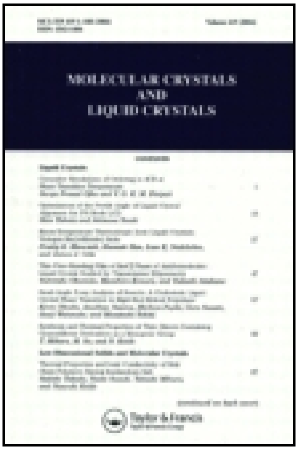

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Control of Cycloreversion Quantum Yields of Diarylethenes by Introduction of Substituents at the Reactive Carbons

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Control of Cycloreversion Quantum Yields of Diarylethenes by Introduction of Substituents at the Reactive Carbons

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Several diarylethene derivatives having various substituents at the reactive carbons were prepared and the quantum yields were measured. Although the cyclization quantum yields were scarcely affected by the introduction of substituents, the cycloreversion quantum yields varied depending on the substituents.

Keywords: diarylethene; photochromism; quantum yield; substituent effect

INTRODUCTION

Photochromic compounds undergo reversible isomerization between two isomers having different absorption spectra upon irradiation with appropriate wavelength of light [1]. Among these photochromic compounds, diarylethenes have attracted much attention because they undergo thermally irreversible and fatigue-resistant photochromic reactions. Various diarylethene derivatives have been synthesized so far in an attempt to apply them to optoelectronic devices such as memories and switches [2].

Control of quantum yields is one of the most fundamental issues of molecular design. In order to control the cycloreversion quantum yields of diarylethenes we took a novel strategy to introduce various

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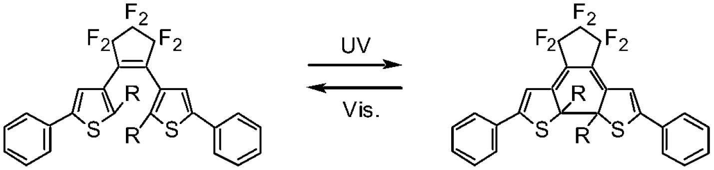
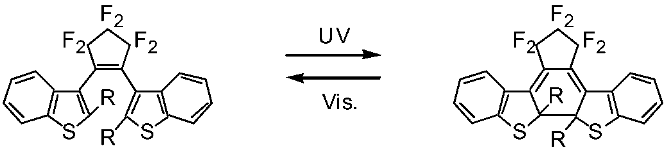


1a: R = OCH_3
2a: R = CN
3a: R = —≡—Ph
4a: R = —≡—$CH_2CH_2CH_3$
5a: R = CH=C$(CH_3)_2$
6a: R = CH_2OCH_3
7a: R = CH_3

1b: R = OCH_3
2b: R = CN
3b: R = —≡—Ph
4b: R = —≡—$CH_2CH_2CH_3$
5b: R = CH=C$(CH_3)_2$
6b: R = CH_2OCH_3
7b: R = CH_3



8a: R = OCH_3
9a: R = CN
10a: R = —≡—Ph
11a: R = —≡—$CH_2CH_2CH_3$
12a: R = CH_3

8b: R = OCH_3
9b: R = CN
10b: R = —≡—Ph
11b: R = —≡—$CH_2CH_2CH_3$
12b: R = CH_3

SCHEME 1 Chemical structure and photochromism of diarylethene derivatives.

substituents at the reactive carbons [3]. Herein we report on photochromic properties of several diarylethene derivatives having various substituents at the reactive carbons as shown in Scheme 1.

RESULTS AND DISCUSSION

Photochromic Reaction

The synthesis of diarylethene derivatives was carried out according to the general synthetic procedure [4]. Each diarylethene underwent photochromism upon irradiation with appropriate wavelength of light in hexane. Colorless solutions of the diarylethene derivatives turned blue, purple, red, and orange, depending on the substituents at the

TABLE 1 Absorption Maxima of Closed-ring Isomers and Quantum Yields in Hexane

	λ_{max}/nm[a]	$\Phi_{a\to b}$[b]	$\Phi_{b\to a}$[c]
1	625	0.44	1.7×10^{-5}
2	545	0.42	0.41
3	575	0.17	0.32
4	575	0.41	0.27
5	625	0.25	0.23
6	580	0.50	0.0062
7	575	0.59	0.013
8	547	0.34	0.030
9	496	0.28	0.59
10	520	0.13	0.55
11	520	0.21	0.58
12	517	0.35	0.35

[a] Absorption maxima of the closed-ring isomers in the visible region.
[b] Cyclization quantum yield.
[c] Cycloreversion quantum yield.

reactive carbons. The absorption maxima of close-ring isomers are summarized in Table 1.

Quantum Yield

The cyclization and cycloreversion quantum yields in hexane at room temperature are shown in Table 1. The cyclization quantum yields are close to the values of methyl derivatives **7a** and **12a**, and scarcely affected by modification of substituents at the reactive carbons. Conversely, the cycloreversion quantum yields varied depending on the substituents. Methoxy groups extremely suppressed the cycloreversion reactivity to less than 10^{-4}. However, cyano and π-conjugated groups enhanced the reactivity. The substituent effect was independent of the aryl groups, and similar tendency was observed for benzothiophene derivatives. The cycloreversion quantum yields of **2b** and **9b** were obtained to be 0.41 and 0.59 which are 30 and 1.7 times larger than those of **7b** and **12b**, respectively. We can control the cycloreversion reactivity of the diarylethenes as much as 24000 times.

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