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Structurally Versatile Novel Photochromic Bisarylindenone and Its Acetal: Achievement of Large Cyclization Quantum Yield

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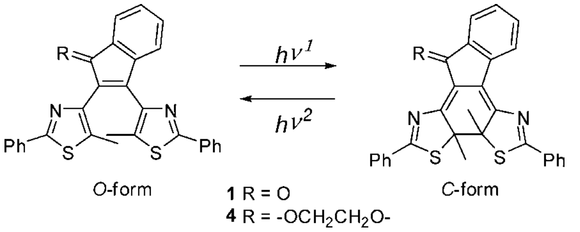
ABSTRACT



1 R = O
4 R = $-OCH_2CH_2O-$

Bisarylindenones and an acetal derivative, a novel thermally irreversible photochromic family based on 6π-electrocyclization with three easily modifiable functional groups, have been synthesized. 2,3-Bis(5-methyl-2-phenyl-4-thiazolyl)indenone showed photochromic back-and-forth reactions with two different visible lights. Its ethylene acetal recorded 0.81 as the photocyclization quantum yield in hexane, which is the largest value known to date for 6π-electrocyclization in solution.

In order to meet the requirements of various applications and research demands for photodriven switches,[1] the development of novel photochromic compounds classified as a new structural family is vital. Although diarylethenes[2] are well-designed and, indeed, a superior class of thermally irreversible photochromic compounds, one drawback is that structural modifications are mainly carried out on the aryl groups on the right and left ends of the molecule[3] and a modification of the central ethene moiety is sometimes inconvenient. Nowadays, most diarylethenes are hexafluorocyclopentene-based and its structural modification is almost impossible. First-generation diarylethenes have maleic anhydride[4] and maleimide[5] structures; however, their extensive structural modifications have been difficult. When the central ethene is incorporated in an aryl group,[6] it usually becomes thermally reversible because of the large loss of aromatic stabilization energy upon photocyclization. Other modifications have proved that the central ethene moiety can act as a switchable functional group[7] or the monomer for polymerization.[8]

We envision that if the central ethene moiety were a functional group that could be modified structurally as well as electronically in easily accessible ways, the diversity of

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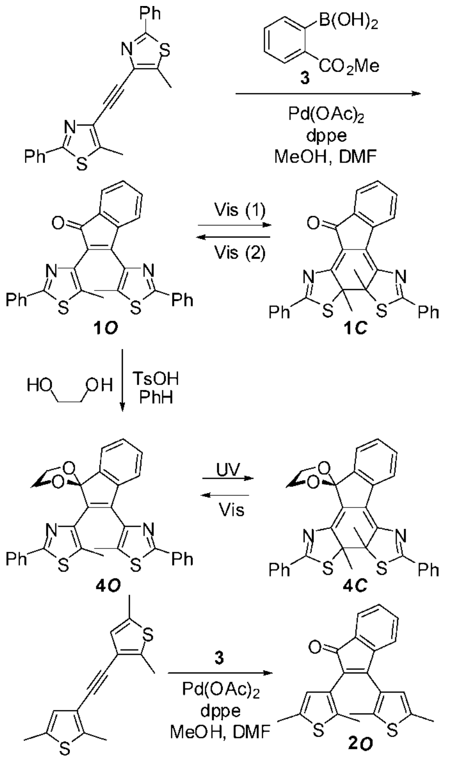
the thermally irreversible photochromic molecules could be widely extended. We chose a carbonyl group and a phenyl group as such easily modifiable functional groups. However, as a number of 2,3-bisaryl-1,4-naphtho- and benzoquinones[9] and 3,4-bis(2-methyl-5-phenyl-3-thienyl)-3-cyclobutene-1,2-dione[10] were reported to be nonphotochromic, we decided to synthesize 2,3-bisarylindenones. These compounds have three easily modifiable functional groups: two aryl groups and the indenone group possessing a carbonyl and a phenyl group.[11]

We employed 5-methyl-2-phenyl-4-thiazolyl and 2,5-dimethyl-3-thienyl groups as the aryl groups and synthesized 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)indenone (**1*O***) and 2,3-bis(2,5-dimethyl-3-thienyl)indenone (**2*O***). When they cyclize by photoirradiation, the closed forms (**1*C*** and **2*C***) as the result of photoinduced 6π-electrocyclization possess large conjugate systems, which may show the absorption bands at longer wavelengths in the visible region.

