A Novel Photochromic System of 4,5-Dialkenylthiophenes Constructed by the Samarium Diiodide Promoted Coupling Reactions of Thiophene-2-carboxylate with Aryl Ketones

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ABSTRACT

The SmI2-promoted coupling reaction of ethyl thiophene-2-carboxylate with aryl ketones (2 equiv), followed by acid-catalyzed dehydration and oxidative aromatization, gave dialkenylthiophenes 1b–d, which underwent electrocyclizations upon irradiation with 300-nm light in CH3CN solution to give the corresponding closed-ring species with absorption λmax ≈ 425 nm. The interconversion between dialkenylthiophenes and their corresponding closed-ring species constitutes a novel photochromic system bearing an ester group for potential uses in linkage and wavelength tuning.

Photochromism is a light-induced reversible isomerization between two forms having different absorption spectra. The photochromic system based on the interconversion of 1,3,5-hexatriene to cyclohexadiene has been extensively investigated, partly as a result of their potential applications to optical memories and switches. The photocyclization of stilbene to dihydrophenanthrene is a well-known photochromic system. According to the Woodward–Hoffmann rule, the double bond of stilbene should have (Z)-configuration to conform a concerted conrotatory cyclization in the photochemical conditions. Dihydrophenanthrene can return rapidly to stilbene in the dark; however, it can also undergo oxidative aromatization in the presence of oxygen. By replacing the phenyl rings with thiophene rings, 1,2-di(3-thienyl)ethene undergoes a photocyclization reaction to give the closed-ring species with an improved stability.


result is attributed to the low aromatic stabilization energy difference between the open- and closed-ring isomers of thiophene by comparison with that of benzene.\textsuperscript{1b,2c} Irie and co-workers further demonstrate that the light-induced cyclization of 1,2-bis(2,4-dimethylthien-4-yl)perfluorocyclopentene gives a stable colored species.\textsuperscript{1b} The cyclopentene ring incorporates the requisite double bond of the \((Z)\)-configuration, and the methyl groups at the 2- and 2′-positions prevent the closed-ring species from oxidative aromatization.

We report herein a novel photochromic system (eq 1) based on the interconversion between 4,5-dialkenylthiophenes 1a–d and their closed-ring isomers 2a–d. Dialkenylthiophene 1a–d were readily prepared by a three-step sequence (Scheme 1): (i) coupling of ethyl thiophene-2-carboxylate (3) with aryl ketones 4–7 (2 equiv) by the promotion of SmI\(_2\), giving diols 8–11,\textsuperscript{5} (ii) acid-catalyzed dehydration, giving dienes 12–15, and (iii) oxidation by DDQ (1 equiv), giving dialkenylthiophenes 1a–d. The central double bonds of 1a–d were confined in the thiophene ring to adopt a (Z)-configuration required by the concerted electrocyclizations.

The UV—vis spectrum of dialkenylthiophene 1a\textsuperscript{6} exhibited \(\lambda_{\max }\) at 242 nm (\(e = 38800\)) and 289 nm (\(e = 13800\)). Upon irradiation of 1a (colorless solution) with 300-nm light, an orange color immediately appeared, indicating the existence of new species. The reaction course of 1a in CDCl\(_3\) (ca. 0.1 M) was recorded by the \(^1\)H NMR spectra.\textsuperscript{7} After irradiation for 10 min, closed-ring species 2a (ca. 30\%) was produced as inferred from a new set of proton signals, in which a singlet at 0.299 was ascribed to the methylene protons of tetrahydrobenzothiophene moiety. The ratio of 2a increased as the irradiation progressed to 60 min. However, several other compounds including benzothiophene 16\textsuperscript{8} and 6,7-dihydrobenzothiophene 17\textsuperscript{9} were also produced at the expense of 2a (Scheme 2).

