

Diastereoselection in Crystalline State Photochromism of a Diarylethene Having a Chiral Substituent

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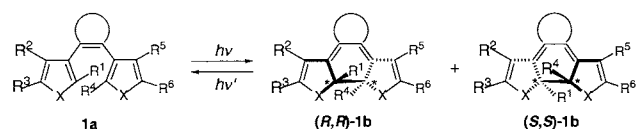
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A diarylethene having a chiral substituent underwent a diastereoselective photocyclization reaction in the crystalline phase, while the selectivity was not observed in solution.

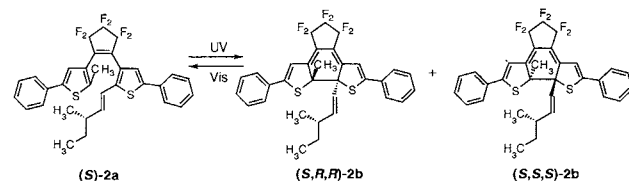
Various types of photochromic compounds, such as spirobenzopyrans, azobenzenes, fulgides and diarylethenes, have been reported.¹ Among the compounds, diarylethenes show very special reactivities. Both isomers are thermally stable and some of them undergo photochromic reactions even in the crystalline phase.²

The closed-ring form of a diarylethene have two enantiomers (*R,R* and *S,S*) originating from two asymmetric carbon atoms.³



Scheme 1. Photochromism of compound **1a**. The photogenerated closed-ring form of **1a** has two enantiomer, (*R,R*)-**1b** and (*S,S*)-**1b**.

Although a photocyclization reaction of diarylethene in solution results in the formation of two enantiomers in equal amounts, preferential formation of one of the diastereomers was observed in slightly polar solvents when a chiral substituent is introduced into the diarylethene.³ Such enrichment of one of the enantiomers or diastereomers is expected in various chiral environments,⁴ in cavities of optically active host molecules⁵ and in crystals with chiral space group.⁶ Here we report diastereoselection in the photocyclization reaction of (*S*)-**2a** which has a chiral substituent in the crystalline phase.



Scheme 2. Photochromism of (*S*)-**2a**. The photogenerated closed-ring form of (*S*)-**2a** has two diastereomers, (*S,R,R*)-**2b** and (*S,S,S*)-**2b**.

The synthesis of optically active diarylethene (*S*)-**2a** was performed according to the general synthetic procedure.^{2,7} A chiral 3-methyl-1-pentenyl substituent was introduced at 2-position of the thiophene ring by Grignard reaction of (*S*)-(+)-methylbutylbromide with a 2-formyl diarylethene derivative.

(*S*)-**2a** crystallized as colorless prisms from a mixed solvent of hexane and chloroform. The crystal structure was determined by X-ray crystallography (Figure 1).⁸ (*S*)-**2a**

adopted orthorhombic chiral space group $P2_12_12_1$. The distance between C(1) and C(10), that are reaction carbon atoms, was 3.649 Å, which is sufficiently short for the reaction. The open-ring forms were packed in the crystal in only one conformer.

Upon irradiation with 366 nm light, (*S*)-**2a** underwent a photochromic reaction both in hexane solution and in the crystalline phase. Figure 2 shows the absorption spectral change of compound (*S*)-**2a** in hexane. Upon irradiation with 366 nm light a 580 nm band increased and reached the photostationary state in 1 min. An isosbetic point was observed at 340 nm. The conversion from the open- to the closed-ring form was 87% in the photostationary state. Upon irradiation with 578 nm light for 3 min, the spectrum converted back to the original one.

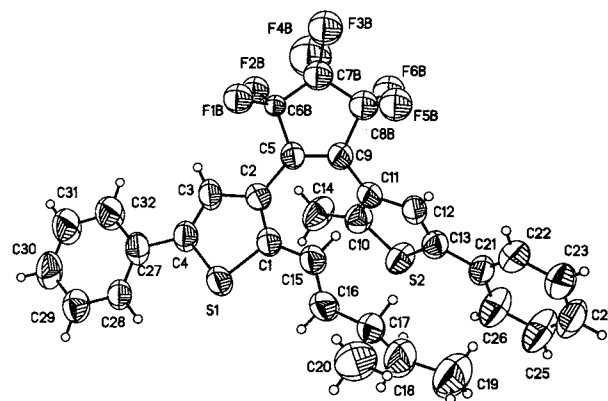


Figure 1. ORTEP drawings of the absolute configuration of (*S*)-**2a**. Selected torsion angle [°]: C(3)-C(4)-C(27)-C(32) -5.2(9), C(3)-C(2)-C(5)-C(9) -140.2(5), C(5)-C(9)-C(11)-C(10) 54.8(7), C(12)-C(13)-C(21)-C(26) 173.7(5).