The synthesis of 2,3-bisarylindenones **1*O*** and **2*O*** was carried out, as shown in Scheme 1, by employing Tsukamoto's Pd-catalyzed [2 + 3] ring-closing reaction[12] as the key step using 2-methoxycarbonylphenylboronic acid **3** and bisarylethyne.[13]

Scheme 1. Synthetic Outline and Photochromic Reactions of **1**, **2**, and **4**



We prepared two corresponding symmetric ethynes according to known procedures and reacted them with boronic acid **3** using Pd(OAc)$_2$ as the catalyst. The yields were 25 and 27% for **1*O*** and **2*O***, respectively. Because the low yield is due to the deactivation of the catalyst, the recovered organic materials (a mixture of starting ethyne and the product) by fast silica gel column chromatography were subjected to the same reaction two more times. The yield of **1*O*** in this manner was 73%.

In acetonitrile, **1*O*** showed an absorption maximum at 433 nm, in addition to the maxima in the UV region at 262 and 311 nm (Figure 1). The color of the solution was yellow.[13] The absorption band in the visible region tailed to over 550 nm. Since we confirmed that the longest absorption maximum wavelength of 2,3-diphenylindenone was 433 nm in toluene, the absorption in the visible light region is characteristic of 2,3-bisarylindenones. Upon irradiation of 436 nm light, new absorption maxima appeared at 542, 429, 363, 307, and 253 nm, and the color of the solution turned brown. This is attributable to the formation of the cyclic form **1*C***. HPLC analysis revealed that the conversion ratio to **1*C*** at the photostationary state (pss) of 436-nm light irradiation was 58%. The cyclized form was thermally so stable that it showed no change after 1.5 months storage in the dark at room temperature.

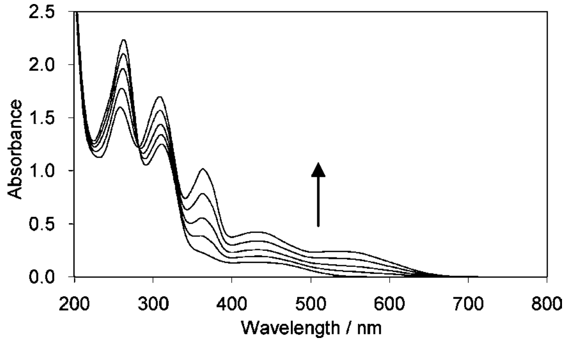


Figure 1. Absorption spectral change of **1** during irradiation of 436 nm light in acetonitrile. Concentration: 0.558 × 10^{-4} mol dm^{-3}. Light intensity: 2.4 mW cm^{-2}. Irradiation time: 0−12 min.

When the 436-nm pss solution was irradiated with 579 nm light, the color turned yellow, and HPLC analysis proved that **1*O*** was recovered again. However, due to the long absorption tail of **1*O*** in the visible region, the ratio of **1*O***/**1*C*** at the pss of 579-nm light irradiation was 99/1.

The absorption spectral properties of **1** are listed in Table 1, and the quantum yields of the photochromic reactions of **1** are listed in Table 2.

Thus, a novel photochromic system, in which back-and-forth reactions can be driven by visible light of two different wavelengths, was created.

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Table 1. Absorption Spectral Data of **1**[a] and **4**[b]

compd	λ_{max}/nm (ε/10^3 dm^3 mol^{-1} cm^{-1})
1O	262 (40.0) 311 (22.4) 433 (2.51)
1C	253 (18.9) 307 (34.5) 363 (28.3) 429 (11.1) 542 (7.37)
4O	229 (29.9) 319 (22.2)
4C	290 (27.2) 353 (14.7) 511 (10.0)

[a] CH_3CN. [b] Hexane.

In contrast, **2*O*** showed poor photochromism[13] and was decomposed gradually upon 436-nm light irradiation.

Table 2. Quantum Yields of the Photoreactions of **1**[a] and **4**[b]

			shorter wavelength light[a]		longer wavelength light[b]	
compd	solvent	$E_T(30)$/kcal mol^{-1}	Φ_{OC}	Φ_{CO}	Φ_{CO}	CR[c]/%
1	CH_3CN	45.6	0.10	0.016	0.0051	58
4	hexane	31.0	0.81	0.011	0.0089	99
	toluene	33.9	0.72	0.024	0.0091	97
	AcOEt	38.1	0.70	0.037	0.012	96
	CH_3CN	45.6	0.63	0.063	0.023	91
	EtOH	51.9	0.68	0.017	0.012	97

[a] 436 nm for **1**, 313 nm for **4**. [b] 579 nm for **1**, 512 nm for **4**. [c] CR: Conversion ratio to the colored form at the photostationary state of the cyclization reaction.

