ChemComm
www.rsc.org/chemcomm

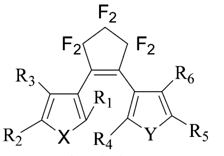
Photochromism of a novel 6π conjugate system having a bis(2,3′-benzothienyl) unit

Tadatsugu Yamaguchi,*[a] Yuji Fujita[a] and Masahiro Irie[b]
[a] *Fukuoka Industrial Technology Center, 3-2-1 Kamikoga, Chikushino, Fukuoka 818-8540, Japan. E-mail: tyama@fitc.pref.fukuoka.jp; Fax: +81-92-925-7724; Tel: +81-92-925-7721*
[b] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan. E-mail: irie@cstf.kyushu-u.ac.jp; Fax: +81-92-642-3568; Tel: +81-92-642-3556*

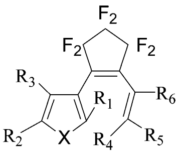
Received (in Cambridge, UK) 26th January 2004, Accepted 1st March 2004
First published as an Advance Article on the web 19th March 2004

A novel photochromic molecule having a bis(2,3′-benzothienyl) unit has been synthesized. The derivative underwent a thermally irreversible photochromic reaction upon alternate irradiation with UV and visible light.

Diarylethene derivatives are known to undergo thermally irreversible photochromic reactions.[1–4] Recently, Branda *et al.*[5] and Yokoyama *et al.*[6] independently prepared 1-aryl-1,3-butadiene derivatives and showed that the non-symmetric derivatives also undergo efficient 6π-electrocyclization reactions.

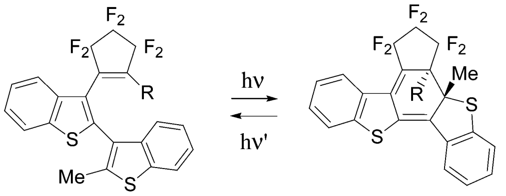


Diarylethene



1-Aryl-1,3-butadiene

Monosubstituted perfluorocyclopentenes can be selectiviely prepared by controlling the ratio of perfluorocyclopentene and n-butyllithium. These mono-substituted compounds are useful intermediates for non-symmetrical diarylethene derivatives. During the course of preparation of such non-symmetric diarylethene derivatives, we found (2-(2-methylbenzothien-3-yl)benzothien-3-yl)perfluorocyclopentene **1a** undergoes a photochromic reaction. Here we report on new thermally irreversible photochromic compounds having a bis(2,3′-benzothienyl) unit.



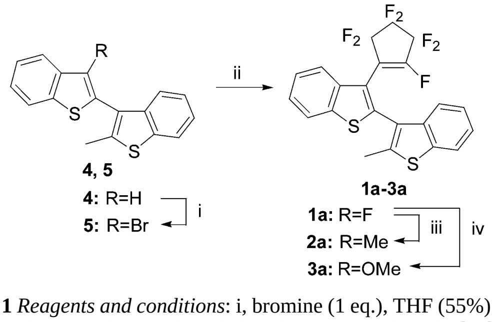
1a-3a

1a: R=F
2a: R=Me
3a: R=OMe

1b-3b

1b: R=F
2b: R=Me
3b: R=OMe

Synthesis of the compounds **1a, 2a** and **3a** was carried out as shown in Scheme 1. Compound **4** was prepared according to the Suzuki coupling reaction starting from 2-methyl-3-iodobenzothiophene and benzothiophene.[7] Compound **5** was prepared by the bromination of **4** in 55% yield.[8] The coupling reaction between **5** and octafluorocyclopentene gave the **1a** in 18% yield.[9] **1a** (1 eq.) was treated with methyllithium diethyl ether solution (1 eq.) or sodium methoxide (1 eq.) at room temperature to give methyl or methoxy substituted derivatives **2a** and **3a**, respectively. The structures of **2a** and **3a** were determined with ^{1}H NMR and X-ray crystallography.[10,11]



Scheme 1 *Reagents and conditions*: i, bromine (1 eq.), THF (55%); ii, 1) n-BuLi (1 eq.), THF, 2) C_5F_8 (1 eq.) (18%); iii, MeLi (1 eq.), diethyl ether (61%); iv, NaOMe (1 eq.), THF (48%).

The single crystal of **3a** was obtained by recrystallization from the mixed solvent of hexane and ethyl acetate. X-Ray crystallographic analysis was performed with a crystal of 0.3 × 0.3 × 0.2 mm dimensions using Mo Kα (60 kV, 30 mA).[12] The final *R* value was 0.0464 for 3769 reflections ($I > 2\sigma(I)$). The ORTEP drawing of **3a** is shown in Fig. 1. The ORTEP drawing confirms that **3a** has two benzothiophene and methoxy moieties.

