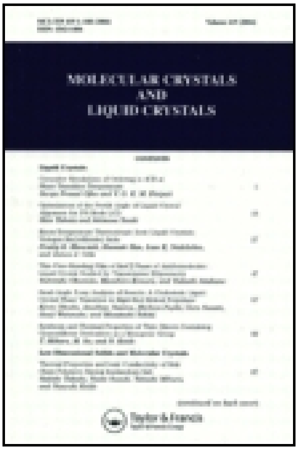

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1,3-Bisarylbutadienes: Novel Thermally Irreversible Photochromic System

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1,3-Bisarylbutadienes: Novel Thermally Irreversible Photochromic System

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*Novel thermally irreversible photochromic compounds **1O**, **2O** and **3O** based on 1,3-bisarylbutadiene system were synthesized. The closed ring-forms **1C** and **2C** showed absorption maximum at 445 nm, while the closed ring-form **3C**, a methyl group of **2C** on C-5 of thienyl ring was replaced with a formyl group, showed the absorption maximum at 500 nm.*

Keywords: bathochromic shift; bisarylbutadiene; fatigue resistivity; photochromism; thermal irreversibility

INTRODUCTION

Although a great number of photochromic compounds have been reported [1–3], very few are known to be thermally irreversible. They are fulgides [4], diarylethenes [5], and phenoxynapthacenequinones [6]. However, if the catalog of thermally irreversible photochromic compounds is thicker, it would be more convenient to select an appropriate one for the particular purpose. Therefore, we have designed and synthesized thermally irreversible and fatigue resistant photochromic 1,3-bisarylbutadiene system exemplified by **1**, based on

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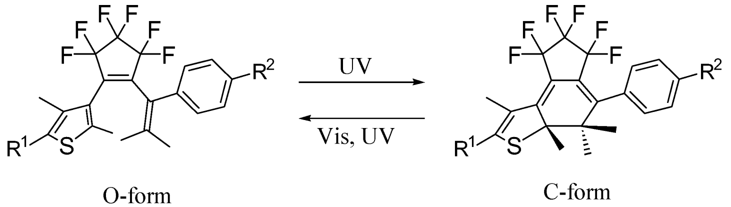


SCHEME 1 Photoreactions of 1,3-arylbutadienes.

the photochemical 6π-eletrocyclization [7,8]. The photochromic reaction of 1,3-arylbutadienes is shown in Scheme 1.

Thermal irreversibility and fatigue resistivity are the fundamental and important properties for practical application to the rewritable optical recording media. It is also desired to develop a series of photochromic compounds that have sensitivity in several different wavelength regions. We here report the synthesis of **2** and **3**, the colored forms of which were supposed to have absorption maxima at longer wavelengths.

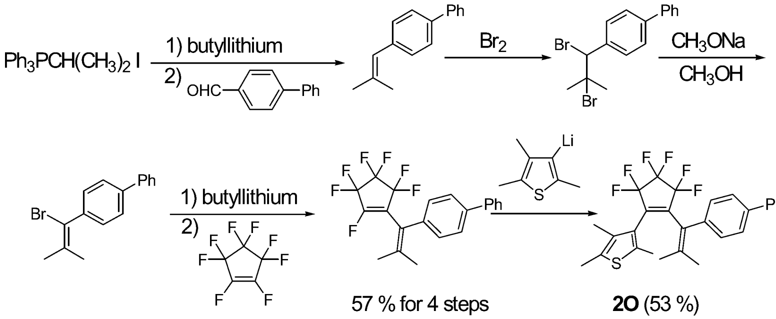
RESULTS AND DISCUSSION

1. Synthesis of 2O

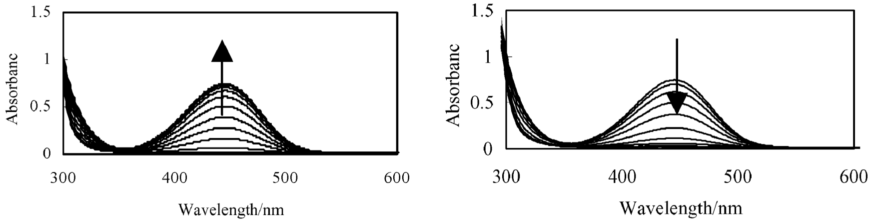
Synthesis of **2O** was carried out as shown in Scheme 2 in 53% yield, according to the similar procedures described elsewhere [9].

