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Subsequent Chemical Reactions of Photochromic 4,5-Dibenzothienylthiazoles

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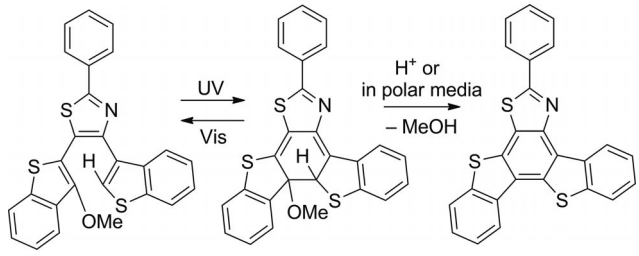
4,5-Dibenzothienylthiazole derivatives having leaving groups at the reactive 2-positions of benzothiophene rings have been synthesized, and their photochromic ring-closing reaction followed by spontaneous elimination and substitution reactions have been studied. A 4,5-dibenzothienylthiazole having an ethoxy group and a hydrogen atom at each 2-position of the benzothienyl ring underwent elimination to generate a condensed aromatic structure upon the addition of acid. 4,5-Dibenzothienylthiazoles having an ethoxy or methyl groups at the 2-position of the benzothienyl rings showed photochromism both in hexane and in methanol solutions with photocyclization quantum yields as high as 60 %. Upon the addition of acid to the methanol solutions of closed-ring isomers of dibenzothienylthiazoles, the substitution of the ethoxy group with a methoxy group occurred. The generation and rearrangement of the carbocation intermediate formed by elimination of the ethoxy group from the closed-ring isomers were apparent from the chemical structure of methoxy-substituted products.

Introduction

Electrocyclizations of a hexatriene moiety to form a cyclohexadiene structure, which is categorized as a pericyclization reaction, has been widely studied as a typical photochromic reaction.[1] Since the discovery of diarylethenes, which undergo cyclization and cycloreversion reactions under photo-irradiation, extensive studies have focused on the synthetic organic chemistry of their derivatives and related compounds. One of the typical features of diarylethene derivatives is their relatively high photochromic sensitivity even in single-crystalline and amorphous states.[2,3] Some diarylethenes show photochemical quantum yields as high as 100 % in the crystalline state.[2d] Recent development of terarylenes,[4] which are composed of three heteroaromatic units to form a hexatriene backbone with photochromic reactivity, has led to efficient photocyclization reaction systems by means of the control of molecular folding by supramolecular interactions with the aid of heteroaromatics.[5] Among these systems, a 2,3-dithiazolylbenzothiophene with the controlled photochromically active conformation, which is tethered by multiple intramolecular interactions, has been reported to show a photon-quantitative ring-closing reaction.[5c] This motivated us to explore the specific chemical reactivity in ring-closed cyclohexadienes as a way to enable efficient photochemical processes such as, photoacid generators[6] for efficient optical photolithography,[7] bio-probing and bio-controlling caged compounds,[8] and so on. In an early report by Lehn and co-workers, substitution reactions specific for the ring-closed isomer of diarylethenes were demonstrated.[9] Other forms of selective chemical reactivity for the ring-closed forms of diarylethenes and terarylenes have been reported as photo-gated reactions.[10] It should be noted that the ring-closing reaction of diarylethenes and terarylenes involves conversion of the orbital of the reacting carbon atoms from sp^2 to sp^3 with steric distortion, bringing about the specific reactivity of closed-ring isomers. Recently, the authors have reported the elimination of methanol from the ring-closed form of a terarylene derivative to form condensed fluorescent aromatics which never returned to the original open-ring isomer with visible light irradiation (Scheme 1).[11] This elimination reaction quantitatively proceeded either in highly polar solvents such as acetone or in the presence of acid. Thus, the set of reactions including photocyclization and subsequent spontaneous dark reactions provides efficient routes not only to polycyclic aromatics for which oxidative dehydroge-



Scheme 1. Photochromism and elimination reaction of the closed-ring isomer of a terarylene with leaving groups at the photoreactive carbon atoms.[11]

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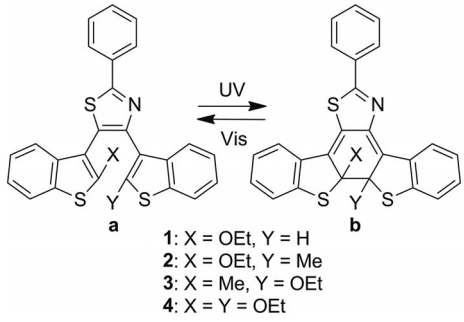
nation is often employed,[12,13] but also to sequential photoreleasing systems[10b] that trigger further chemical reactions in a remote manner.