![Scheme 1](image)

2-carboxylate (3) with aryl ketones 4–7 (2 equiv) by the promotion of SmI\(_2\), giving diols 8–11,\textsuperscript{5} (ii) acid-catalyzed dehydration, giving dienes 12–15, and (iii) oxidation by DDQ (1 equiv), giving dialkenylthiophenes 1a–d. The central double bonds of 1a–d were confined in the thiophene ring to adopt a (Z)-configuration required by the concerted electrocyclizations.

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![Scheme 2](image)

Compound 16 was likely obtained by an oxidative aromatization of 2a similar to that proposed in the conversion


(6) Compounds 1a–d and 8–18 were fully characterized by spectral methods (IR, UV, MS, HR-MS, \(^1\)H and \(^{13}\)C NMR). The details are reported in Supporting Information, whereas some pertinent physical and spectral properties are herein listed. Compound 1a: solid, mp 109–111 °C; UV (CH\(_2\)Cl\(_2\)) \(\lambda_{\max }\) (\(e\)) 249 nm (38800), 289 nm (13800); FL (CHCl\(_3\), \(c = 2 \times 10^{-4}\) M) \(\lambda_{\text{em}} = 415\) nm on excitation at 364 nm; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 7.77 (1\ H, s), 7.70 (2\ H, m), 7.54 (4\ H, m), 7.44–7.36 (6\ H, m), 7.16 (1\ H, dd, \(J = 8.5, 1.5\) Hz), 7.10 (1\ H, dd, \(J = 8.5, 1.5\) Hz), 5.57 (1\ H, s), 5.50 (1\ H, s), 5.41 (1\ H, s), 5.35 (1\ H, s), 4.38 (2\ H, q, \(J = 7.3\) Hz), 1.39 (3\ H, t, \(J = 7.3\) Hz). Compound 1b: UV (CH\(_2\)CN) \(\lambda_{\max }\) (\(e\)) 249 nm (34400), 300 nm (16800). Compound 1d: UV (CH\(_2\)CN) \(\lambda_{\max }\) (\(e\)) 251 nm (34900), 300 nm (13700).

(7) The photochemical reactions were conducted in a Rayonet photochemical reactor using 300 or 450-nm lamps. The corresponding NMR and UV—vis time course spectra are included in Supporting Information.
of dihydrophenanthrene to phenanthrene. When the photochemical reaction of 1a was conducted in deoxygenated CD3CN solution, the formation of 16 was inhibited. Compound 17 might be derived from 2a by an H-shift. Attempts to isolate 2a failed, presumably because of its instability. Attempts to trap the transient closed-ring species o-thiophenequinodimethane, by N-phenylmaleimide in the photochemical reaction of dialkenylthiophene 1a (300-nm, CH3CN, 25 °C, 48 h) also failed, even though the existence of 2a could be inferred from a newly occurring NMR signal at δ 2.99 (s). However, 2a was alternatively generated by the thermal electrocyclization of 1a in refluxing toluene and successfully trapped by N-phenylmaleimide to give a [4 + 2] cycloaddition product 18. Although the trapping experiment under thermal conditions should not be strictly correlated to the photochemical reaction of 1a, this result lent a clue to intermediate 2a in support of the newly NMR signal at δ 2.99 found under photochemical conditions.

The drawbacks of oxidative aromatization and H-shift would be avoided in the photochemical cyclization of trienes 1b–d as they have C-5 and C-6 positions substituted by methyl groups. When a colorless acetonitrile solution (1.1 × 10−5 M) of 1b was irradiated with 300-nm light at room temperature, the 290-nm absorption of 1b decreased along with the growth of a new 429-nm absorption attributed to the formation of the yellow closed-ring species 2b (Figure 1). The corresponding 1H NMR spectra also showed a newly occurring singlet (δ 6.64) ascribed to the H-3 of 2b. According to the NMR study, the maximal content of the closed-ring species 2b was estimated to be 15% in the reaction mixture under the photochemical conditions (30 min at −20 °C in CD3CN solution).

