ORGANIC LETTERS

2003
Vol. 5, No. 10
1769−1772

Diastereoselective Cyclization in Chiral Diarylethene Crystals: Polymorphism and Selectivity

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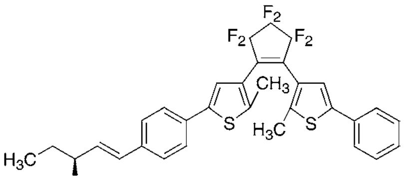
Received March 12, 2003

ABSTRACT



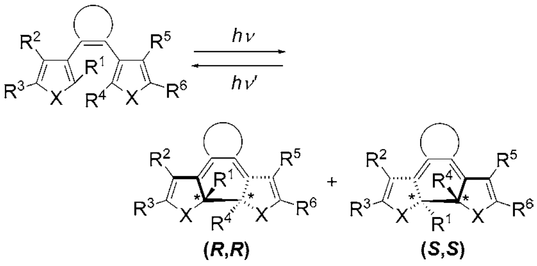
(*S*)-1a

An optically active photochromic diarylethene, (*S*)-1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(4-(3-methyl-1-penten-1-yl)phenyl)-3-thienyl]-perfluorocyclopentene ((*S*)-1a), was synthesized. (*S*)-1a formed two crystalline phases, α- and *β*-phases. The diarylethene underwent a photochromic reaction in solution and even in the single-crystalline phase. In solution, no diastereoselection was observed. On the other hand, in the *β*-crystalline phase, only one diastereomer (*S*,*R*,*R*)-1b was produced. No such diastereoselection was observed in the α-crystalline phase.

In recent years, there has been considerable scientific interest in crystalline-phase photochemistry.[1] One unique aspect of the crystalline-phase reaction is the topochemical reactivity. The crystal lattices provide microenvironments for the reactions with stereo-, regio-, and enantiospecificity. Enantiospecific reactions take place in chiral crystals containing chiral auxiliaries such as chiral host molecules[2] or covalently bonded chiral substituents.[3] It should be noted that so-called absolute asymmetric synthesis is possible when achiral molecules spontaneously crystallize in a chiral space group.[4]

Photochromic diarylethenes undergo reversible cyclization/cycloreversion photoreactions upon alternate irradiation with UV and visible light.[5] 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

Scheme 1. Photochromism of Diarylethene[a]



[a] Photogenerated closed-ring form has two enantiomers, (*R*,*R*)- and (*S*,*S*)-.

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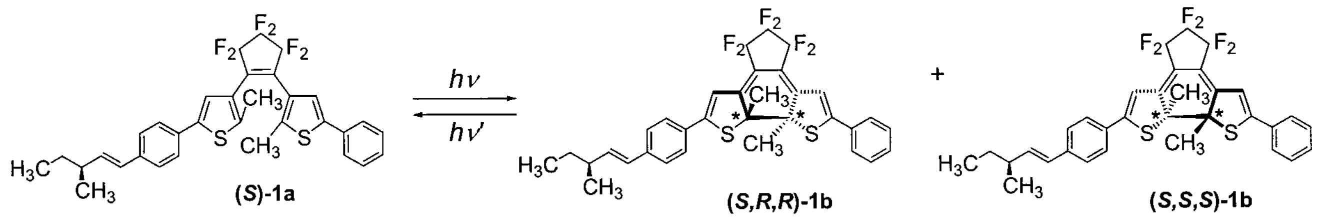
(1) (a) *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: Weinheim, Germany, 1991. (b) Keating, A. E.; Garcia-Garibay, M. A. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York, 1998; Vol. 2, pp 195−248. (c) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433. (d) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480. (e) Gamlin, J. N.; Jones, R.; Leibovitch, M.; Patrick, B.; Scheffer J. R.; Trotter J. *Acc. Chem. Res.* **1996**, *29*, 203. (f) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.

(2) (a) Aoyama, H.; Hasegawa, M.; Omote, Y. *J. Am. Chem. Soc.* **1979**, *101*, 5343. (b) Toda, F.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1986**, *29*, 4299. (c) Hosomi, H.; Ohba, S.; Tanaka, K.; Toda, F. *J. Am. Chem. Soc.* **2000**, *122*, 1818.

