



Synthesis of photochromic 2,3-bis(5-methyl-2-phenyl-4-thiazolyl)-1,4-naphthoquinone derivatives

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ABSTRACT

2,3-Bis(5-methyl-2-phenyl-4-thiazolyl)-1,4-naphthoquinone **1-O**, its monoethylene acetal **2-O** and methylated derivatives **3-O** and **4-O** were synthesized and their photochromic properties were investigated. While bisarylnaphthoquinone **1-O** was nonphotochromic, its monoacetal **2-O** and methylated derivatives **3-O** and **4-O** displayed good photochromism. Among them, the isomer **4-O** recorded a remarkable diastereomeric excess (98.40%) with high conversion ratio (96.20%) upon UV irradiation.

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1. Introduction

Thermally irreversible photochromic compounds such as fulgides and diarylethenes have received a great attention due to their possible application as a molecular-level switches [1]. The diarylethenes [2] are superior to the fulgides [3] in terms of thermal stabilities and fatigue resistance. On the other hand, structural modifications of diarylethenes are limited only on the aryl moieties. Recently a number of new photochromic systems similar to the diarylethenes such as bisarylindene [4], terarylene [5], bisaryl-1,10-phenanthroline [6], and 4,5-bisarylimidazolium [7] have been reported. Diarylethenes and related photochromic analogs undergo reversible ring closure/ring opening photoreactions upon irradiation with different wavelengths of light. The ring closure photoreaction of diarylethenes produces a racemic mixture of two isomers. More recently a considerable attention has been focused on the enrichment of one of the stereoisomer in the photochromic reaction.

Indeed, a number of diastereoselective photochromism in the diarylethenes was already achieved by different approaches. Main strategy for diastereoselectivity is to place a chiral substituent on the molecule. The chiral center helps one of the conformations of the ring-opened forms favorable compared to others by steric and electronic effects [8] in solution or complete conformation fixation

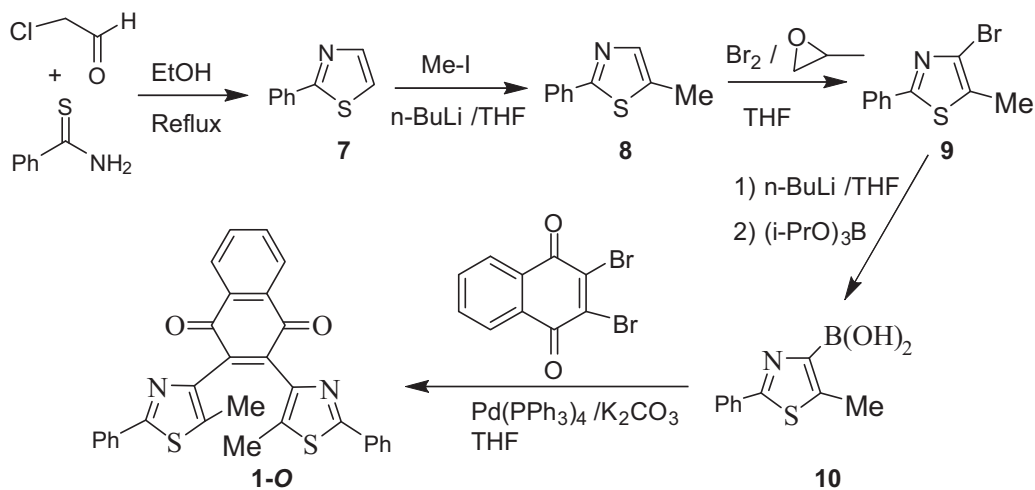
in the crystalline state [9], the later cause an absolute asymmetric photocyclisation. Similar work also was conducted in amorphous state [10] and in gel states by Irie et al. [11].