In this study, we investigated subsequent reactions which follow the efficient photochromic ring-closing reaction of terarylenes using a series of 4,5-dibenzothienylthiazoles with various substituents at the 2-position of a benzothienyl ring. The chemical reactivity of the substituents was investigated in association with the photocyclization reaction in the presence of acid; new stereospecific reactions giving complex polycyclic structures are also demonstrated. Compounds **1**–**4** have a similar basic terarylene structure of 2-phenyl-4,5-dibenzothienylthiazole, which has been demonstrated to show relatively high photocyclization reaction efficiency above 60%,[5a] with different substituents at the 2-position of benzothienyl rings (Scheme 2). Compound **1** has an ethoxy group and a hydrogen atom at the respective 2-positions of each benzothienyl ring and was expected to undergo ethanol elimination in a manner similar to that shown in Scheme 1. Unlike **1**, compounds **2** and **3** had methyl groups at each 2-position opposite to the ethoxy group; in each case the methyl group was anticipated to suppress the concerted elimination reaction. Given that the elimination reaction from the ring-closed intermediate proceeds through the agency of a carbocation intermediate, **2** and **3** were expected to give alcoholysis products with an alkoxy substituent corresponding to the alcohols used as solvents in the presence of acid. The subsequent chemical reaction is discussed in terms of the chemical structure of products determined by ^{1}H NMR, mass spectra, and X-ray crystal structures.



Scheme 2. Photochemical interconversion of 4,5-dibenzothienylthiazoles.

Results and Discussion

Compounds **1**–**4** were synthesized by conventional cross-coupling reactions of 4,5-dibromo-2-phenylthiazole and various pinacolboranes of benzothiophene, and their chemical structures were confirmed by ^{1}H NMR, ^{13}C NMR, mass spectra, and elemental analysis.

As shown in Figure 1, compound **1** showed both photoinduced coloration and de-coloration reactions in hexane. We observed a colorless solution of the open-ring isomer **1a** turn orange upon irradiation with UV light (λ = 313 nm) and showing an absorption maximum at 530 nm. The colored solution was bleached by visible light irradiation ($\lambda >$ 400 nm) and returned to the original colorless solution of **1a**. However, the closed-ring isomer **1b** was difficult to isolate from the colored solution since the subsequent elimination reaction occurred in the reverse-phase HPLC column when using polar solvents as eluent. The hexane solution containing the ring-closed **1b** became yellow immediately following addition of a small amount of trifluoroacetic acid (TFA), and the absorption band at 530 nm completely disappeared. The absorption profile of the product was found to be clearly different from that of **1a**, indicating the formation of a new compound. Neither UV nor visible irradiation to the yellowish solution caused further spectral change. The single yellow component was isolated by HPLC and identified as condensed structure **1c** in Scheme 3 on the basis of ^{1}H NMR and mass spectra, which corresponds well with the previous result (Scheme 1). Gradual

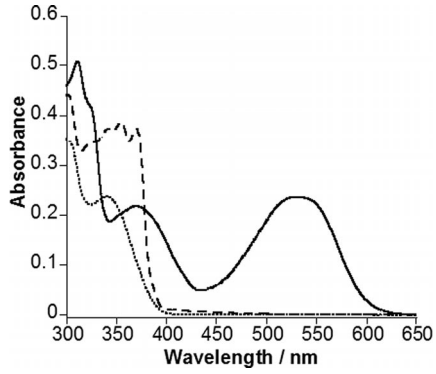
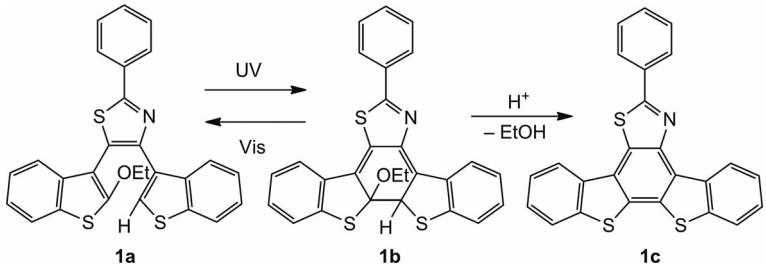


Figure 1. Absorption spectrum change of **1** in hexane: open form (dotted line), photostationary state under irradiation with 313 nm light (solid line) and after the addition of TFA (dashed line).