10.1021/ol034440h CCC: $25.00

Scheme 2



diarylethene, enrichment of one of the diastereomers hardly takes place.[6]

Some diarylethenes undergo photochromic reactions in the single-crystalline phase.[7] 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.[8] Although a diastereomeric mixture of the closed-ring isomers was produced in solution, highly diastereoselective photocyclization took place in the single-crystalline phase. The origin of the selectivity is ascribed to the restricted conformation of the open-ring isomer in the crystal and topochemical control. In this letter, we have prepared a diarylethene (*S*)-**1a** having a chiral substituent at the end of the molecule and examined the diastereoselection (Scheme 2).

The synthesis was performed by 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(4-formylphenyl)-3-thienyl]perfluorocyclopentene as the intermediate.[9] Grignard reaction with 2-methylbutylmagnesium bromide followed by dehydration reaction provided **1a**. The structure of **1a** was confirmed by NMR, mass spectroscopy, and elemental analysis.[10]

Figure 1 shows the photochromic reaction of **1** in hexane. Upon irradiation with 313 nm light, absorption at 586 nm increased and reached a photostationary state. The solution turned blue, which is the color of the closed-ring isomer **1b**.[11] The conversion at the photostationary state was 98%. Upon irradiation with 578 nm light, the closed-ring isomer **1b** was completely returned back to the open-ring isomer **1a**.

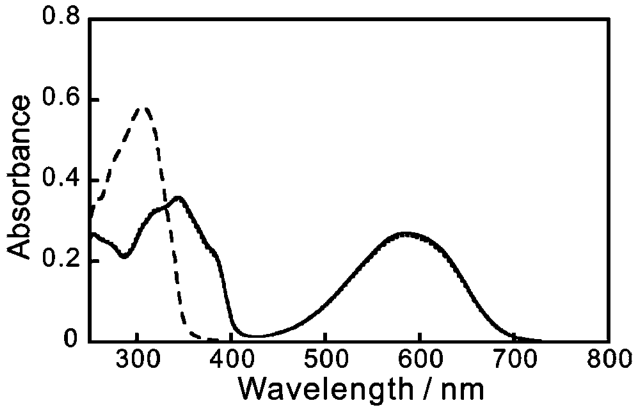


Figure 1. Absorption spectra of **1** in hexane (1.4 × 10^{-5} M). Open-ring isomer (dashed line), closed-ring isomer (solid line), in the photostationary state (dotted line).

Needle crystals of (*S*)-**1a** were obtained by recrystallization from acetone. Two kinds of crystals, α- and *β*-phase crystals, were obtained. The crystal structures are shown in Figure 2.[12] Both crystals adopted chiral space group $P2_1$. There are two molecules in the asymmetric unit of α-(*S*)-**1a**. One molecule has a *P* configuration in the hexatriene of the dithienylethene moiety, and the other molecule has an *M*

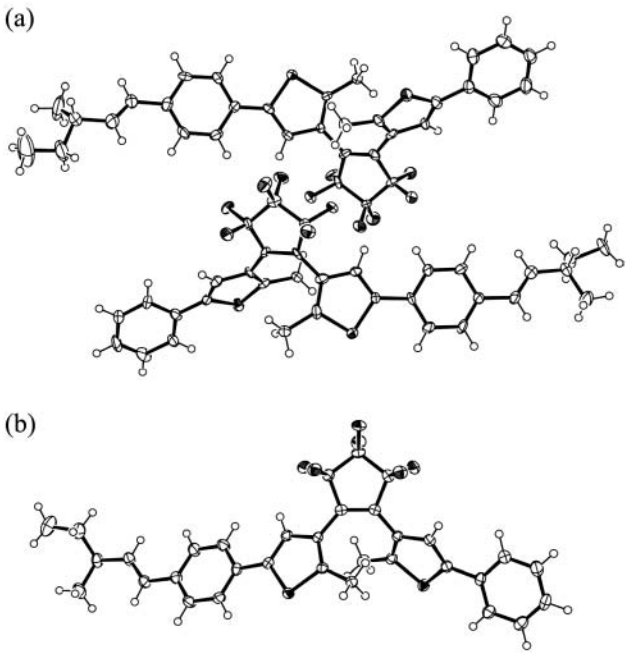


Figure 2. ORTEP drawing of the absolute configuration of (a) α-(*S*)-**1a** and (b) *β*-(*S*)-**1a**. The asymmetric units are presented.

