

Absolute Stereochemistry and CD Spectra of Resolved Enantiomers of the Colored Form of a Photochromic Dithienylethene

Yasushi Yokoyama,* Naoya Hosoda, Yasuko T. Osano,[†] and Chizuko Sasaki[†]

Department of Materials Chemistry, Faculty of Engineering, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240-8501

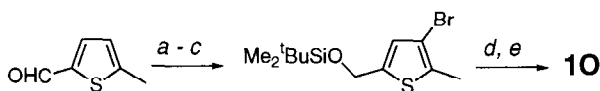
[†]Analytical Sciences Laboratory, Yokohama Research Center, Mitsubishi Chemical Corporation,
Kamoshida-cho, Aoba-ku, Yokohama 227-8502

(Received July 10, 1998; CL-980524)

The colored form of photochromic 1,2-bis(5-hydroxymethyl-2-methyl-3-thienyl)hexafluorocyclopentene was resolved into enantiomers by HPLC. The absolute stereochemistry of an enantiomer was determined on its bis(4-chlorobenzoate). The CD spectra and optical rotation of the resolved colored form were measured.

The research interest on the combination of photochromism and chirality has been growing rapidly¹⁻⁶ because they can act as the switch of the chiral properties of themselves and of the chiral interaction with the environment in which the molecules are located. We have recently reported the optical resolution of an indolylfulgide^{1b} and the diastereoselective photochromism of a binaphthol-condensed indolylfulgide.^{1c} As the extension of our research, we wished to develop the chemistry of chiral photochromism with thermally stable and fatigue resistive diarylethenes.⁷ We here report the first determination of the absolute stereochemistry of an enantiomer of the colored form of a dithienylethene and correlation of the absolute stereochemistry with the CD spectra.

Synthesis of dithienylethene **10** was done as shown in Scheme 1, in five steps with 82% overall yield.⁸ It showed usual thermally irreversible photochromism between **10** and **1C** in toluene.



a: Br₂/THF (quant.). b: NaBH₄/methanol (98%). c: tBuMe₂SiCl, Et₃N, DMAP/DMF (95%). d: BuLi/hexane/THF then octafluorocyclopentene (99%). e: Bu₄NF/THF (89%).

Scheme 1.

The procedure of optical resolution of **1C** was as follows. Irradiation of 313-nm light to the ethyl acetate solution of **10** (216 mg) for 13 h afforded a mixture of **10** and **1C**. After they were separated by silica-gel column chromatography, **1C** (140 mg) was resolved by HPLC equipped with a chiral preparative-

scale column (cellulose tris(3,5-dimethylphenylcarbamate): Daicel Chem. Ind., CHIRALCEL® OD-H, 4.6 mm (diameter) x 25 cm (length)) using hexane/2-propanol (95/5) as the eluent, to give 67 mg of fast-moving enantiomer **1C-f** and 66 mg of slow-moving enantiomer **1C-s**.

All attempts to obtain suitable crystals of resolved **1C** and its dibenzoate for X-ray crystallographic analysis in various solvents were in vain. Fortunately, crystals of **2C-s**,⁸ bis(4-chlorobenzoate) of **1C-s**, crystallized from hexane, were found to be suitable for X-ray crystallographic analysis.

X-ray crystallographic analysis of **2C-s** was performed with a crystal of 0.5 x 0.4 x 0.2 mm dimension using MoK α (40 kV, 40 mA). The crystal has the following lattice constants: $a = 13.807(3)$ Å, $b = 23.012(4)$ Å, $c = 10.724(4)$ Å, $\alpha = 95.95(2)^\circ$, $\beta = 108.90(2)^\circ$, $\gamma = 100.66(2)^\circ$, $V = 3119(2)$ Å³, and belonging to space group $P1$, $Z = 4$. The final R value was 0.057 for 7896 reflections ($I > 2\sigma(I)$). Absolute configurations of the chiral carbon atoms were determined both to be S with CuK α radiation (40 kV, 80 mA) by the X-ray anomalous dispersion technique.

The four molecules (A—D) of (S,S)-**2C** within an asymmetric unit have all different conformations, with the torsion angles of C—CH₂—O—C moieties in two of the 4-chlorobenzoate groups (+anüberiplanar (+ap) and +ap for A, +antclinal (+ac) and +ap for B, -ap and -ap for C, and -ap and -ac for D) and with the different puckering of hexafluorocyclopentane rings. No significant values were observed for bond distances and angles. The ORTEP drawing of molecule A is shown in Figure 1, and the selected torsion angles are listed in Table 1.

Thus, the absolute stereochemistry of the slow-moving enantiomer **1C-s** was determined to be (S,S)-**1C**.