2. Photoreaction of 1 and 2

Photoreaction of **2O** was carried out as previously reported for **1O** [7]. When a toluene solution of **2O** was irradiated with 313-nm light, the



SCHEME 2 Synthesis of **2O**.



(a) (b)

FIGURE 1 Change in absorption spectra of **2**. Concentration/mol dm^{-3}: $2.16 \times 10^{\times 4}$ in toluene (a) Light intensity/mW cm^{-2}: 0.37 (313 nm), irradiation time/min: 0, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9. (b) Light intensity/mW mW cm^{-2}: 0.24 (405 nm), irradiation time/min: 0, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7.

color of the solution turned yellow, and a new absorption band in the visible region. The absorption maximum of **2C** was 445 nm which was the same as that of **1C**.

The change in absorption spectra of **2** according to the time of 313-nm light irradiation and 405-nm light irradiation were shown in Figure 1. The quantum yields of photoreactions and the spectroscopic data of **2** in toluene is shown in Table 1, together with those of **1**. Apparently the introduction of an additional phenyl group was ineffective, because of the poor conjugation of those two non-coplanar phenyl groups caused by steric congestion.

3. Synthesis of 3O

Unterhalt et al. [10] reported the oxidation of an alkyl group on a benzothiophene ring by cerium sulfate oxidation. The oxidation

TABLE 1 Absorption Spectral Data and Quantum Yields of Photoreactions of **1C**, **2C**, and **3C** in Toluene

	Absorption spectral data of colored forms		Quantum yields of photoreactions			
			313 nm		405 nm	O: C at Pss[1]
	λ_{max}/nm	$\varepsilon_{max}/mol^{-1}\ dm^3\ cm^{-1}$	Φ_{OC}	Φ_{CO}	Φ_{CO}	
1	445	9.9×10^3	0.43	0.14	0.16	37 : 63
2	445	10.9×10^3	0.61	0.18	0.14	68 : 32
3	500	10.2×10^3	0.34	0.16	0.08[2]	41 : 59

[1] Ratio of O-form and C-form at photostationary state of 313-nm light irradiation.
[2] 505-nm light irradiation.

occurred exclusively on the alkyl group on C-2 of the benzothiophene, to produce a carbonyl group.

We carried out this oxidation reaction of **2O** with the same reaction conditions – with cerium (IV) sulfate in acetic acid. Two new photochromic compounds **3O** in 41% and **4O** in 39% yields were obtained.

4. Structure Determination of 3O

^{1}H NMR spectrum ($CDCl_3$) of **2O** showed five singlet methyl signals at δ 1.47, 1.66, 1.75, 1.92, and 2.19. The oxidation product **3O** showed singlet methyl signals at δ 1.67 (3H, s), 1.85 (3H, s), and 1.95 (6H, s). In addition, a new signal appeared at δ 9.86 (1H, s), assigned to a formyl hydrogen. Also, a strong carbonyl absorption at 1667 cm^{-1} in IR spectrum was observed. Thus, an electron-withdrawing formyl group was introduced by the oxidation of a methyl group.

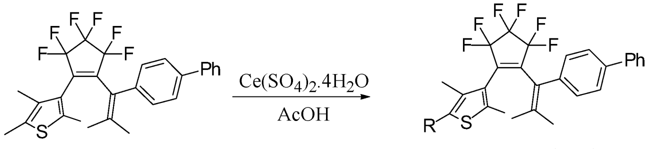
Reduction of **3O** with $NaBH_4$ in methanol followed by acetylation gave **4O**. Thus, the structure of **4O** was determined to be the acetoxymethyl derivative of **3O**.

Photoreaction of **3O** was carried out to examine the photochromic properties of **3** and to elucidate the effect of the electron-withdrawing substituent. Irradiation of 313-nm light to a toluene solution of **3O** produced **3C**, possessing the absorption maximum at 500 nm. Thus the formyl group worked to lengthen the absorption maximum of the colored form. This also indicated that the formyl group takes part in the conjugation in the structure of **3C**. Therefore the oxidized methyl group should have been located on C-4 or C-5 on the trimethyl thiophene ring. Other methyl groups of **2**, after photoirradiation, are located on the sp^3 carbon atoms.