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(3) (a) Schultz, A. G.; Taveras, A. G.; Taylar, R. E.; Tham, F. S.; Kulling, R. K. *J. Am. Chem. Soc.* **1992**, *114*, 8725. (b) Sakamoto, M.; Takahashi, M.; Hokari, N.; Fujita, T.; Watanabe, S. *J. Org. Chem.* **1994**, *59*, 3131. (c) Ito, Y.; Kano, G.; Nakamura, N. *J. Org. Chem.* **1998**, *63*, 5643.

(4) Sheffer, J. R.; Garcia-Garibay, M. A. In *Photochemistry of Solid Surfaces*; Matsuura, T., Anpo, M., Eds.; Elsevier: Amsterdam, 1989.

(5) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2001**, *123*, 9896. (c) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759.

(6) (a) Yamaguchi, T.; Uchida, K.; Irie, M. *J. Am. Chem. Soc.* **1997**, *119*, 6066. (b) Murguly, E.; Norsten, T. B.; Branda, N. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1752.

(7) (a) Irie, M.; Uchida, K.; Eriguchi, T.; Tsuzuki, H. *Chem. Lett.* **1995**, 899. (b) Kobatake, S.; Yamada, T.; Uchida, K.; Kato, N.; Irie, M. *J. Am. Chem. Soc.* **1999**, *121*, 2380. (c) Shibata, K.; Muto, K.; Kobatake, S.; Irie, M. *J. Phys. Chem. A* **2002**, *106*, 209−214.

configuration. Two molecules were pseudoracemates.[13] In the β-phase crystal, there was only one molecule in the asymmetric unit, which has a *P* configuration. For all open-ring isomers, the distances between reactive carbons were in the range between 3.42 and 3.47 Å, which are sufficiently short for the cyclization to take place in the crystalline phase.

Both crystals showed photochromic reactivity. The colorless single crystal of α- and β-phase crystals turned dark blue upon irradiation with 366 nm light. When observed under polarized light, the blue color intensity was regularly changed by rotating the crystal sample. This dichroic behavior suggests that the closed-ring isomers are regularly packed in the crystal. The blue color disappeared upon irradiation with 578 nm light.

Diastereoselectivity in the photocyclization process was examined in solution as well as in the two crystalline phases. The photoirradiated sample was analyzed with a chiral HPLC column (Daicel CHIRALCEL OD-RH, 2-propanol). The HPLC charts are shown in Figure 3. As can be seen from Figure 3a, the closed-ring 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**.

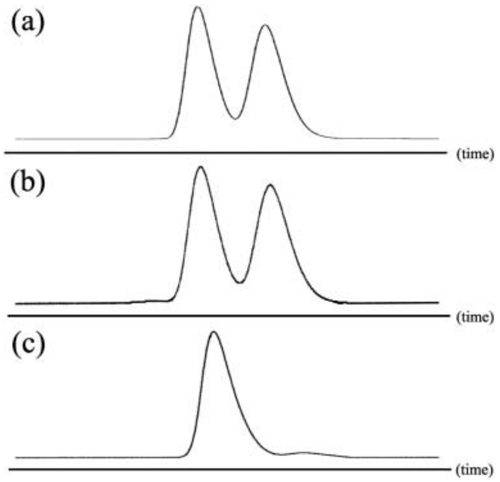

Figure 3. HPLC chromatogram of **1a** monitored at 586 nm. (a) Photocyclization in hexane solution. (b) Photocyclization reaction in the α-single-crystalline phase. (c) Photoirradiation in the β-single-crystalline phase.

In the α-crystalline phase, diastereoselectivity was not observed (Figure 3b). The two diastereomers were produced in equal amounts. On the other hand, when the β-phase crystal was irradiated with 366 nm light, one of the diastereomers was produced predominantly (Figure 3c). The diastereomeric excess was as high as >90%. On the basis of the structure of the open-ring isomers in the crystal, the main product is supposed to be (*S*,*R*,*R*)-**1b**.

