



Diastereoselective photocyclization of a photochromic diarylethene having a benzo[*b*]phosphole *P*-oxide group



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ABSTRACT

A photochromic diarylethene derivative **1** having a chiral benzo[*b*]phosphole *P*-oxide at the aryl moiety underwent a diastereoselective photocyclization reaction in acetonitrile upon irradiation with ultraviolet (UV) light. It was found that the diastereomeric excess (d.e.) value changes depending on the conversion ratio from the open- to closed-ring isomer as well as the irradiation wavelength. This is attributed to the difference in the photocycloreversion quantum yields of diastereomers of the closed-ring isomer. The diarylethene showed a high photocyclization quantum yield owing to a high population of photoreactive conformers of the open-ring isomer by the steric effect of the benzo[*b*]phosphole *P*-oxide group.

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1. Introduction

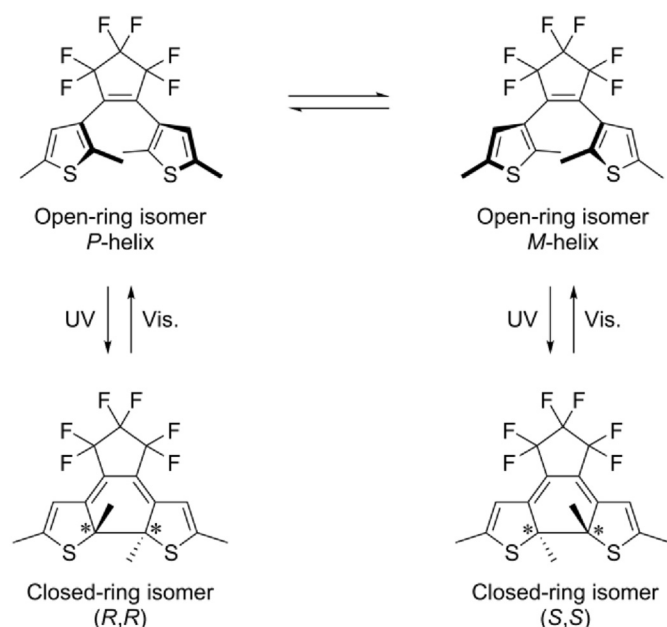
Photochromism is defined as a reversible transformation of a chemical species between two isomers having different absorption spectra upon photoirradiation [1]. Among various types of photochromic molecules, diarylethenes are one of the most promising candidates for the applications to molecular devices because of their thermally irreversible and fatigue resistant properties [2,3]. Upon photoisomerization, the diarylethene derivatives reversibly change not only their absorption spectra but also various properties, such as luminescence, refractive indices, electric conductance, magnetism, and bulk crystal shapes. The photostimulated changes in the properties can be potentially applied to photoactive molecular devices, such as optical memory media, optical switches, and light-driven actuators. The chirality of diarylethene further expands the applications. For example, optical rotation and liquid-crystalline properties can be controlled by photoisomerization of chiral diarylethene derivatives, demonstrating the potential applications to optical memory with non-destructive readout performance and photoswitchable liquid-crystalline materials [4–7]. In addition, chemical and biological applications, such as photoresponsive asymmetric catalyses [8] and tools for photocontrolling

the bioactivity [9–11], also have been proposed. For such applications, it is important to construct chiral photochromic systems that undergo highly efficient and stereoselective photoisomerization reactions.

The diarylethene derivatives undergo reversible cyclization and cycloreversion reactions between open- and closed-ring isomers upon irradiation with UV and visible light. The photoinduced conrotatory cyclization of the open-ring isomer produces two enantiomers of the closed-ring isomer with (*R,R*) and (*S,S*) absolute configurations originating from two asymmetric carbon atoms at the reactive center (Scheme 1) [12,13]. The (*R,R*) and (*S,S*) enantiomers are generated respectively from photoreactive antiparallel conformers of the open-ring isomer having *P*- and *M*-helicity in the central hexatriene moiety. Generally, in solution, the *P*- and *M*-helical conformers exist in equal amounts under thermal equilibrium conditions and the cyclization upon UV irradiation results in the formation of a racemic mixture of the closed-ring isomers. The enantioselective photocyclization has been observed for several specific diarylethenes, in which the racemization of the optically resolved helical conformers is sterically hindered [14–16], as well as for organized systems, such as gels [17,18], single crystals [19–21], and complexes with biomacromolecules [22,23]. When the diarylethene molecule possesses auxiliary chirality, the photocyclization reaction produces a pair of diastereomers instead of enantiomers. The diastereoselective photocyclization of the chiral diarylethene can be controlled by changing the population ratio of

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Scheme 1. Photoisomerization of a diarylethene. The photocyclization reactions from *P*- and *M*-helical conformers of the open-ring isomer produce (*R,R*) and (*S,S*) enantiomers of the closed-ring isomer, respectively.

the two helical conformers in solution [24–41]. The fully diastereoselective cyclization has been achieved based on elaborate molecular designs utilizing the steric effect of auxiliary chiral moieties with either point or facial chirality [29,30].

The conformational control of the diarylethene is also essential to prepare highly efficient photochromic systems. The conrotatory photocyclization of the open-ring diarylethene takes place from an antiparallel conformation with C_2 symmetry and a parallel conformer with mirror symmetry cannot undergo photocyclization. Therefore, the photocyclization quantum yield depends on the population ratio of the antiparallel and parallel conformers. Various approaches to increase the population of the antiparallel conformers have been reported [42–47]. These results indicate that the precise control of the ground-state conformation of the opening diarylethene is essential to prepare superior chiral photo-switches with high sensitivity and stereoselectivity.