In this work, our achievement is to synthesis new photochromic diarylethenes which were derived from a non-photochromic diarylnaphthoquinone. The diarylnaphthoquinone are structurally more modifiable than the diarylethenes. Some diarylbenzoquinones or naphthoquinone which possess different aryl groups were already synthesized via slightly different methods to examine their biological activity [12] or their photochromism [13]. However, so far photochromic diarylquinone or naphthoquinone or their derivatives have not yet been reported. The new photochromic isomers which possess one (**3-O**) or two (**4-O**) chiral units showed diastereoselective photochromism. In this case the chiral center on the molecule of *O*-form caused fixation of the conformation via hydrogen bonding between OH groups derived from the carbonyl groups and nitrogen atoms on the thiazole rings. When the fixed conformation of *O*-form is irradiated with UV light a diastereoselective ring closure is expected.

2. Results and discussion

2,3-Bis(5-methyl-2-phenyl-4-thiazolyl)-1,4-naphthoquinone **1-O** was prepared by the Suzuki Coupling reaction [14] (Scheme 1). The requisite thiazolyl boronic acid [10] was prepared from 4-bromo-5-methyl-2-phenylthiazole **9** and B(O-*i*Pr)₃ with *n*-BuLi. Commercially available 2,3-dibromo-1,4-naphthoquinone was used as the quinone portion. Structural modifications of **1-O** on

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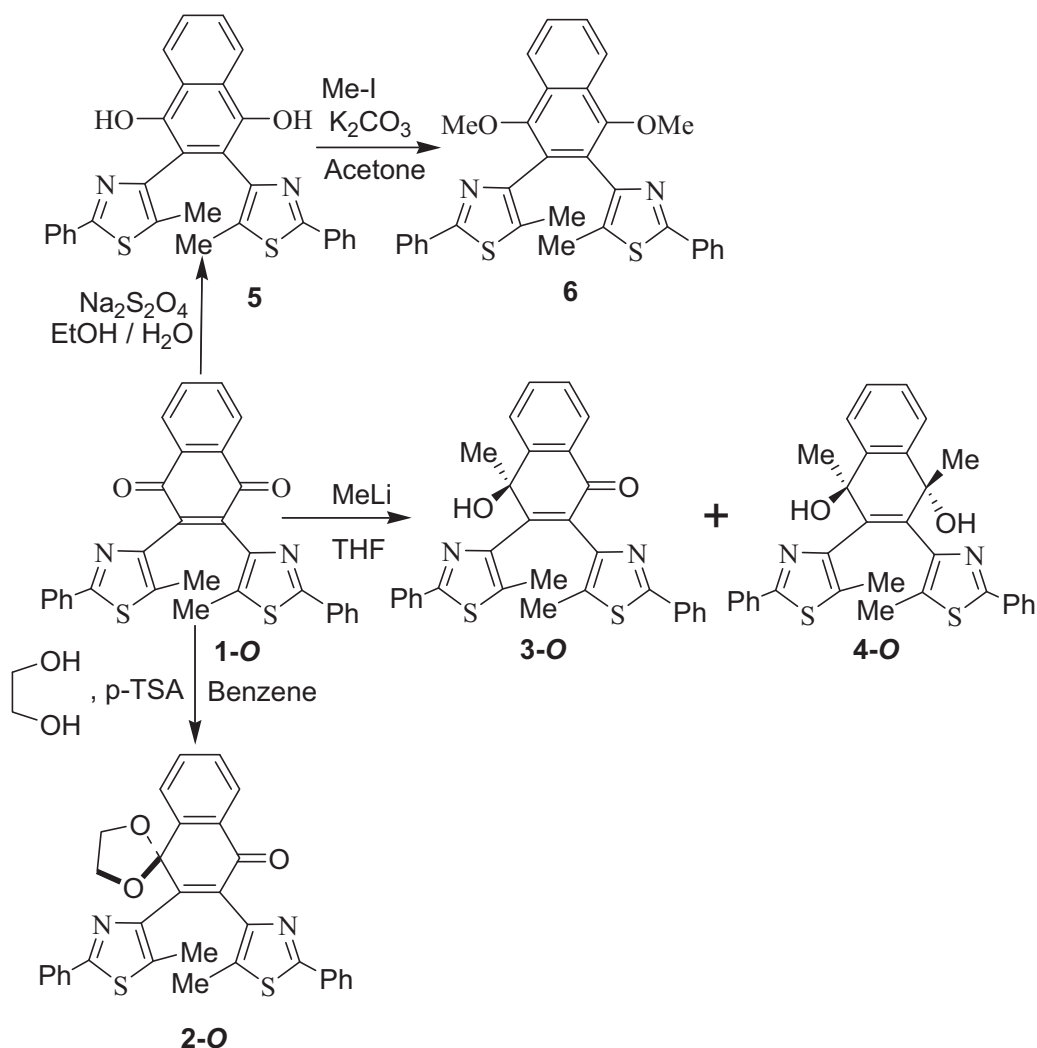