The closed-ring isomer photogenerated in the β-single-crystalline phase was separated using a chiral prepacked column (Daicel CHIRALPAK OD-H, hexane). The recrystallization of the separated closed-ring isomer in hexane solution gave the black plate crystals. X-ray analysis of the obtained crystal was carried out.[14] The final configuration of the photogenerated samples irradiated in the crystalline state of the β-crystal is shown in Figure 4. Molecules possessed the (*S*,*R*,*R*)-configuration.[15]

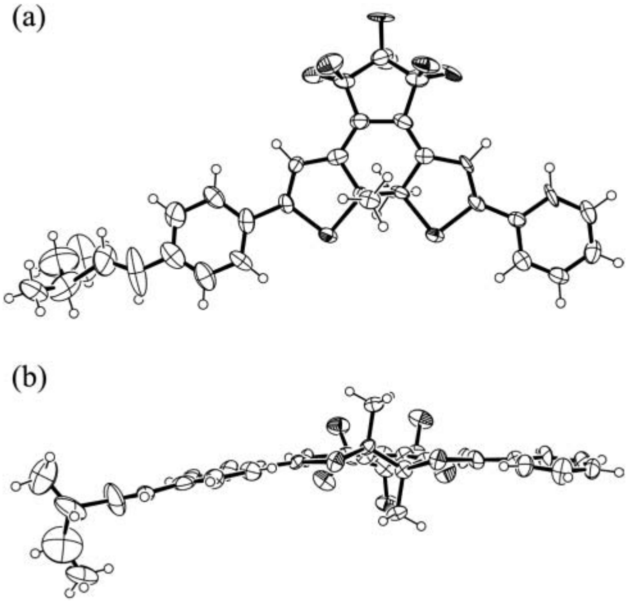

Figure 4. ORTEP drawing of the absolute configuration of (*S*,*R*,*R*)-**1b**. The asymmetric units are presented. (a) Top view. (b) Side view.

CD spectra of two diastereomers were measured. Figure 5 shows the CD spectra of the open-ring isomer (*S*)-**1a** and

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(8) (a) Kodani, T.; Matsuda, K.; Yamada, T.; Kobatake, S.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 9631. (b) Matsuda, K.; Yamamoto, S.; Irie, M. *Tetrahedron Lett.* **2001**, *42*, 7291.

(9) For details of the synthesis, see Supporting Information.

(10) **(*S*)-1a:** pale yellow crystal; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.91 (t, $J = 7$ Hz, 3H), 1.09 (d, $J = 7$ Hz, 3H), 1.42 (quintet, $J = 7$ Hz, 2H), 1.96 (s, 3H), 1.97 (s, 3H), 2.20−2.23 (m, 1H), 6.13 (dd, $J = 16$ Hz, 8 Hz, 1H), 6.34 (d, $J = 16$ Hz, 1 H), 7.27−7.57 (m, 7H), 7.46 (d, $J = 8$ Hz, 2H), 7.54 (d, $J = 8$ Hz, 2H); UV−vis (hexane) λ_{max} (ϵ) 307 (44 000). Anal. Calcd for $C_{33}H_{28}F_6S_2$: C, 65.76; H, 4.68. Found: C, 65.79; H, 4.75.

(11) **(*S*)-1b (Mixture of (*S*,*R*,*R*)-1b and (*S*,*S*,*S*)-1b):** ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.92 (t, $J = 8$ Hz, 3H), 1.10 (d, $J = 7$ Hz, 3H), 1.43 (quintet, $J = 7$ Hz, 2H), 1.38−1.47 (m, 1H), 2.18 (s, 6H), 6.21 (dd, $J = 16$ Hz, 8 Hz, 1H), 6.36 (d, $J = 16$ Hz, 1H), 6.66 (s, 1H), 6.68 (s, 1H), 7.27−7.60 (m, 9H); UV−vis (hexane) λ_{max} (ϵ) 586 (20 000), 344 (27 000).

