

## Photochromic Properties of Diarylethene Maleimide Derivatives in Polar Solvents

Tadatsugu Yamaguchi\* and Masahiro Irie\*<sup>†</sup>

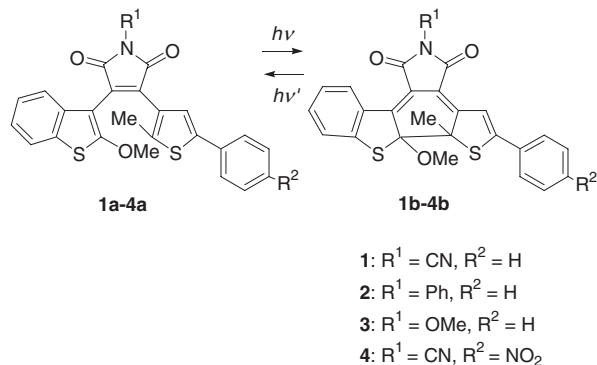
Chemical and Textile Industry, Fukuoka Industrial Technology Center,  
3-2-1 Kamikoga, Chikushino, Fukuoka 818-8540

<sup>†</sup>Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,  
6-10-1Hakozaki, Higashi-ku, Fukuoka 812-8581

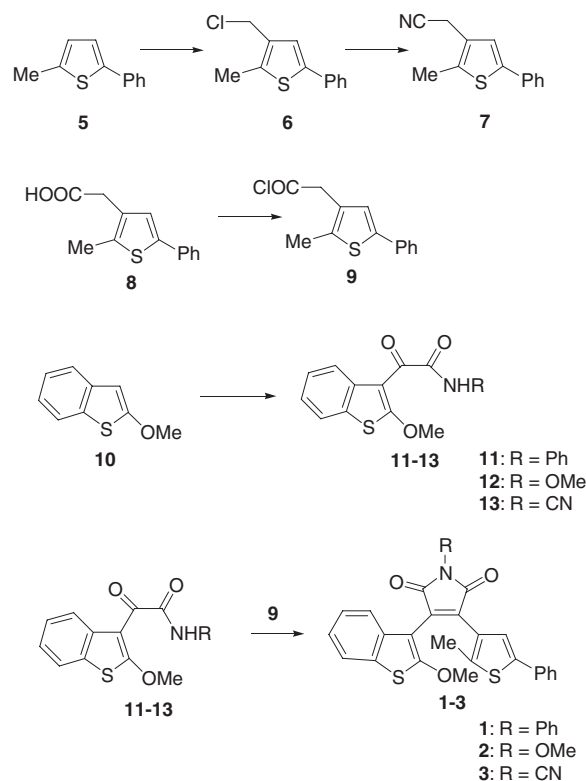
(Received July 29, 2004; CL-040895)

Diarylmaleimide derivatives having methoxy, phenyl, or cyano group as a nitrogen substituent were synthesized in an attempt to prepare photochromic compounds which exhibit photochromic reactivity even in polar solvents. Although the derivatives having methoxy or phenyl group did not undergo photochromism in polar solvents, the derivative having a cyano group showed photochromism even in polar solvents.

Various kinds of diarylethenes that undergo thermally irreversible and fatigue-resistant photochromic reactions have been developed.<sup>1-3</sup> One of potential application fields of photochromic compounds is a fluorescent probe in biological systems, such as a FRET probe.<sup>4</sup> For such application the photochromic compound should have sensitivity in visible region and the reactions should take place even in polar solvents, because UV light induces the damages of the biological systems. Diarylmaleimides<sup>5,6</sup> as well as diarylmaleic anhydrides<sup>7-9</sup> exhibit reversible photoisomerization reactions upon irradiation with visible light. However, their photochromic reactions are strongly prohibited in polar solvents. This is due to an intramolecular electron transfer (TICT) from the donor aryl moiety to the electron acceptor maleic anhydride or maleimide moiety.<sup>5,8</sup> In this work, the diarylmaleimide derivatives having methoxy, phenyl, or cyano groups as a nitrogen substituent were synthesized in an attempt to control photochromic reactivity in polar solvents. Methoxy substituent was also introduced at 2-position of benzothiophene to decrease the cycloreversion quantum yield.<sup>10</sup>