The photochemical properties of 1c (Ar = Ph) and 1d (Ar = p-MeOC6H4) were similar to that of 1b (Ar = 2-naphthyl), even though they had different aryl groups. Irradiation of 1c and 1d with 300-nm light in CH3CN solution afforded the closed-ring species 2c and 2d, which showed absorption maxima at 422 and 425 nm, respectively. On the basis of these results, the moiety of o-thiophenequinodimethine carboxylate in 2b–d was likely the main contributing chromophore. The absorption change in 2b–d was trivial, as their aryl substituents might not be coplanar to the chromophore.

We also demonstrate that the closed-ring species 2b–d are photochemically reversible. When a mixture of 1b/2b and 1d/2d was irradiated with 450-nm light, respectively, 2b and 2d disappeared and returned rapidly (within 1 min) to the open-ring species (1b and 1d). The interconversion between 1c and 2c was realized by alternate irradiation with UV (300-nm) and visible (419-nm) lights at 10-s intervals. In a preliminary experiment, the absorption intensity at 424 nm showed a significant change after irradiation of 1c/2c for several cycles (see Supporting Information).

The ring-closure and ring-opening reactions as shown in eq 1 should be both photochemically and thermally allowed. The closed-ring species were unstable on standing at room temperature, and they returned to the open-ring species in the dark. For example, a mixture of 1b/2b (ca. 85:15) obtained by irradiation of 1b with 300-nm light for 40 s in CH3CN was removed from the light source and allowed to stand at room temperature in the dark. According to the absorption intensity changes at 290 and 429 nm, 2b returned to 1b to a considerable degree (~20%) in the first minute and 2b completely disappeared in 40 min. A mixture of 1c/2c (ca. 82:18) also behaved similarly to give exclusively 1c after standing at room temperature for 24 h in the dark. This interconversion was monitored by 1H NMR spectra, in which the characteristic H-3 signal of 1c (singlet at δ 7.52) increased as that of 2c (singlet at δ 6.22) disappeared.

In summary, the interconversion between dialkenylthiophenes 1b–d and their corresponding closed-ring species constitutes a novel photochromic system. The preparation of 1b–d is simple by using readily available starting materials via a three-step sequence (Scheme 1), though the yield is not yet optimized. The ester group in trienes 1b–d may serve as a linker to polymeric supports or undergo functional group transformation to tune the photochemical properties. The closed-ring species 2b–d are unstable and return to 1b–d in the dark even at room temperature. The photochemical and thermal stability of these substrates must be improved in order to reach a practical application of this novel dialkenylthiophene/dihydrobenzothiophene system.

The elegant diarylethene photochromic system developed
by Irie and co-workers\textsuperscript{1b,d} has demonstrated high quantum yield, thermal stability, and fatigue resistance. This system incorporates a central ring of perfluorocyclopentene with substitution of two aromatic rings. When the open isomer changes to the closed isomer upon irradiation, the two aromatic rings must change simultaneously to form another conjugated chromophore. In contrast, our current photochromic system utilizes a thiophenyl ring as the central moiety. The synthesis of the photo-/thermochromic substrates of dialkenylthiophenes is relatively easy by using the commercially available starting materials of thiophene-2-carboxylate and aryl ketones. Furthermore these two aryl groups are not incorporated into the contributing \textit{o}-thiophenequinodimethane chromophore of the closed-ring species. This unique structure bearing two independent chromophores thus provides a good opportunity to build the photochromic system having a fluorescent sensing property. For example, one can replace the naphthyl ring in 1b by an appropriate coumarin as the acceptor chromophore for the light emitted from the closed-ring species, which is generated by UV-light irradiation. Modification of the ketone moieties in our current system would not be difficult. We are currently engaged in this endeavor to demonstrate such energy-transfer mechanism in a photochromic system.

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**Supporting Information Available:** Detailed experimental procedures, NMR and UV–vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.