(12) **Crystal Data for α-(*S*)-1a:** mp = 130.5−131.0 °C, $C_{33}H_{28}F_6S_2$, FW = 602.67, monoclinic $P2_1$, $a = 15.7480(15)$ Å, $b = 8.6888(8)$ Å, $c = 21.240(2)$ Å, $\beta = 102.789°$, $V = 2834.2(5)$, $Z = 4$, R ($I > 2\sigma$) = 0.0479, wR_2 (all data) = 0.1125, $\chi = 0.06(13)$. ***β*-(*S*)-1a:** mp = 127.0−130.0 °C, $C_{33}H_{28}F_6S_2$, FW = 602.67, monoclinic $P2_1$, $a = 10.3986(16)$ Å, $b = 8.6686(13)$ Å, $c = 16.054(3)$ Å, $\beta = 100.890°$, $V = 1421.1(4)$, $Z = 2$, R ($I > 2\sigma$) = 0.0351, wR_2 (all data) = 0.0833, $\chi = -0.02(5)$.

(13) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley & Sons: New York, 1981.

(14) **Crystal Data for (*S*,*R*,*R*)-1b:** $C_{33}H_{28}F_6S_2$, FW = 602.67, monoclinic $P2_1$, $a = 10.555(6)$ Å, $b = 25.402(13)$ Å, $c = 10.647(6)$ Å, $\beta = 91.697(6)°$, $V = 2853(3)$, $Z = 4$, R ($I > 2\sigma$) = 0.0931, wR_2 (all data) = 0.2971, $\chi = -0.09(16)$.

(15) We obtained the (*S*,*S*,*S*)-**1b** crystal by separating the closed-ring isomer photogenerated in solution. The result of the X-ray crystallography is shown in Supporting Information.

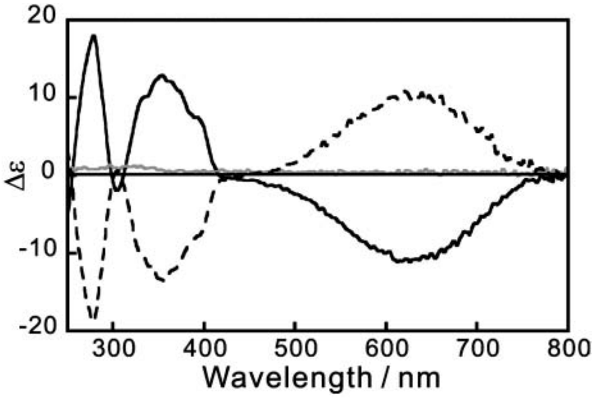

Figure 5. CD spectra of **1** in hexane. Open-ring isomer (*S*)-**1a** (gray line), closed-ring isomer (*S*,*R*,*R*)-**1b** (solid line), and (*S*,*S*,*S*)-**1b** (dashed line).

the closed-ring isomers (*S*,*S*,*S*)-**1b** and (*S*,*R*,*R*)-**1b**. The open-ring isomer has almost no CD signal. The CD signal of the closed-ring isomers was much larger than that of the open-ring isomer. The two spectra of closed-ring diastereomers are mirror images. This result indicates that the CD spectra of the closed-ring diastereomers 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.[16] The sign of the Cotton effect in the visible region was opposite from our result. 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.[8b]

In conclusion, a chiral diarylethene (*S*)-**1a** was synthesized. The diastereoselection was not observed in the photocyclization reaction in solution. The molecule formed two kinds of crystals, α- and *β*-phases. In the α-(*S*)-**1a** crystal, no diastereoselection was observed, but in the *β*-(*S*)-**1a** crystal, only one closed-ring diastereomer was produced. It was proved that the diastereoselectivity was dependent on the crystal packing.

Acknowledgment. This work was supported by CREST of Japan Science and Technology Corporation and by a Grant-in-Aid for the 21st Century COE program (Functional Innovation of Molecular Informatics) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting Information Available: Experimental procedure for (*S*)-**1a**, the result of the X-ray crystallography of (*S*,*S*,*S*)-**1b**, and X-ray crystallographic data for α-(*S*)-**1a**, *β*-(*S*)-**1a**, (*S*,*R*,*R*)-**1b**, and (*S*,*S*,*S*)-**1b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OL034440H

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[16] Yokoyama, Y.; Hosoda, N.; Osano, Y. T.; Sasaki, C. *Chem. Lett.* **1998**, 1093.