Scheme 1. Synthesis of 2,3-bis(phenylthiazolyl)-1,4-naphthoquinone **1-O**.

the carbonyl group such as the acetal formation and mono- and di-methylation have been carried out (Scheme 2).

Acetal formation of **1-O** using 1,2-ethanediol in the presence of *p*-toluenesulfonic acid (*p*-TSA) as a catalyst in dry benzene gives photochromic acetal **2-O** in a low yield. However, from the acetal

formation, a substantial amount of the starting **1-O** was recovered so that if the recovered compound was re-used for the synthesis the percentage of the yield could be improved. The stability of acetal derivatives **2-O** in the silica gel column was low and slight decomposition was observed during purification in the column. Many



Scheme 2. Modification of 2,3-bis(phenylthiazolyl)-1,4-naphthoquinone **1-O** on carbonyl groups.

Table 1
Absorption spectral data of **1-O** and its photochromic derivatives in toluene before and after irradiation. Compound **1-O** and **2-O** (1×10^{-4} mol dm $^{-3}$); **3-O** (7.29×10^{-5} mol dm $^{-3}$) and **4-O** (4.82×10^{-5} mol dm $^{-3}$). Cell length: 1 cm.

Compounds	O-form λ_{\max}/nm ($\epsilon_{\max}/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$)	Colored isomer (pss) λ_{\max}/nm (absorbance)	Cr/% at pss
1	425 (3190)	485 (0.812)	–
2	–	490 (0.182)	–
3	305 (24,700)	529 (0.557)	96.51
4	315 (20,100)	505 (0.392)	96.20

attempts to protect both carbonyl groups by ethylene acetal have failed.

The carbonyl group of **1-O** was also reacted with one equivalent of MeLi. From the reaction flask three photochromic spots were observed on TLC and the primary two of these were isolated. Since the molecule possesses two carbonyl groups, three isomers are possible upon methylation. If both carbonyl groups are methylated, cis and trans isomers may result. The possibility of the occurrence of the trans isomer is more likely due to the chelation effect of the alkoxy group generated by the first addition of MeLi to the cationic part of the second MeLi, so that the isolated isomers were interpreted as **3-O** (monomethylated) and **4-O** (trans-dimethylated), respectively.

One of our main interest was to synthesize bisaryl-1,4-hydronaphthoquinone **5** and to investigate its photochromic properties as well as the H-bond effect between OH groups and N atoms of phenyl-thiazole moieties in compound **5**. Therefore, hydronaphthoquinone **5** was prepared quantitatively by treatment of **1-O** with excess sodium dithionate in equal amounts of water and diethyl ether. During the purification on silica gel, compound **5** was partially oxidized back to the compound **1-O**. To improve the stability of compound **5**, the OH groups were protected as the methyl ethers to give compound **6**. Unfortunately, even at a very low temperature (-78°C), both **5** and **6** were not photochromic. This could be explained by the presence of stable aromatic rings. During the photocyclisation process of the **5-O** and **6-O**, the three aromatic rings should lose their aromaticity to give highly conjugated colored photochromes, yet this may be energetically very difficult.