Scheme 3. Photoreaction and subsequent elimination reaction of **1**.

formation of **1c** from **1b** was also observed in methanol in the absence of both acid and light.

Photochromic properties of 4,5-dibenzothienylthiazoles **2a** and **3a** with opposing ethoxy and methyl groups at each benzothienyl 2-position and **4a** with two opposing ethoxy groups were then investigated. The values for λ_{max} and ε of **2**, **3** and **4** are summarized in Table 1 with photochromic cyclization quantum yields evaluated by the standard procedure with 3,3,4,4,5,5-hexafluoro-1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)cyclopentene[14] in hexane as a standard. Relatively high quantum yields were obtained for compounds **2**–**4** in their cyclization reactions, which were almost comparable with those reported for 4,5-dibenzothienylthiazoles.[5a] The colorless solutions of **2a**–**4a** turned to red-purple, bluish-purple and blue upon irradiation at 313 nm. These colors are due to the formation of closed-ring isomers **2b**–**4b**. The conversion ratios between **2a** and **2b**, between **3a** and **3b** and between **4a** and **4b** at their photostationary states, achieved by irradiation with UV light (λ = 313 nm) were estimated to be 86, 81 and 90%, respectively. Upon irradiation with visible light, the closed-ring isomers reverted to **2a**–**4a** with a decrease of absorption band in the visible region. 4,5-Dibenzothiazoles **2**–**4** showed the photochromic reactions in methanol as well as in hexane. Since isosbestic points were clearly observed in both hexane and methanol, the well-defined two-component reaction schemes between the open-ring and the closed-ring isomers are apparent under these conditions. Unlike **1**, the ring-closed forms **2b**–**4b** were successfully isolated by reverse-phase HPLC using methanol as an eluent, and their structures were elucidated by ^{1}H NMR spectroscopy. These ring-closed forms seemed to be stable in methanol. The existence of clear isosbestic points in the absorption spectral change (Figure 2) in methanol solutions also supports the stability of the ring-closed form in methanol.

Table 1. Absorption maxima (λ_{max}) and coefficients (ε) of the open- and closed-ring isomers of **1**–**4**, together with the ring-closing quantum yields (Φ_{a-b}) in hexane solution.

Entry	Compound	λ_{max} [nm] (ε [10^4 M^{-1} cm^{-1}])	Φ_{a-b}
1	**1a**	310 (1.1)	–[a]
2	**1b**	530[b] (–)[a]	–
3	**2a**	340 (1.2)	0.53
4	**2b**	545[b] (0.94)	–
5	**3a**	336 (1.0)	0.64
6	**3b**	554[b] (0.98)	–
7	**4a**	344 (0.90)	0.62
8	**4b**	566[b] (1.1)	–

[a] Not determined because **1b** could not be isolated. [b] Absorption maximum in the visible region.

In order to evaluate the mechanism of ethoxy group elimination from the benzothiophene 2-position, TFA was added to methanolic solutions of **2b** and **3b**. The absorption band at 545 nm derived from the closed-ring isomer **2b** decreased following addition of TFA, and a new absorption band appeared at 368 nm (Figure 3a). Similarly, the absorption band for **3b** observed at 554 nm decreased following

