent effect on the diastereoselectivity of these compounds. In *n*-hexane, although the *de* values were still high, they are all slightly lower than those observed in ethyl acetate. This difference can be interpreted by the enhanced interaction of the solvent molecules with the polar side arms. As for the stable helical conformation, the side arms are expected to be sticking out of the molecule. For this conformation, the polar solvent molecules can interact strongly. When the molecule takes the other unstable helical conformation, the polar side arms are located inside the molecule so that the solvent effect is less pronounced. Therefore the difference in the free energy is larger and the ratio is more biased in ethyl acetate. The *de* values of **1** in polar acetonitrile and ethanol were also 98%, with conversion ratios of 77% and 81%, respectively.

Another way to alter the population of the diastereomeric helical conformers is to change the temperature. We therefore carried out the photochemical reaction of **1** at −70 °C. When the diastereomeric ratio was examined by HPLC the minor diastereomer of **1C**, which was observed when the reaction was carried out at room temperature, was not detected. Thus, 100% diastereoselectivity was achieved and similarly, **2** showed 99% *de*. However, **3** showed only 89% *de* at −70 °C, which is lower than the value of 95% *de* at room temperature. When the photoirradiation of **3** was carried out at 67 °C the *de* value was raised to 98%, although a small amount (1.6%) of an aromatized compound **7** [26] was generated, which was not observed during the photoirradiation at room temperature. These phenomena of increased *de* values as the irradiation temperature is increased are not consistent with the results of **1** and **2**. This strange behavior of **3** is not well-understood at this stage, but may be due to the difference in the activation energy at the excited state of each diastereomeric C form[28] on the way back to the O form upon UV irradiation, and the frozen conformations of the O form of **3**.[29]

In conclusion, we have shown the extremely high diastereoselectivity in polar solvents for photochemical 6π electrocyclizations of diarylethenes, which have two side arms that control the stereochemistry. The cyclization of **1** at a lower temperature gave an exceptional 100% diastereoselectivity. This structural modification can be applied to any diarylethene derivative possessing two alkyl groups on the bondforming carbon atoms at both ends of the hexatriene moiety. By simply replacing the alkyl groups with 1-methoxymethoxyethyl groups having the same absolute stereochemistry, an extremely high diastereoselective ring closure upon UV irradiation can be achieved.

Experimental Section

Syntheses and characterization of diarylethenes **1**–**3** are described in the Supporting Information.

Photochromic reactions were carried out in quartz cells with a 10 mm path length: 313 nm light irradiation: with a 500 W high-pressure mercury lamp with 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); 366 nm light irradiation: with a 500 W high-pressure mercury lamp with filters (a 5 cm water filter, a 5 cm aqueous $CuSO_4{\cdot}5H_2O$ solution, a UV-35 glass filter, a UV-D35 glass filter, and a UV-D36A glass filter); 437 nm light irradiation: with a 500 W high-pressure mercury lamp with filters (a 5 cm water filter, a V-40 glass filter, a Y-43 glass filter, and a V-44 glass filter); 483 nm light irradiation: with a 500 W xenon lamp with filters (a 5 cm water filter, a 5 cm toluene filter, an IRA-25S glass filter, a Y-47 glass filter, and a KL-47 interference glass filter); 515 nm light irradiation: with a 500 W xenon lamp with 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.

A high performance liquid chromatograph equipped with a UV/Vis detector and a chiral column (Daicel chiralpak IA or Daicel chiralcel OD-H, both of 4.6 mm diameter and 250 mm length) was used to determine the conversion ratios and the diastereomeric excess values of the diarylethene derivatives.

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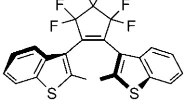
[29] In the ^1H NMR spectrum (270 MHz in $CDCl_2CDCl_2$) the coalescence temperature of the signals corresponding to the methyl group at C2 of 1,2-bis(2-methyl-3-benzothienyl)hexafluorocyclopentene (**8**; site exchange of antiparallel and parallel conformations) was 85 °C. Coalescence of signals corresponding to any proton in **3** was not observed at temperatures lower than 125 °C (270 MHz in $CDCl_2CDCl_2$). Therefore the conformational change to establish the Boltzmann equilibrium at low temperature (such as −70 °C) is not possible within a short time even for **8**, and is naturally not possible for more crowded **3**.



8O