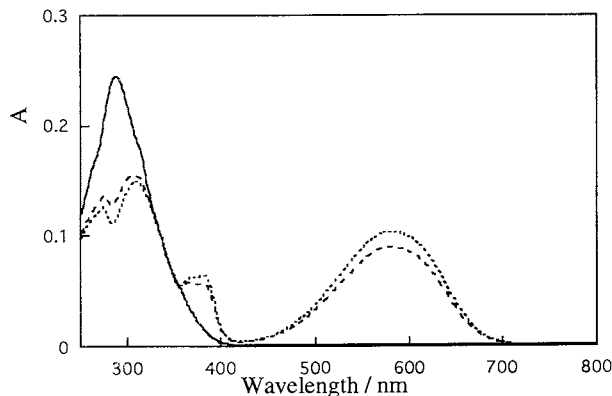


Figure 2. Absorption spectra of (*S*)-**2a** in hexane ($c = 7.5 \times 10^{-6}$ M): open-ring form (solid-line), closed-ring form (dotted-line), and in the photostationary state under irradiation with 366 nm light (dashed-line).

The photochromic reaction was also observed in the crystalline phase. The colorless single crystal of (S)-2a turned dark blue upon irradiation with 366 nm light in 5 seconds. The blue color disappeared by irradiation with 578 nm light.

Diastereoselectivity in the cyclization process was examined in solution and in the crystalline phase. The photoirradiated sample was analyzed with a reversed phase HPLC column (Mightysil RP-18 GP, CH₃CN/H₂O = 75:25 volume ratio). The closed-ring forms, (S,R,R)-2b and (S,S,S)-2b, are diastereomers. Therefore, it is possible to separate them with an ordinary HPLC column. The closed-ring forms produced in an acetonitrile solution by irradiation with 366 nm light were a mixture of equal amounts of two diastereomers, (S,R,R)-2b and (S,S,S)-2b. However, the ratio of the two diastereomers dramatically changed in the crystalline phase reaction, as shown in Table 1.

Based on the structure of the open-ring forms in the crystal, the main product is deduced to (S,R,R)-2b. The reaction was diastereoselective when the conversion was less than 3%. The d.e.(diastereomer excess) value slightly decreased when the conversion increased over 10%. Taking into account that the photocyclization is regulated by the crystal lattice, the slight decrease of selectivity is attributed to that the crystal lattice is getting distorted as the reaction proceeds.

Table 1. Asymmetric induction in the crystalline state photochromism of (S)-2a

Conversion /% ^a	d.e. /% ^b
1.7	>99 ^c
2.9	>99 ^d
9.3	97.2 ^e
11.9	96.7 ^e
13.2	95.0 ^e

^aDetermined by HPLC by using Superspher Si60 (MERCK).

^bDetermined by HPLC by using Mightysil RP-18 GP (KANTO CHEMICAL). ^cIrradiation with 366 nm light. ^dIrradiation with 405 nm light. ^eIrradiation with 435 nm light.

In conclusion a diastereoselective photocyclization reaction was observed in the single crystal of diarylethene (S)-2a. The reaction is considered to be regulated by the crystal lattice.

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- 7 Physical properties of (S)-2a: m.p. 116.7-117.2 °C; ¹H NMR (200 MHz, CDCl₃): δ = 0.62 (t, J = 6.2 Hz, 3 H), 0.78 (d, J = 10 Hz, 3 H), 1.10-1.23 (m, 2 H), 1.78-1.92 (m, 1 H), 1.94 (s, 3 H), 5.85-5.99 (m, 2 H), 7.21-7.65 (m, 12 H); UV/Vis (hexane): λ_{max}(ε) = 288 (33000) FAB HRMS (m/z): [M]⁺ calcd for C₃₂H₂₇F₆S₂ 589.1458; found 589.1443.
- 8 Crystallographic data for (S)-2a: FW = 588.65, Orthorhombic space group P2₁2₁2₁, a = 9.624(3) Å, b = 12.031(4) Å, c = 25.398(7) Å, V = 2940.7(15) Å³, Z = 4, μ(MoKα) = 0.239, D = 1.330 g cm⁻³, R = 0.0654, wR₂ = 0.1800.