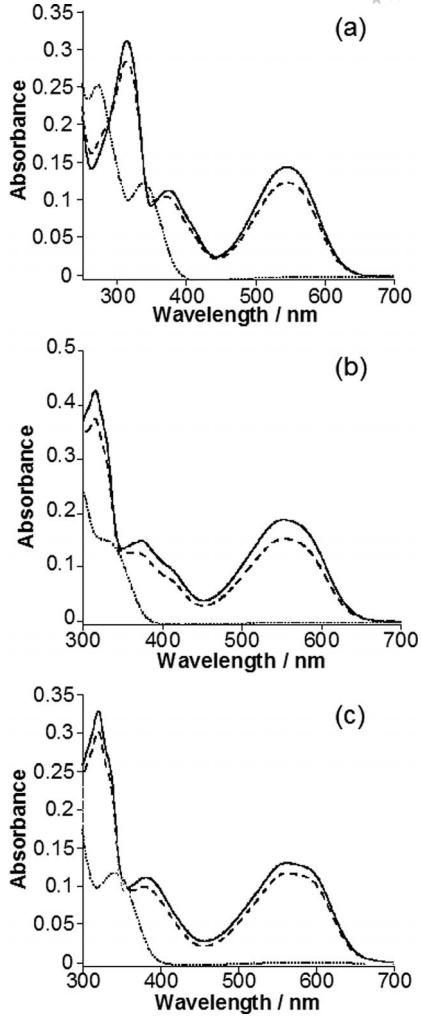


Figure 2. Absorption spectra for **2** (a), **3** (b) and **4** (c) in methanol: open-form **a** (dotted lines), closed-form **b** (solid lines) and photostationary state under irradiation with 313 nm light (broken lines). The concentrations of **2**, **3** and **4** were 1.0×10^{-5}, 1.44×10^{-5} and 1.29×10^{-5} M, respectively.

addition of TFA, and a new absorption band appeared at 253 nm (Figure 3b). These acid-induced spectral changes were observed in the dark. The absorption profiles of final products were different from those of starting materials **2a** and **3a**, indicating the formation of new components. The isosbestic points at 400 nm (for **2**) and 280 nm (for **3**) were clearly found, supporting the involvement of two-component chemical reactions with the addition of TFA. The final products no longer showed photochromic changes upon irradiation with either UV or visible light. The reaction mixtures were characterized by a reverse-phase HPLC with a flow rate of 3 mL/min. The fact that no closed-form molecules **2b** (66 min) or **3b** (65 min) were observed (Supporting Information, Figure S1) indicates a conversion ratio of almost 100%, which is consistent with the observed changes in absorption spectra (Figure 3). Each reaction mixture of **2b** and **3b** with TFA gave single HPLC peaks at 57 and 71 min, respectively; these are different from the retention times of **2a** (46 min) and **3a** (51 min), respectively. Mean-

while, addition of TFA to methanol solutions of open-ring isomers **2a** and **3a** did not induce any observable changes in absorption or ^{1}H NMR spectra, demonstrating a ring-closed form-selective reaction. Although **4b** with two ethoxy groups at the reactive benzothiophene carbon atoms showed a similar spectral change to those observed for **2b** and **3b** with an isosbestic point by the addition of TFA (Supporting Information, Figure S3), the reaction mixture gave a complicated HPLC chromatogram with multiple peaks.

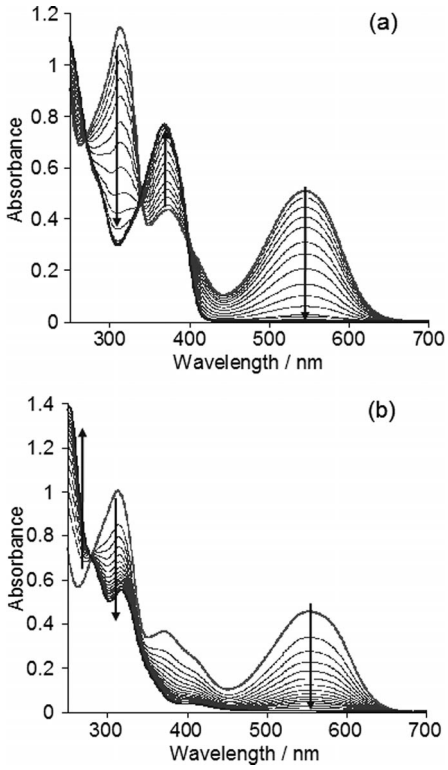


Figure 3. Absorption spectral changes of **2b** (a) and **3b** (b) after the addition of TFA. Spectra were recorded every 5 min after the addition of TFA.