Diarylmaleimide derivatives **1a-3a** were synthesized according to Scheme 1. The detail procedure has been reported in Ref 6. 2-Methyl-5-phenylthiophene was reacted with chloromethyl methylether and with sodium cyanide to give compound **7** in 47% yields. The carboxylic acid **8** was obtained by the hydrolysis of **7** in 95% yields. *N*-alkylglycoylamide derivatives (**11-13**) were synthesized from **10**. Cyanamide, methoxyamide or aniline was prepared by the same procedure as used in



**Scheme 1.** Synthesis of diarylethene maleimide derivatives **1-3**.

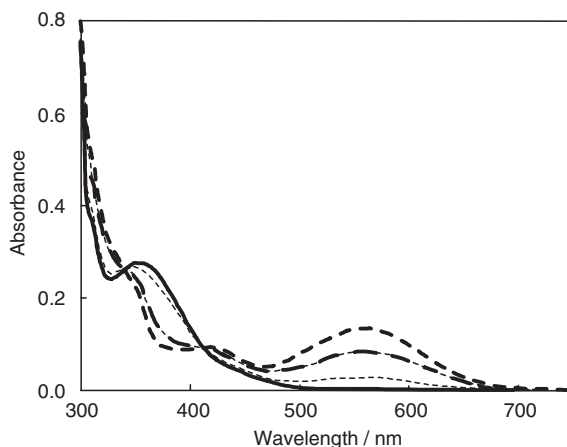
Ref. 6. The coupling reaction of **9** with *N*-alkylglycoylamide (**11-13**) gave diarylethenes **1-3** in 12-20% yields. A nitrophenyl derivative **4** was also synthesized to improve the photoreactivity. The synthetic route of **4** was the same as that of **1**. 2-methyl-5-(4-nitrophenyl)thiophene was used instead of 2-methyl-5-phenylthiophene.

Table 1 summarizes conversions from the open to the closed

**Table 1.** Conversion rates of **1-4** from open-ring to closed-ring isomer upon irradiation with 436-nm or 365-nm light in various solvents

Irradiation Wavelength	Conversion Rate/%				
	Hexane	Toluene	DMF	Acetonitrile	Ethanol
<b>1</b> 436 nm	— <sup>a</sup>	45	13	5	3
<b>2</b> 436 nm	43	28	0	0	0
<b>3</b> 436 nm	45	26	0	0	0
<b>4</b> 436 nm	— <sup>a</sup>	70	43	16	10
<b>4</b> 365 nm	— <sup>a</sup>	82	73	70	30

<sup>a</sup>insoluble.



**Figure 1.** Absorption spectra of **4a** (solid line) **4b** (dashed line) and in the photostationary state under irradiation with 436-nm light (dotted line) and 365-nm light (dott-dashed line) in acetonitrile solution ( $1.72 \times 10^{-5}$  mol/L).

closed-ring isomers at the photostationary state in various solvents. Upon irradiation with 436-nm light, the open-ring isomer **1a** converted to the closed-ring isomer **1b**, which has the absorption maximum at 547 nm. The conversion rate of **1** was 45% in toluene. The blue color disappeared upon irradiation with >560-nm light. In polar solvents such as acetonitrile the rate was decreased to 5%.

Compounds **2** and **3** underwent reversible photoisomerization reactions upon irradiation with 435-nm and >560-nm light in hexane and toluene solutions. The conversion rates of **2** and **3** were dramatically decreased by changing the solvent from hexane to toluene. These compounds did not show any spectral change upon irradiation with any wavelength in acetonitrile. The result suggests that the reactivity in polar solvents is dependent on the nitrogen substituent. The cyano group is the best substituent for the photoreaction in polar solvents.

In order to improve the photoreactivity in polar solvents, an electron withdrawing nitro group was introduced at the para-position of the phenyl group. The electron withdrawing group is known to decrease the photocycloreversion quantum yield.<sup>11</sup> Figure 1 shows the absorption spectral change of **4** in acetonitrile. Upon irradiation with 436 nm, the open-ring isomer **4a** converted to the closed ring isomer **4b** with the absorption band at 570 nm. The conversion rate of **4** was 30%. Upon irradiation with >560-nm light, the closed-ring isomer returned back to the open-ring isomer. The conversion rate was increased to 70% under irradiation with 366 nm, at which the absorption coefficient of the open-ring isomer is larger than that of the closed-ring isomer.