Compound **1-O** was not photochromic either. A yellow-orange solution of **1-O** in toluene exhibited an absorption maximum at 425 nm. During irradiation with 313 nm or 436 nm light, the color intensity of the solution increased greatly. When the colored solution (λ_{\max} at 485 nm) in the photostationary state (pss) was irradiated with visible light (570 nm), neither color nor spectral change was observed, thus leading to the conclusion that the ring closure is not reversible, or other unidentified photochemical side reaction(s) may have occurred. However, when one or both carbonyl groups in **1-O** were protected or methylated, the molecule acquired photochromic character, so that **2-O**, **3-O**, and **4-O** are photochromic.

Upon irradiation with UV light, the nearly colorless solutions of **2-O**, **3-O**, and **4-O** in toluene underwent photocyclisation to form highly colored photochromes **2-C**, **3-C**, and **4-C**, which reversed back to **2-O**, **3-O**, and **4-O** upon exposure to white light. The absorption spectral data of **1-O**–**4-O** and their photochromic isomers are listed in Table 1. The ring-closing photoreaction (313 nm) from **4-O** to pss and the ring-opening photoreaction (>410 nm) from pss to **4-O** in toluene are shown in Fig. 1.

The ring-closed photochrome **3-C** at pss ($\lambda_{\max} = 529$ nm) displayed bathochromic shift by 24 nm compared to the photochrome **4-C** ($\lambda_{\max} = 505$ nm). This can be explained by the conjugation effect of the carbonyl group to the main chromophore on the molecular backbone. However, photochrome **2-C** displayed a shorter absorption maximum wavelength ($\lambda_{\max} = 490$ nm) compared to others.

This may be interpreted by the structural deformation of the conjugate system due to the steric compression caused by the highly complex and congested ring system.

The conversion ratios from **3-O** to **3-C** and **4-O** to **4-C** at the pss of 313-nm light irradiation were determined by HPLC and were found to be 96.51% and 96.20% respectively. The HPLC chromatogram of the colored C-forms (**3-C** and **4-C**) at the pss showed two main diastereomers, and the diastereomeric excesses (de) were found to be 65.16% and 98.40%, respectively.

The reason that **4-O** exhibits high diastereomeric excess (de) during the ring-closing photoreaction is not clear at this stage. However, this could be explained by noting the electronic and steric effect of the adjacent N atoms (and Me groups) on the thiazole ring and the OH groups in the molecule (Scheme 3).

Compound **4-O** can take two conformations before ring closure. Presumably, in the major conformation, the N atoms of thiazole and the OH groups are in the close proximity in the molecule, so that they could make two sets of hydrogen bonds.

On the other hand, in the minor conformation formation of the hydrogen bonds between the OH and N atoms is not possible. Therefore the major conformation is thermally more stable than the