The reaction products derived from **2b** and **3b** by the addition of TFA in methanol were isolated by HPLC as **2c** and **3c**, respectively, and were characterized with the aid of ^{1}H NMR and mass spectra. Figure 4 shows the ^{1}H NMR spectral change in the aliphatic region in going from **2b** to **2c** and from **3b** to **3c**. Signals at δ = 3.72, 3.39 and 1.08 ppm assigned to an ethoxy group in **2b** disappeared in **2c**, whereas the methyl group proton signals on another reactive carbon atom at δ = 2.1 ppm remained, and a new singlet signal appeared at δ = 3.00 ppm (3 H). A similar result was also observed in the ^{1}H NMR spectral change from **3b** to **3c**. The new singlet at δ = 3 ppm was assigned as the methoxy group, which takes the place of the ethoxy group of **2b** and **3b** by alcoholysis in methanol. The change in molecular mass with the decrease of 14 observed by mass measurement also supported the replacement of an ethoxy group with a methoxy group. The possibility of simple substitution reactions has been excluded since **2c** and **3c** failed to show any photochromic capability.

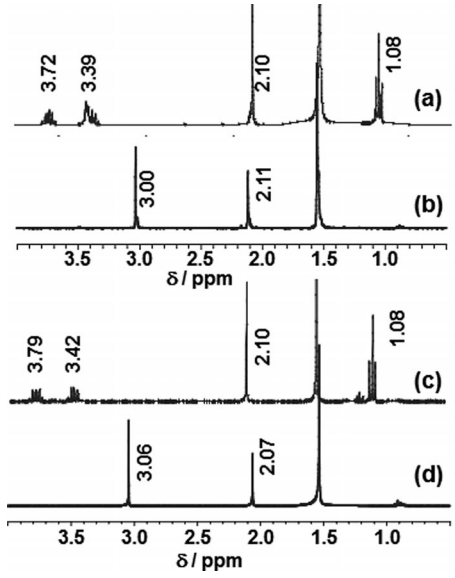


Figure 4. ^{1}H NMR spectra for **2b** (a), **2c** (b), **3b** (c) and **3c** (d) in CD_2Cl_2. For clarity, only parts of the aliphatic region (δ = 0.5–4.0 ppm) are shown.

Fortunately, **2c** and **3c** crystallized from their hexane solutions as colorless crystals enabling us to identify the absolute structures of **2c** and **3c** by single-crystal X-ray analysis (Figure 5).[15] Although **2c** and **3c** are indeed methoxy-substituted products, the methoxy group regiochemistry was found to be different from that of the ethoxy groups in **2a** and **3a**, respectively. The methoxy group in **2c** was introduced at C10 (Figure 5a), and the methoxy group in **3c** was found to reside at C20 (Figure 5b). This suggests the generation of intermediates **(2b–OEt)$^+$** and **(3b–OEt)$^+$** by the elimination of the ethoxy group as ethanol from **2b** and **3b**, respectively, and subsequent carbocation rearrangements. According to the resonance structures depicted in Scheme 4, the positive charge seems to be mainly localized on the C3, C10 and C19 positions for **(2b–OEt)$^+$** and C2, C17 and C20 positions for **(3b–OEt)$^+$**. Considering the relative stability of the three possible resonance structures **X**, **Y** and **Z** for carbocation intermediates in Scheme 4 in terms of the number of aromatic rings involved, canonical structures **Z** seem to be the most stable ones for both **(2b–OEt)$^+$** and **(3b–OEt)$^+$**.

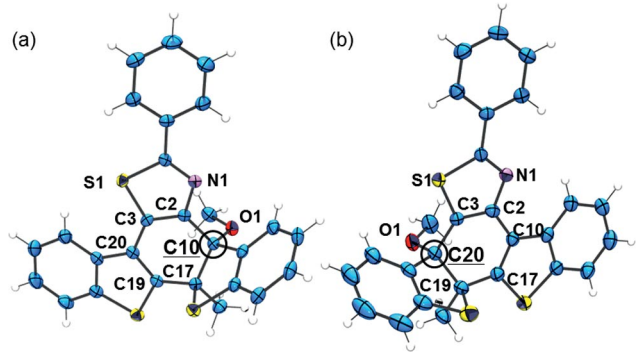
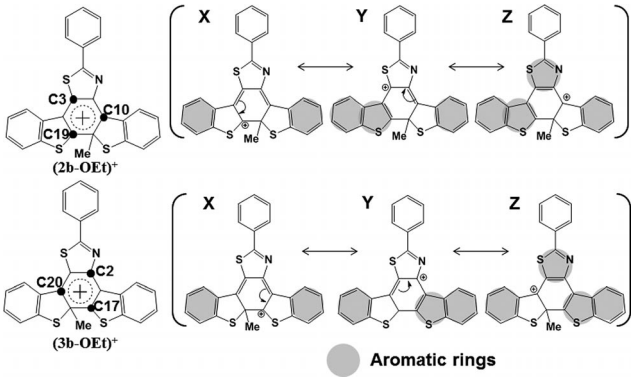