The chiroptical properties of photochromic compounds may be useful for non-destructive readout of records when they are used as the rewritable recording media.^{1c} We therefore measured CD spectra of both enantiomers of **1C**. As shown in Figure 2, two negative Cotton effects were observed at about 520 nm and 320 nm for (S,S)-**1C**. The mirror-imaged Cotton effects were observed for (R,R)-**1C**.

The specific optical rotation value of (S,S)-**1C** (98% ee) at 820 nm ($[\alpha]_{820}$), where the compound has no absorption, was -251° (CH₃CN, 0.0480 g/100 ml at 25 °C).

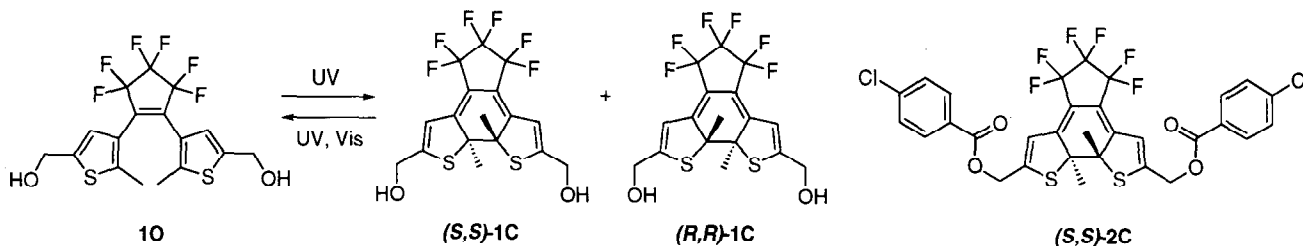
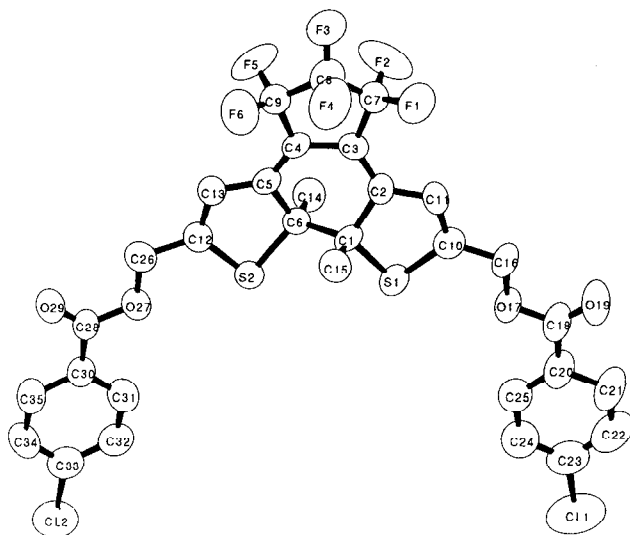
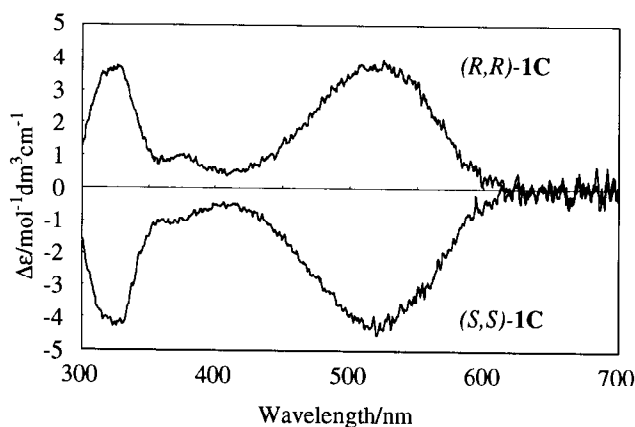


Table 1. Selected torsion angles of (*S,S*)-**2C** in crystals

Molecule	C ₄ -C ₃ -C ₇ -C ₈	C ₃ -C ₇ -C ₈ -C ₉	C ₇ -C ₈ -C ₉ -C ₄	C ₁₀ -C ₁₆ -O ₁₇ -C ₁₈	C ₁₂ -C ₂₆ -O ₂₇ -C ₂₈
A	22.5 (1.0)	-27.5 (1.0)	22.6 (1.0)	179.0 (1.0) (+ap)	179.2 (0.7) (+ap)
B	17.6 (1.2)	-26.0 (1.2)	25.1 (1.1)	125.2 (1.0) (+ac)	170.4 (0.9) (+ap)
C	15.7 (1.2)	-22.7 (1.3)	21.0 (1.4)	-176.2 (0.7) (-ap)	-176.8 (0.8) (-ap)
D	24.0 (1.0)	-27.5 (1.0)	22.2 (1.2)	-173.5 (0.8) (-ap)	-118.3 (1.0) (-ac)

**Figure 1.** ORTEP drawing of (*S,S*)-**2C** (molecule A).**Figure 2.** CD spectra of (*R,R*)- and (*S,S*)-**1C** in acetonitrile.