The quantum yields, the absorption maxima of the open- and the closed-ring isomers, and their absorption coefficients are summarized in Table 2. The cyclization quantum yields of **1–4** are relatively high in toluene. As expected, the cyclorever-

**Table 2.** Absorption characteristics and photoreactivity of diarylethene in toluene

Compound	$\epsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$		Quantum yield	
	Open Form	Closed-ring Form	Cyclization	Cycloreversion
<b>1</b>	3.24 (410 nm)	4.78 (547 nm)	0.27 (436 nm)	0.49 (547 nm)
<b>2</b>	3.08 (412 nm)	4.30 (550 nm)	0.27 (436 nm)	0.20 (550 nm)
<b>3</b>	4.02 (422 nm)	5.76 (542 nm)	0.17 (436 nm)	0.42 (542 nm)
<b>4</b>	3.03 (415 nm)	4.55 (570 nm)	0.20 (436 nm)	0.068 (550 nm)

sion quantum yield of **4b** was very small ( $\Phi = 0.068$ ). Both cyano and nitro substituent contribute to increase the conversion rate.

## References and Notes

- H. Dürr and H. Bouas-Laurent, "Photochromism Molecules and Systems," Elsevier, Amsterdam (1990).
- M. Irie, "Photo-Reactive Materials for Ultrahigh-Density Optical Memory," Elsevier, Amsterdam (1990).
- M. Irie, *Chem. Rev.*, **100**, 1685 (2000).
- L. Giordano, T. M. Jovin, M. Irie, and E. A. Jares-Erijman, *J. Am. Chem. Soc.*, **124**, 7481 (2002).
- T. Yamaguchi, K. Uhida, and M. Irie, *J. Am. Chem. Soc.*, **119**, 6066 (1997).
- K. Uchida, Y. Kido, T. Yamaguchi, and M. Irie, *Bull. Chem. Soc. Jpn.*, **71**, 1101 (1998).
- M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988).
- M. Irie and K. Sayo, *J. Phys. Chem.*, **96**, 7671 (1992).
- K. Uchida, Y. Nakayama, and M. Irie, *Bull. Chem. Soc. Jpn.*, **63**, 1311 (1990).
- K. Shibata, S. Kobatake, and M. Irie, *Chem. Lett.*, **2001**, 618.
- K. Matsuda, Y. Shinkai, T. Yamaguchi, K. Nomiya, M. Isayama, and M. Irie, *Chem. Lett.*, **32**, 1178 (2003).
- 1a**: Orange crystals; mp. 84–85 °C;  $^1\text{H NMR}$  (200 MHz)  $\delta$  2.57 (s, 3H), 3.70 (s, 3H), 6.79–7.87 (m, 10H). EIMS  $m/z$  456 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{16}\text{N}_2\text{O}_3\text{S}_2$ : C 65.77, H 3.53, N 6.14%. Found: C 65.75, H 3.53, N 6.06%.
- 2a**: Orange crystals; mp. 78–79 °C;  $^1\text{H NMR}$  (200 MHz)  $\delta$  2.52 (s, 3H), 3.72 (s, 3H), 6.84–7.73 (m, 15H). EIMS  $m/z$  507 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{30}\text{H}_{21}\text{NO}_3\text{S}_2$ : C 70.98, H 4.17, N 2.76%. Found: C 70.97, H 4.21, N 2.72%.
- 3a**: Orange crystals mp. 159–160 °C;  $^1\text{H NMR}$  (200 MHz)  $\delta$  2.50 (s, 3H), 3.72 (s, 3H), 4.07 (s, 3H), 6.77–8.11 (m, 10H). EIMS  $m/z$  461 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{19}\text{NO}_4\text{S}_2$ : C 65.06, H 4.15, N 3.03%. Found: C 65.16, H 4.22, N 2.89%.
- 4a**: Orange crystals; mp. 78–80 °C;  $^1\text{H NMR}$  (200 MHz)  $\delta$  2.46 (s, 3H), 3.80 (s, 3H), 6.83–8.20 (m, 10H). EIMS  $m/z$  501 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{25}\text{H}_{15}\text{N}_3\text{O}_5\text{S}_2$ : C 59.87, H 3.01, N 8.38%. Found: C 59.97, H 3.07, N 8.25%.