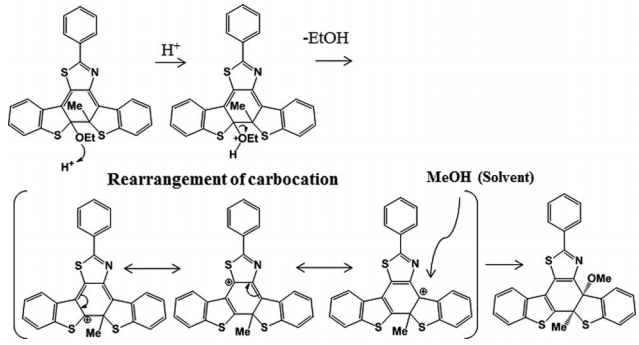
Figure 5. ORTEP drawings (showing 50% probability displacement ellipsoids) of the crystals of **2c** (a) and **3c** (b).



Scheme 4. Resonance structures of carbocation intermediates **(2b–OEt)$^+$** and **(3b–OEt)$^+$**.

The distribution of the positive charge in **(2b–OEt)$^+$** and **(3b–OEt)$^+$** was also simulated using density function theory (DFT) calculations at the B3LYP/6-31++G* level. The positive charges were found to be more localized at C10 for **(2b–OEt)$^+$** and at C20 for **(3b–OEt)$^+$** (Supporting Information, Figure S4) than for other possible carbon atoms. This finding was consistent with structures elucidated for products **2c** and **3c**. It also should be noted that X-ray crystallographic data revealed only *cis*-substituted compounds, although *trans*-compounds could be generated according to the reaction mechanism. However, ^{1}H NMR and HPLC results never suggested the formation of diastereomeric products. In order to compare the stability of *cis* and *trans* forms of **2c**, Merck Molecular Force Field (MMFF94) calculations were performed. The *cis* structure was calculated based on the X-ray single-crystal structure. According to the MMFF calculations, the *cis* structure is much more stable than the *trans* structure by 22 kcal/mol. CH/O interactions between methyl and methoxy groups in the *cis* form may stabilize the *cis* form. Moreover, substantial strain in the fused aromatic rings may destabilize the *trans* form. The methoxy group, once attached to the *trans* position, might be readily eliminated under acidic conditions to bias the chemical equilibrium towards the more stable *cis* form.

On the basis of these results we consider that a plausible mechanism for the elimination reaction in acidic conditions is as shown in Scheme 5. The ethoxy group on the 2-position of benzothiophene leaves as ethanol in the presence of TFA. The carbocation, which can assume a number of different resonance structures, then selectively reacts with methanol at the most positively charged carbon atom. This S_N1-like reaction mechanism seems to be dominant under the acidic conditions because of the poor leaving group ability of the methoxylate anion under neutral conditions. However, it should also be mentioned that the contribution of a concerted reaction, where the elimination of ethanol and the addition of the methoxy group occur simultaneously, cannot be ruled out completely. Although **2b** and **3b** were stable in neutral methanol, **1b** spontaneously formed **1c**. This specific reactivity of **1b** may originate from a particularly facile deprotonation due to a unique H-bonding network, which enables concerted elimination of ethanol from **1b** under neutral conditions; such a scenario clearly warrants further study.



Scheme 5. Suggested reaction mechanism for the elimination of ethanol followed by the introduction of a methoxy group in **2**.