No crystals showed photochromism but in hexane all cyclized and changed color upon UV irradiation. Compound **1a** underwent rapid degradation after several cycles in hexane, whereas **2a** and **3a** undergo reversible photochromism more than 10 times. Therefore the photochromic performance was examined for **2a** and **3a**. Fig. 2

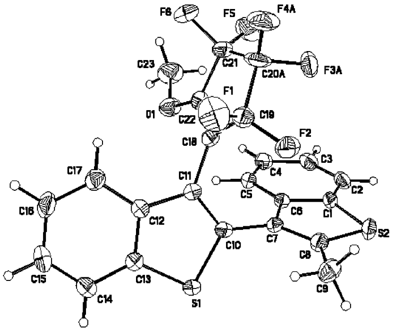


Fig. 1 ORTEP drawing of **3a** showing 50% probability displacement ellipsoids.

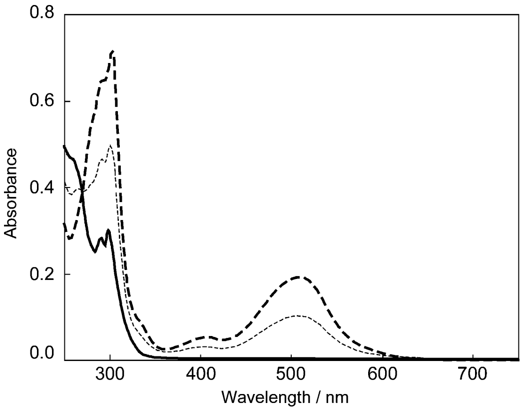


Fig. 2 Absorption spectra of **3a** (solid line) and **3b** (dashed line) in hexane (2.54 × 10^{-5} mol l^{-1}) and in the photostationary state (broken line) under irradiation with 313 nm light.

DOI: 10.1039/b401207k

shows the absorption spectral change of **3** upon irradiation with 313 nm light in hexane. Diarylethene **3a** has an absorption shoulder at 300 nm (ε 1.18 × 10^4 $dm^3\ mol^{-1}\ cm^{-1}$). Upon irradiation with 313 nm light, the colorless solution of **3a** turned brilliant red, in which a visible absorption band was observed at 510 nm (ε 7.58 × 10^3 $dm^3\ mol^{-1}\ cm^{-1}$).

The conversion at the photostationary state from **3a** to **3b** was 52%. The colored isomer was isolated with HPLC and recrystallized from hexane. X-Ray crystallographic analysis of the colored crystal was carried out and the ORTEP drawing of the isomer is shown in Fig. 3.[13] The structure was confirmed to be **3b**. The colored form disappeared upon irradiation with visible light (λ > 480 nm). Both isomers were stable at 50 °C in hexane and at 70 °C for more than 1 week in toluene. The absorption intensity of **3b** decreased to 70% of the first cycle after 10 photocyclization/cycloreversion cycles in the presence of air.[14]

In case of **2a**, similar photochromic behavior was observed in hexane. The conversion upon irradiation with 313 nm light at the photostationary state was 60%. The absorption intensity of **2b** decreased to 70% of the first cycle after 100 photocyclization/cycloreversion cycles in the presence of air.[14] Table 1 summarizes the absorption maxima and the molar coefficients of the open- and closed-ring isomers in hexane. The cyclization and cycloreversion quantum yields were also measured and are included in Table 1. The cyclization quantum yields of **2a** and **3a** are almost similar. The cycloreversion quantum yield of **3b** ($\Phi = 0.085$) was smaller than that of **2b** ($\Phi = 0.15$). In diarylethene derivatives, a methoxy group at the 2-position is known to decrease the cycloreversion quantum yield.[15] A similar substitution effect was observed for **3b**.

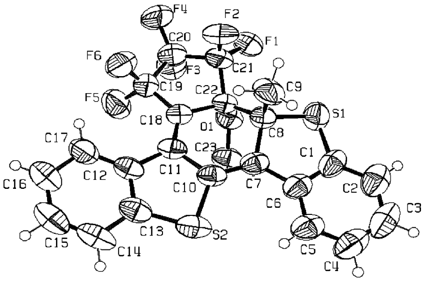


Fig. 3 ORTEP drawing of **3b** showing 50% probability displacement ellipsoids.

Table 1 Absorption characteristics and photoreactivity of dithienylethene in hexane

Compound	$\varepsilon/10^4\ dm^3\ mol^{-1}\ cm^{-1}$		Quantum yield	
	a	**b**	Cyclization (313 nm)	Cycloreversion (517 nm)
2	1.2 (300 nm)	0.79 (504 nm)	0.41	0.15
3	1.2 (300 nm)	0.76 (510 nm)	0.40	0.085

In conclusion, a new type of 6π conjugated system having a bis(2,3′-benzothienyl) unit has been synthesized and its photochromic reactivity has been examined. These compounds underwent efficient photochromic reactions in hexane. The colored isomers were thermally stable. Further modification of the structure is now in progress in our laboratory.