In summary, we have resolved the colored form of a dithienylethene, determined the absolute stereochemistry of one of the enantiomers by X-ray crystallographic analysis of a derivative, and correlated the structure with the CD spectrum and the optical rotation value. These knowledge are of particularly useful for further investigation of photochromism of optically active diarylethene derivatives. Theoretical study about the relationship between the absolute structure of photochromic molecules and the change of CD spectra is now under way.

We thank Mr. Hiroaki Izumi of our laboratory for technical assistance. This work has been done with the financial support

of a Grant-in-Aid for Scientific Research (No. 08651022) from Ministry of Education, Science, Sports and Culture, and Nissan Science Foundation, which are greatly acknowledged.

References and Notes

- 1 a) Y. Yokoyama, T. Iwai, Y. Yokoyama, and Y. Kurita, *Chem. Lett.*, **1994**, 225. b) Y. Yokoyama, Y. Shimizu, S. Uchida, and Y. Yokoyama, *J. Chem. Soc., Chem. Commun.*, **1995**, 785. c) Y. Yokoyama, S. Uchida, Y. Yokoyama, Y. Sugawara, and Y. Kurita, *J. Am. Chem. Soc.*, **118**, 3100 (1996).
- 2 a) B. L. Feringa, W. F. Jager, B. de Lange, and E. W. Meijer, *J. Am. Chem. Soc.*, **113**, 5468 (1991). b) B. L. Feringa, N. P. M. Huck, and H. A. von Doren, *J. Am. Chem. Soc.*, **117**, 9929 (1995). c) N. P. M. Huck, W. F. Jager, B. de Lange, and B. L. Feringa, *Science*, **273**, 1686 (1996).
- 3 a) M. Takeshita, K. Uchida, and M. Irie, *Chem. Commun.*, **1996**, 1807. b) T. Yamaguchi, K. Uchida, and M. Irie, *J. Am. Chem. Soc.*, **119**, 6066 (1997).
- 4 M. Negishi, O. Tsutsumi, T. Ikeda, T. Hiyama, J. Kawamura, M. Aizawa, and S. Takehara, *Chem. Lett.*, **1996**, 319.
- 5 K. Yang, B. Campbell, G. Birch, V. E. Williams, and R. P. Lemieux, *J. Am. Chem. Soc.*, **118**, 9557 (1996).
- 6 A. Miyashita, A. Iwamoto, T. Kuwayama, H. Shitara, Y. Aoki, M. Hirano, and H. Nohira, *Chem. Lett.*, **1997**, 965.
- 7 M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **71**, 985 (1998).
- 8 **1C**: Mp 125 – 128 °C. ¹H NMR (270 MHz, CDCl₃, TMS) δ/ppm 1.60 (2H, s), 1.88 (6H, s), 4.76 (4H, s), 6.95 (2H, s). IR (KBr) ν/cm⁻¹ 3292, 2928, 1273, 1049, 985. UV (toluene) no absorption maxima over 300 nm. The end absorption ends at 350 nm. MS (EI, 70 eV) *m/z* (rel intensity) 428 (M⁺, 100), 411 (51), 395 (43), 365 (43), 333 (34). Found: *m/z* 428.0332. Calcd for C₁₇F₆H₁₄O₂S₂ 428.0339.
1C (racemic): Mp 127 – 130 °C. ¹H NMR (270 MHz, CDCl₃, TMS) δ/ppm 1.88 (2H, s), 2.06 (6H, s), 4.53 (4H, s), 6.25 (2H, s). IR (KBr) ν/cm⁻¹ 3219, 2928, 1343, 1113, 1047, 968. UV (toluene) λ_{max}/nm 519 ε_{max}/mol⁻¹dm³cm⁻¹ 5860. MS (EI, 70 eV) *m/z* (rel intensity) 428 (M⁺, 65), 395 (42), 365 (33), 149 (100). Found: *m/z* 428.0344. Calcd for C₁₇F₆H₁₄O₂S₂ 428.0339.
(S,S)-2C: Mp 122 – 125 °C. ¹H NMR (270 MHz, CDCl₃, TMS) δ/ppm 2.09 (6H, s), 5.18 (4H, s), 6.29 (2H, s), 7.46 (4H, d, *J*/Hz = 8.58), 8.00 (4H, d, *J*/Hz = 8.57). IR (KBr) ν/cm⁻¹ 2926, 1729, 1270, 1092, 757. MS (EI, 70 eV) *m/z* (rel intensity) 704 (M⁺, 15), 547 (29), 532 (59), 392 (100).