As described above, the carbonyl and phenyl groups can be easily modified. The electronic influence of the carbonyl group was changed by acetalization in a manner similar to that of Belser and Kühni for 3,4-bis(2-methyl-5-phenyl-3-thienyl)-3-cyclobutene-1,2-dione.[10] In their case, acetalization of both carbonyl groups could realize photochromic properties.

We tried to synthesize acetals of 1,2-ethanediol and 1,3-propanediol. While 1,3-propanediol did not give the corresponding 1,3-dioxane due to steric congestion, 1,2-ethanediol reacted with **1*O*** to give the corresponding 1,3-dioxolane **4*O*** in 76% yield based on the consumed **1*O***.

Photochromism of **4*O*** was investigated in various solvents with different polarities, and the photocyclization quantum yield in hexane was proved to be the largest. The changes observed in the absorption spectra by photochromic reactions in hexane are shown in Figure 2. The conversion ratio to **4*C*** at the pss of 313-nm light irradiation was 99%. The absorption spectral data and quantum yields of the photoreactions are summarized in Tables 1 and 2, respectively.

Acetalization induced a blue shift of the absorption spectra as well as an increase in the photocyclization quantum yield. The photocyclization quantum yield value of 0.81 recorded in hexane is, to the best of our knowledge, the largest one based on 6π-electrocyclization in solution,[14,15] which has exceeded previous large quantum yield values, such as 0.77 reported by Kawai and co-workers[16] and 0.79 reported by our group.[17]

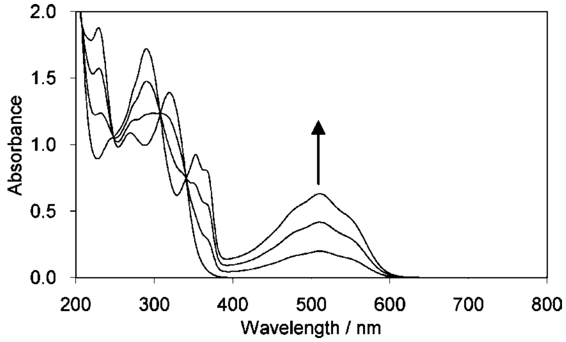

Figure 2. Absorption spectral changes of **4** during irradiation of 313 nm light in hexane. Concentration: 0.628 × 10^{-4} mol dm^{-3}. Light intensity: 0.24 mW cm^{-2}. Irradition time: 0−20 min.

The reason the cyclization quantum yield of **4*O*** is so large is not yet known and is currently under investigation. However, we assume that the two sets of intramolecular nitrogen−hydrogen interactions (a thiazole nitrogen atom and the proximate hydrogen atom on the indenone phenyl group, and a thiazole nitrogen atom and a hydrogen atom on the carbon atom adjacent to an oxygen atom in the acetal group) may play an important role in constraining the conformation of **4*O*** in favor of the cyclization.[18] The solvent effect on the quantum yield of ring closure of **4*O*** can be explained by the polar N−H interactions. It recorded the highest value in hexane while it decreased as the solvent polarity became larger (Table 2). As the polar solvent molecules prevent effective N−H interactions, the distribution of the conformers becomes less biased, thus decreasing the quantum yield.

In conclusion, we have synthesized a novel thermally irreversible photochromic system based on 6π-electrocyclization with three easily modifiable functional groups. Bisarylindenone **1** showed photochromic back-and-forth reactions with visible light of different wavelength. The photochromic and absorption spectral properties can be switched by its acetalization. Significantly, the photocyclization quantum yield of acetal **4*O***, i.e., 0.81 in hexane, is the largest value known to date for 6π-electrocyclization in solution. Achievement of the large quantum yield may be explained by the intramolecular interactions of nitrogen and hydrogen atoms to fix the conformation in favor of photochemical cyclization.

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(13) See the Supporting Information.

(14) In order to secure the quantum yield values, we used Parker's $K_3Fe(C_2O_4)_3$ chemical actinometer to determine the intensity of the lights used for photochromic reactions.

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(18) A preliminary result obtained by DFT calculations suggests that two antiparallel (i.e., photocyclizable) conformations are particularly stable (more than 98% population at 25 °C), in which the two sets of N−H distances are around 0.26 nm, almost the same as the sum of van der Waals radii of N and H. Theoretical aspects of this problem will be reported separately.

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Supporting Information Available: Details of the synthesis of **1*O***, **2*O***, and **4*O***, UV−vis spectral change of **1*O***, **2*O***, and **4*O*** by photoirradiation, HPLC chromatograms during photoreactions of **1*O*** and **4*O***, pictures of solution of **1*O***/**1*C***(pss) and **4*O***/**4*C***(pss), and ^{1}H NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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