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Diastereoselective cyclization of a diarylethene having a chiral N-phenylethylamide substituent in crystals

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Abstract—A diarylethene which has an *N*-phenylethylcarbamoyl substituent at the periphery of 1,2-bis(2-methyl-5-phenyl-3-thienyl)hexafluorocyclopentene was synthesized. The diarylethene underwent a photochromic reaction both in solution and in the single-crystalline phase. The chiral substituent at the end of the molecule contributed to the intermolecular hydrogen bond formation in the crystal and the crystal adopted the chiral space group $P2_1$. In the crystalline phase photocyclization reaction, only one closed-ring diastereomer was produced, while the diastereoselection was not observed in solution. © 2001 Elsevier Science Ltd. All rights reserved.

Photochromic compounds change their geometrical and electronic structures upon irradiation with light of appropriate wavelengths.¹ When one of the isomers is chiral, chiroptical properties are also changed by the photochromic reaction.² Photochromic diarylethenes undergo cyclization/cycloreversion photoreactions.³ The photochemical conrotatory cyclization produces two enantiomeric closed-ring isomers (R,R and S,S) originating from asymmetric carbon atoms (Scheme 1). The photocyclization in solution, in general, results in the formation of two enantiomers in equal amounts. Even when a chiral substituent is introduced into the diarylethene, enrichment of one of the diastereomers hardly takes place.⁴

Some diarylethenes undergo photochromic reactions in the single crystalline phase.⁵ We have prepared a diarylethene with a chiral substituent at the reactive carbon and examined diastereoselection in solution as well as in the crystalline phase.⁶ Although a racemic mixture of the closed-ring isomers was produced in solution, photocyclization was highly diastereoselective in the single-crystalline phase. The origin of the selectivity is the restricted conformation of the open-ring isomer in the crystal. In this letter we have introduced a chiral substituent at the periphery of the molecule which can form intermolecular hydrogen bonds to control the crystal structure.

We chose 1,2-bis(2-methyl-5-phenyl-3-thienyl)hexafluorocyclopentene as the photochromic core because this compound is known to undergo the photochromic reaction in the single-crystalline phase.⁷ An *N*phenylethylcarbamoyl group was introduced at *para* position of the phenyl group, and is capable of intermolecular hydrogen bond formation. The resulting molecule is (S)-1a, as shown in Scheme 2. Compound 1a was prepared from 1-(2-methyl-5-phenyl-3-thienyl)-2 -(2-methyl-5-(4-formylphenyl)-3-thienyl)hexafluorocyclopentene. Jones oxidation followed by treatment with thionyl chloride afforded acyl chloride. (S)-Phenylethylamine was mixed with the acyl



Scheme 1. Photochromism of diarylethene. The photogenerated closed-ring form has two enantiomers, (R,R) and (S,S).

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Scheme 2.

chloride to give (S)-1a. The overall yield from aldehyde to amide was 60%, and the structure was confirmed by NMR, mass spectroscopy, and elemental analysis.⁸

Upon irradiation with UV light, (S)-1a underwent a cyclization reaction in hexane. Fig. 1 shows the absorption spectral change of compound (S)-1a in hexane. Upon irradiation with 313 nm light a 582 nm band increased and reached the photostationary state in 5 min. This is due to the formation of the closed-ring isomer.⁹ The color of the solution changed from colorless to blue. An isosbestic point was observed at 318 nm. The conversion from the open- to the closed-ring isomers was 96% in the photostationary state. Upon irradiation with 578 nm light, the spectrum converted back to that of the starting material.

Very thin white needles of (S)-1a were obtained from hexane. The absolute crystal structure was determined by X-ray crystallography and the crystal packing is shown in Fig. 2.¹⁰ (S)-1a adopted monoclinic chiral space group $P2_1$. The distance between reactive carbons is 3.46 Å, which is short enough for the cyclization reaction to take place in the crystalline phase. The conformation of the open-ring isomer is restricted to Min the hexatriene moiety. The distance between oxygen of CO group and nitrogen of 2 NH group is short enough (2.78 Å) to form hydrogen bonds. The hydrogen bonds control the crystal packing and conformation of (S)-1a as shown in Fig. 2. The crystal also contained solvent hexane.