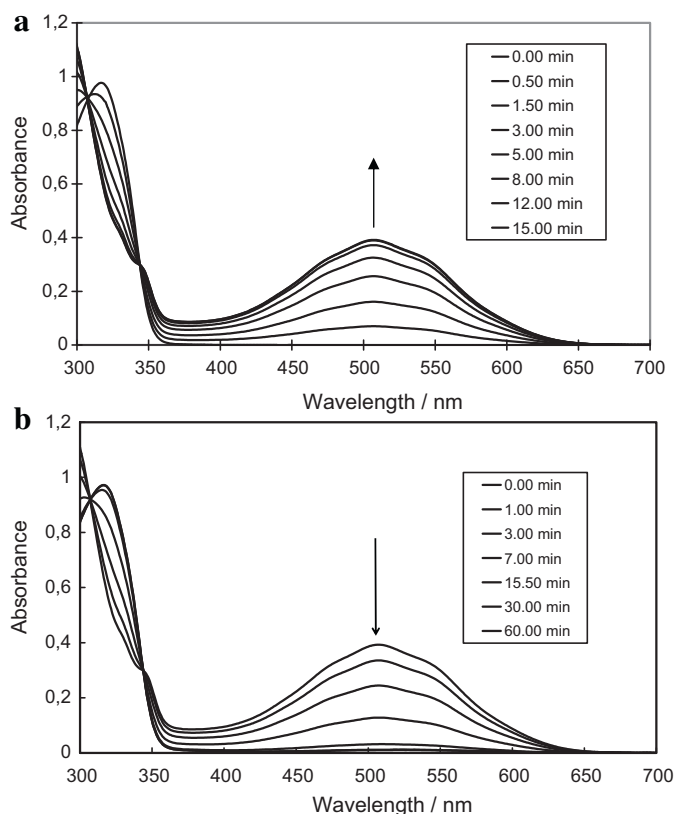
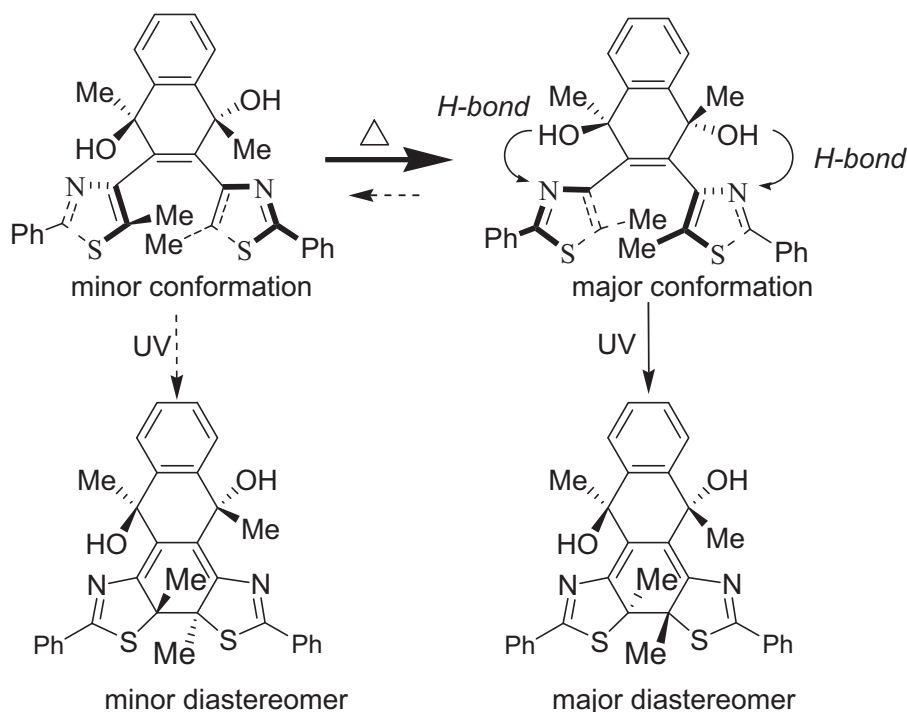


Fig. 1. Absorption spectral change of **4** in toluene (4.82×10^{-5} mol dm $^{-3}$). (a) **4-O** to pss. 313 nm (0.25 mW cm^{-2}). 0–15 min. (b) Pss to **4-O**. $\lambda > 410$ nm. 0–60 min.



Scheme 3. Steric/electronic stereoregulation in compound **4-O**.

minor conformation so that this compound possessing trans orientation of the hydroxyl groups yields extremely high diastereomeric excess.

3. Conclusions

We have succeeded in constructing a new photochromic diarylethenes which were derived from a non-photochromic 2,3-bisaryl-1,4-naphthoquinone by acetalization and methylation reactions. Among the compounds synthesized, the photochrome **4-O** showed a high level of photochromic ring closure (96.20% conversion at pss) with high diastereomer excess (98.40% de) upon 313-nm light irradiation.

Acknowledgements

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Appendix A. Supplementary data

Detailed synthetic procedure (SI-1); UV–Vis spectral data for the photochromic compounds **2-O**, and **3-O** (SI-2–SI-3); and HPLC charts for **3-O** and **4-O** during photoirradiation (SI-4–SI-5–SI-6–SI-7–SI-8–SI-9–SI-10). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.01.016.

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