In this paper, we report on an asymmetric photocyclization of a diarylethene derivative **1** having a chiral benzo[*b*]phosphole *P*-oxide group at the aryl moiety (Scheme 2). Recently, several diarylethene derivatives having a benzo[*b*]phosphole scaffold at either the ethene bridge [48,49] or the aryl moiety [50] were synthesized and their photochromic, fluorescent, and electrochemical properties were examined. Although benzo[*b*]phosphole *P*-oxide has a chiral center at the phosphorus atom, its steric effect on the photoisomerization reactions of the diarylethenes has not been elucidated in detail. Here we examined the asymmetric photocyclization of **1** in solution and the steric effect of the chiral benzo[*b*]phosphole *P*-oxide group on the diastereoselectivity and the photoreaction quantum yields.

2. Results and discussion

2.1. Isolation and identification of stereoisomers

Diarylethene **1** undergoes a thermally irreversible photochromic reaction in acetonitrile [50]. Upon irradiation with UV light, the colorless solution of the open-ring isomer **1a** turns red.

The red color is due to the formation of the closed-ring isomer **1b**. Upon irradiation with visible ($\lambda > 440$ nm) light, **1b** undergoes the cycloreversion reaction to generate **1a** and the red color is completely bleached. The isomers of **1** are shown in Scheme 2. The open-ring isomer **1a** is a racemic mixture of two enantiomers (*R*)-**1a** and (*S*)-**1a** with (*R*) and (*S*) configurations on the asymmetric phosphorus center. There is no enantioselectivity in the synthesis of the benzo[*b*]phosphole *P*-oxide scaffold [50]. Upon irradiation with UV light, **1a** undergoes the cyclization reaction to generate four stereoisomers of **1b** with (*S,S*), (*R,R*), (*S,R*), and (*R,S*) configurations originating from the asymmetric centers on the phosphorus atoms and the two reactive carbon atoms.

To identify the photoproducts, the colored solution after UV irradiation was analyzed by high performance liquid chromatography (HPLC) with a normal-phase silica gel column (Wakosil 5SIL, *n*-hexane : ethyl acetate = 60 : 40 (volume ratio), detection wavelength: 306 nm). As shown in Fig. 1, three peaks were detected in the chromatogram. The second fraction is the racemic mixture of (*R*)-**1a** and (*S*)-**1a**. The first and third fractions were isolated and found by mass spectrometry to be isomeric with **1a**. Fig. 2 shows the absorption spectra of the fractions. Both first and third fractions exhibit red color and have the absorption bands in the visible wavelength region. This result indicates that both fractions are diarylethene closed-ring isomers and they are diastereomers of **1b**. Although the shapes of the spectra are very similar to each other, the absorption maxima are slightly different: 508 nm ($\epsilon = 1.04 \times 10^4$ L mol⁻¹ cm⁻¹) for the first fraction (**1b-1**) and 506 nm ($\epsilon = 1.10 \times 10^4$ L mol⁻¹ cm⁻¹) for the third fraction (**1b-2**). Upon irradiation with visible ($\lambda > 440$ nm) light, the red colors were completely bleached and the absorption spectra of both fractions returned to that of **1a**.

Molecular structures and absolute configurations of **1b-1** and **1b-2** were ambiguously determined by X-ray crystallographic analysis on isolated and independently recrystallized single crystals. Fig. 3 shows the molecular structures of **1b-1** and **1b-2** (also see Fig. S1 in the supplementary data). The first fraction (**1b-1**) is a racemic mixture of (*R*)-(*R,R*)-**1b** and (*S*)-(*S,S*)-**1b**, while the third one (**1b-2**) is a mixture of (*R*)-(*S,S*)-**1b** and (*S*)-(*R,R*)-**1b**. 2D-ROESY NMR measurement also gave information on the absolute configurations of **1b-1** and **1b-2** (see Fig. S2 in the supplementary data). In the NMR spectrum of **1b-1**, two cross-peaks between the *n*-propyl hydrogens and the aromatic hydrogens were observed. This suggests that the *n*-propyl group and the phenyl group on the phosphorus atom are in a *cis* configuration and are proximate to each other. On the other hand, in the NMR spectrum of **1b-2**, a cross-peak between the ethyl hydrogens and the aromatic hydrogens was observed, suggesting that the ethyl and phenyl groups are oriented to the same direction against the molecular plane. These observations are consistent with the absolute configurations of **1b-1** and **1b-2** revealed by X-ray crystallographic analysis.

2.2. Diastereoselectivity in the photocyclization reaction

Diastereoselectivity in the photocyclization reaction of **1** in acetonitrile was examined at room temperature. The contents of products upon UV irradiation were analyzed by HPLC (Wakosil 5SIL, *n*-hexane : ethyl acetate = 60 : 40 (volume ratio)). The detection wavelength was 306 nm, at which an isosbestic point of **1a**, **1b-1**, and **1b-2** is located. Fig. 4a shows the relationship between the d.e. value and the conversion ratio from the open- to closed-ring isomer under irradiation with broad-band UV light ($275 \text{ nm} < \lambda < 430 \text{ nm}$). The negative and positive d.e. values indicate the preferential formation of **1b-1** and **1b-2**, respectively. The d.e. value varies depending on the conversion ratio. In the early stage of the photoreaction, in which the conversion ratio is less than 40%, the

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