The crystal also showed photochromic reactivity. The colorless single crystal of (S)-**1a** turned dark blue upon irradiation with 366 nm light. When observed under polarized light, the blue color intensity regularly changed upon rotation of the crystal sample. This phenomenon suggests that the closed-ring isomers were regularly packed in the crystal. The blue color disappeared upon 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 chiral HPLC column (Daicel CHIRALCEL OD-H, hexane:2propanol:ethanol=90:9:1 volume ratio). The closedring isomers produced in hexane solution by irradiation with 313 nm light were a mixture of equal amounts of two diastereomers, (S,S,S)-1b and (S,R,R)-1b. In the crystalline phase reaction, one of the diastereomers was dominant. Diastereomeric excess was as high as 82% when the conversion was around 10%. The rather low d.e. is attributable to high conversion⁶ and the presence of hexane molecules in the crystal. The hexane molecules possibly cause disorder of the lattice by thermal motion. Based on the structure of the openring isomers in the crystal, the main product is ascribed to (S,S,S)-1b. The direction of the cyclization reaction was regulated by the crystal lattice.



Figure 1. Absorption spectra of (S)-**1a** in hexane $(1.9 \times 10^{-5} \text{ M})$: open-ring form (solid-line), closed-ring form (dotted-line) and in the photostationary state (313 nm) (dashed-line).



Figure 2. Crystal packing of (S)-1a. Hydrogen atoms are omitted for clarity. (a) Top view (along the *b* axis). (b) Side view.



Figure 3. CD spectra of (S,S,S)-1b, (S,R,R)-1b, and (S)-1a measured in hexane.

CD spectra of the two diastereomers were measured. Fig. 3 shows the CD spectra of the open-ring isomer (S)-1a and the closed-ring isomer (S,S,S)-1b, (S,R,R)-1b. The absolute structure was estimated from the X-ray crystallographic structure of the open-ring isomer. The open-ring isomer has a small Cotton effect at 310 nm, which is from the phenylethylamide side chain. The closed-ring isomer has Cotton effect at 270, 310, 380, and 620 nm. The CD signal of the closed-ring isomers was much larger than that of the open-ring isomer. The signals of the two closed-ring isomers are mirror images except the signal contribution from the side chain. This result indicates that the CD signal of the closed-ring isomer mainly originates from the diarylethene moiety. Yokoyama et al. reported the CD spectra of the closed-ring isomers of 1,2-bis(5-hydroxymethyl-2-methyl-3-thienyl)hexafluorocyclopentene whose absolute structure is known.¹¹ The sign of the Cotton effect in the visible region was opposite to that observed for 1b, though the band around 380 nm had the same sign. Our molecule has a phenyl group at the 5-position of the thiophene ring, though the above molecule does not have the phenyl group. This difference is considered to affect the sign of the Cotton effect.

In conclusion, a diastereoselective photocyclization reaction was observed in the single crystal of diarylethene (S)-**1a**. This reaction was regulated by the crystal lattice; CD spectra of the open-ring isomer and the both diastereomers of the closed-ring isomers were measured.

Acknowledgements

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- Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. J. Am. Chem. Soc. 2000, 122, 4871–4876.
- 8. Selected data for (*S*)-**1a**: white needles; ¹H NMR (CDCl₃, 200 MHz): δ 1.43 (d, *J*=2.5 Hz, 3H), 1.97 (s, 3H), 1.99 (s, 3H), 5.35 (quintet, *J*=7 Hz, 1H), 6.33 (d, *J*=8 Hz 1H), 7.26–7.81 (m, 16H); UV–vis (hexane) λ_{max} (ε) 300 (3.9×10⁴); MS *m/z* (M⁺) 667. Anal. found: C, 64.87; H, 4.19; N, 2.16%. Calcd for C₃₆H₂₇F₆NOS₂: C, 64.75; H, 4.08; N. 2.10%.
- Selected data for (1:1 mixture of (S,S,S)-1b and (S,R,R)-1b): ¹H NMR (CDCl₃, 400 MHz): δ 1.64 (d, J=7 Hz, 3H), 2.19 (s, 6H), 5.35 (quintet, J=7 Hz, 1H), 6.34 (d, J=8 Hz 1H), 6.69 (s, 1H), 6.72 (s, 1H), 7.26–7.81 (m, 14H); UV-vis (hexane) λ_{max} (ε) 371 (1.1×10⁴), 383 (1.1× 10⁴), 582 (1.8×10⁴).
- Crystallographic data for (S)-1a: Monoclinic space group P2₁, a=18.2145(15), b=9.6866(8), c=23.834(2), β=106.210(2), V=4038.0(6), Z=4, R (I>4σ)=0.1044, wR₂ (all data)=0.2905, χ=-0.02(17).
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