Notes and references

1 H. Dürr and H. Bouas-Laurent, *Photochromism Molecules and Systems*, Elsevier, Amsterdam, 1990.
2 M. Irie, *Photo-Reactive Materials for Ultrahigh-Density Optical Memory*, Elsevier, Amsterdam, 1994.
3 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
4 K. Uchida and M. Irie, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 985.
5 A. Peters, C. Vitols, R. McDonalds and N. R. Branda, *Org. Lett.*, 2003, **5**, 1183.
6 S. M. Shresta, H. Nagashima, Y. Yokoyama and Y. Yokoyama, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 363.
7 **4**: Colorless crystals; mp. 113–114 °C; ^{1}H NMR (200 MHz) δ 2.65(s, 3H), 7.34–7.43(m, 4H), 7.45(s, 1H), 7.72–7.83(m, 4H). MS (EI) *m*/*z* 290(M$^+$). Anal. Calcd for $C_{17}H_{12}S_2$: C 72.82, H 4.31%. Found: C 72.83, H 4.35%.
8 **5**: Colorless crystals; mp. 122–123 °C; ^{1}H NMR (200 MHz) δ 2.53(s, 3H), 7.29–7.58(m, 4H), 7.78–7.92(m, 4H). MS (EI) *m*/*z* 358(M$^+$). Anal. Calcd for $C_{17}H_{11}BrS_2$: C 56.83, H 3.09%. Found: C 56.62, H 3.13%.
9 **1a**: Colorless crystals; mp. 84–85 °C; ^{1}H NMR (200 MHz) δ 2.43(s, 3H), 7.62–7.66(m, 2H), 7.99–8.03(m, 1H), 8.64–8.67(m, 1H). MS (EI) *m*/*z* 472(M$^+$). Anal. Calcd for $C_{22}H_{11}F_7S_2$: C 55.93, H 2.35%. Found: C 55.97, H 2.41%.
10 **2a**: Colorless crystals; mp. 121–122 °C; ^{1}H NMR (200 MHz) δ 1.64(s, 1.5H), 1.89(s, 1.5H), 2.47(s, 1.5H), 2.69(s, 1.5H), 7.23–7.35(m, 3H), 7.43–7.47(m, 3H), 7.75–7.79(m, 1H), 7.93–7.96(m, 1H). MS (EI) *m*/*z* 468(M$^+$); Anal. Calcd for $C_{23}H_{14}F_6S_2$: C 59.04, H 3.05%. Found: C 58.97, H 3.01%. **2b**: ^{1}H NMR (200 MHz) δ 1.75–1.78(m, 3H), 1.89(s, 1.5H), 1.92(s, 1.5H), 7.19–7.32(m, 4H), 7.41–7.45(m, 2H), 7.60–7.65(m, 1H), 8.05–8.10(m, 1H).
11 **3a**: Colorless crystals; mp. 127–128 °C; ^{1}H NMR (200 MHz) δ 2.43(s, 3H), 3.64(s, 3H), 7.24–7.35(m, 3H), 7.43–7.47(m, 3H), 7.75–7.79(m, 1H), 7.93–7.96(m, 1H). MS (EI) *m*/*z* 484(M$^+$); Anal. Calcd for $C_{23}H_{14}F_6OS_2$: C 57.03, H 2.92%. Found: C 57.02, H 2.91%. **3b**: ^{1}H NMR (200 MHz) δ 1.90(s, 1.5H), 1.94(s, 1.5H), 3.37(s, 3H), 7.16–7.38(m, 4H), 7.48–7.51(m, 2H), 7.60–7.65(m, 1H), 8.21–8.26(m, 1H).
12 Crystal data for **3a**: $C_{23}H_{14}F_6OS_2$, MW = 484.46, monoclinic, space group $P2_1/n$, a = 15.459(3) Å, b = 7.6854(16) Å, c = 18.589(4) Å, α = 90°, β = 105.080(3)°, γ = 90°, V = 2132.5(8) Å^3, Z = 4, D_c = 1.509 g cm^{-3}, R_1 = 0.0464 for 3769 observed reflections with $I > 2\sigma(I)$ from 4460 unique reflections. CCDC 229919.
13 Crystal data for **3b**: $C_{23}H_{14}F_6OS_2$, MW = 484.46, tetragonal, space group $I4_1/a$, a = 25.580(6) Å, b = 25.580(6) Å, c = 12.455(4) Å, α = 90°, β = 90°, γ = 90°, V = 8150(4) Å^3, Z = 16, D_c = 1.579 g cm^{-3}, R_1 = 0.0499 for 1567 observed reflections with $I > 2\sigma(I)$ from 2959 unique reflections. CCDC 229920. See http://www.rsc.org/suppdata/cc/b4/b401207k/ for crystallographic data in CIF or other electronic format.
14 Uchida, Y. Kido, T. Yamaguchi and M. Irie, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1101.
15 S. Takami, T. Kawai and M. Irie, *Eur. J. Org. Chem.*, 2002, 3796.