To identify the oxidized methyl group, ZINDO and PPP-CI calculations were carried out for the possible candidates of **3C**. For PPP-CI calculations, while 4-CHO derivative showed blue shift by 17 nm, 5-CHO derivative showed red shift by 29 nm, based on the calculated absorption maximum of **2C** as 394 nm. Similarly, while ZINDO calculations on 4-CHO derivative showed red shift of only 11 nm, 5-CHO derivative showed red shift by 27 nm, deviated from the calculated absorption maximum of 339 nm for **2C**. Therefore we concluded that the oxidized methyl group of **2** was on C-5 of the trimethylthiophene ring (Scheme 3).

5. Photochromic Reaction of 3O

Photoreaction of **3O** was carried out similarly to that of **1O** and **2O**. The absorption spectral changes of **3** in toluene upon alternate



2O

3O R = CHO (41%)
4O R = CH_2OAc (39%)

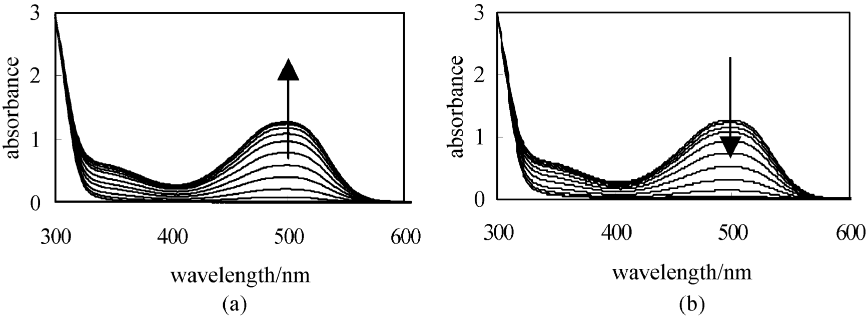
SCHEME 3 Synthesis of **3O** and **4O**.

irradiation of 313-nm and 505-nm lights are shown in Figure 2, and spectroscopic data and quantum yields of photoreactions are summarized in Table 1.

6. Thermal Stability and Fatigue Resistivity of 1, 2 and 3

We have examined the thermal stability and fatigue resistivity of compounds **1**, **2** and **3** in PMMA films. The films containing their photostationary states were kept at 80°C in the dark in the air for 30 days, and the absorption spectrum was measured at intervals. As shown in Figure 3, all these compounds remained constant for 30 days. It is thus proved that **1, 2** and **3** are thermally stable.

As shown in Figure 4, iterative irradiations with 313- and 405- or 505-nm lights were performed for ten times. Although a slight decrease in the absorption of the colored form at photostationary state was observed after the several iterations, it remained at the same level for ten cycles. Thus **1**, **2** and **3** showed an excellent fatigue resistivity.



(a)

(b)

FIGURE 2 Change in absorption spectra of **3**. Concentration/mol dm^{-3}: 2.16×10^{-4} in toluene (a) Light intensity/mW cm^{-2}: 0.33 (313 nm), irradiation time/min: 0, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9,10. (b) Light intensity/mW cm^{-2}: 0.3 (505 nm), irradiation time/min: 0, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8.

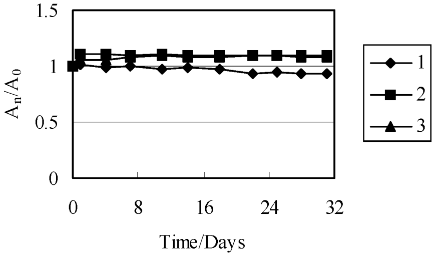


FIGURE 3 Thermal stability of **1C, 2C** and **3C** in a PMMA film at 80°C.

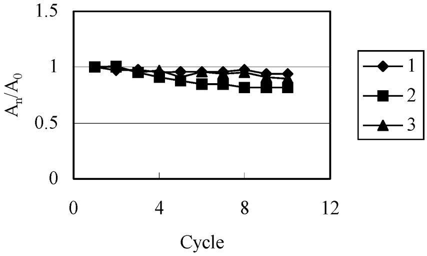


FIGURE 4 Fatigue resistivity of **1, 2** and **3** by irradiating UV and vis light in a PMMA film.

CONCLUSION

A novel thermally stable and fatigue resistive photochromic bisarylbutadiene compounds **1**, **2** and **3** based on 6π-electocyclization were synthesized. The compound **3** with a formyl group at C-5 of the thienyl ring extended the π-conjugation in closed form, and shifted the absorption maximum by 55-nm to the longer wavelength.

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