Conformational Control of Photochromic Reactivity in a Diarylethene Single Crystal

Seiya Kobatake,1,* Yoshimichi Matsumoto,2 and Masahiro Irie2,*

1 Department of Applied and Bioapplied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585 (Japan)
Fax: (+81)6-6605-2797; E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp

2 Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812-8581 (Japan)
Fax: (+81)92-642-3568; E-mail: irie@cstf.kyushu-u.ac.jp
Experimental Section

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Gemini-200 spectrometer and a Jeol A-400 spectrometer, respectively. Tetramethylsilane was used as an internal standard. High performance liquid chromatography (HPLC) was carried out using a Hitachi L-7100/L-7400/D-2500 connected with a silicagel column (Wako Wakosil 5SIL). Mass spectra were taken with a Jeol JMS-AX500 mass spectrometer. Absorption spectra in hexane were measured with a Hitachi U-3410 absorption spectrophotometer. Solvents used were spectroscopic grade and purified by distillation before use. Absorption spectra in a single-crystalline phase were measured using a Nikon E600POL polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Polarizer and analyzer were set in parallel each other. Photoirradiation was carried out using a 100 W mercury short arc lamp. The wavelength of the light used (366 nm) was selected by passing the light through a band pass filter. X-ray crystallographic analysis of single crystals was carried out using a Bruker SMART CCD X-ray diffractometer or a Rigaku RAXIS X-ray diffractometer with MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The cell constants were calculated by the global refinement. The structure was solved by direct methods using SHELXS-86 and refined by full least-squares on $F^2$ using SHELXL-97.

1,2-Bis(2-methoxy-4-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (1a) was synthesized as follows. To dry THF (150 mL) containing 2,4-dibromo-5-methoxy-3-methylthiophene (7.3 g, 0.026 mol) was added a 15% $n$BuLi hexane solution (17 mL, 0.028 mol) at –78 °C. Tributyl borate (10 mL, 0.037 mol) was slowly added to the reaction mixture at –78 °C, and the mixture was stirred for 3 h. Iodobenzene (5.3 g, 0.026 mol), 20 wt% Na$_2$CO$_3$ (aq) (60 mL), and Pd(PPh$_3$)$_4$ (1.0 g, 0.87 mmol) were added to the mixture, and the mixture was refluxed for 5 h at 70 °C to form 5.4 g of 3-bromo-2-methoxy-4-methyl-5-phenylthiophene (3) (Yield: 73%). To the solution of 3 (5.0 g, 0.018 mmol) in dry THF (15 mL), a 15% $n$BuLi hexane
solution (11 mL; 0.018 mol) was added at −78 °C. Then, to the solution was added 1.2 mL (0.0089 mol) of octafluorocyclopentene to yield 2.0 g of 1a (Yield: 38%). 1a: m.p. 117.5-118.5 °C; 1H NMR (200 MHz, CDCl₃, TMS): δ = 2.10 (s, 6H, Me), 3.78 (s, 6H, MeO), 7.2-7.5 ppm (m, 10H, Ph); 13C NMR (100 MHz, CDCl₃): δ = 14.1 (Me), 61.3 (MeO), 110.2 (3-thienyl), 111.5 (CF₂), 116.0 (CF₂), 124.4 (5-thienyl), 127.1 (Ph), 128.6 (Ph), 129.1 (Ph), 130.5 (4-thienyl), 134.1 (Ph), 139.5 (C=C), 163.4 ppm (2-thienyl); FAB HRMS (m/z) [M]+ calcd for C₂₉H₂₂F₆O₂S₂: 580.0965; found: 580.0966; UV/Vis (n-hexane): λ_max (ε) = 288 nm (28600 M⁻¹cm⁻¹).

The closed-ring isomer 1b was isolated by passing a photostationary solution containing 1a and 1b through a HPLC (silica-gel column, hexane/ethyl acetate (98:2) as the eluent). 1b: 1H NMR (200 MHz, CDCl₃, TMS): δ = 1.98 (s, 6H, Me), 3.86 (s, 6H, MeO), 7.2-7.5 ppm (m, 10H, Ph); MS: m/z: 580 [M⁺]; UV/Vis (n-hexane): λ_max (ε) = 617 nm (12000 M⁻¹cm⁻¹).