Conclusions

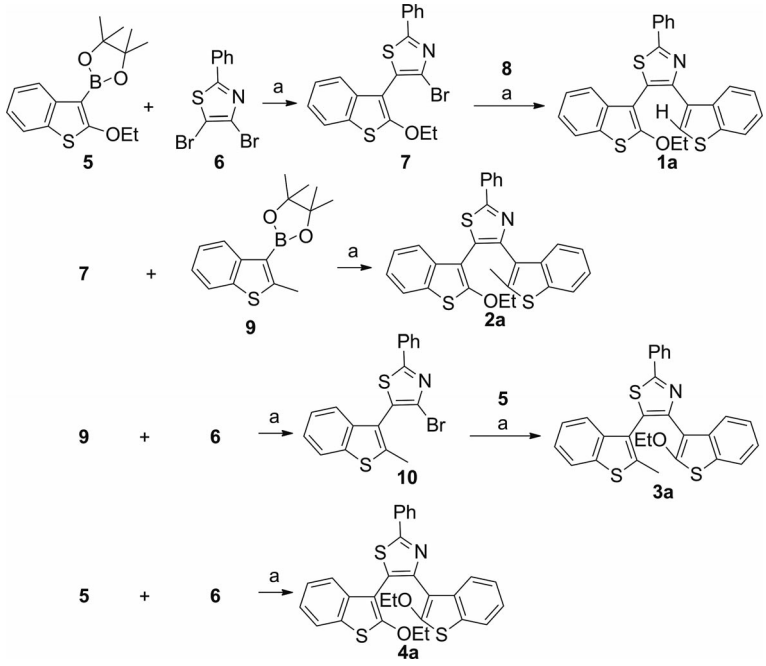
We synthesized 4,5-dibenzothienylthiazoles with leaving groups at the 2-position of each benzothienyl ring and studied the elimination and substitution reactions under alcoholysis conditions. All compounds underwent photochromic reactions in hexane and subsequent reactions specific for ring-closed forms under acidic conditions. Compound **1** having a hydrogen atom and an ethoxy group at reacting carbon atoms underwent an irreversible elimination reaction following the addition of acid as we have already reported.[11] On the other hand, closed isomers **2b** and **3b** having a methyl group on the side opposite to the ethoxy group underwent substitution of the ethoxy group with a methoxy group in methanol. The crystal structures of **2c** and **3c** along with DFT calculations suggest the generation of carbocationic intermediates and the rearrangement of these carbocations to give the most stable *cis*-substituted products.

Experimental Section

General: ^{1}H NMR spectra were recorded with a JEOL AL-300 spectrometer (300 MHz). Preparative and analytical HPLC was performed with a HITACHI LaChrom ELITE HPLC system and a JASCO LC-2000 Plus Series. Mass spectra were measured with a JEOL JMS-T100LC AccuTOF mass spectrometer. Absorption spectra in solution were studied with JASCO V-550 and V-660 spectrophotometers. Irradiations were carried out with a USHIO 500 W ultra-high-pressure mercury lamp as the excitory light source. Monochromic light was obtained by passing the light through a monochromator (Shimadzu SPG-120S, 120 mm, $f = 3.5$). X-ray crystallographic analyses were carried out with a Rigaku R-AXIS RAPID/s imaging-plate diffractometer with Mo-K_α radiation at 296 K.

Synthesis of 1a–4a: Dibenzothienylthiazoles **1a**–**4a** were prepared by cross-coupling reactions as illustrated in Scheme 6.

4-Bromo-5-(2-ethoxybenzo[*b*]thiophen-3-yl)-2-phenylthiazole (7): A 500 mL four-necked flask was charged with 2-(2-ethoxybenzo[*b*]-thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**, 2.2 g,



Scheme 6. Syntheses of compounds **1a**–**4a**. Reagents and conditions: triphenylphosphane, $Pd(PPh_3)_4$, K_3PO_4 (2 M)/H_2O, 1,4-dioxane.

7.2 mmol), 4,5-dibromo-2-phenylthiazole (**6**, 2.3 g, 7.2 mmol), triphenylphosphane (940 mg, 3.6 mmol), $Pd(PPh_3)_4$ (410 mg, 0.36 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (100 mL/200 mL) solution. The mixture was then stirred at 110 °C under N_2. After stirring for 20 h, the reaction mixture was extracted with EtOAc, and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/EtOAc, 20:1) followed by recrystallization from hexane afforded **7** (2.0 g, 67%) as a colorless solid. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 1.42–1.47 (t, J = 7 Hz, 3 H), 4.42–4.43 (q, J = 7 Hz, 2 H), 7.34–7.40 (m, 2 H), 7.54–7.57 (m, 4 H), 7.84–7.86 (d, J = 8 Hz, 1 H), 8.01–8.04 (m, 2 H) ppm.

4-(Benzo[*b*]thiophen-3-yl)-5-(2-ethoxybenzo[*b*]thiophen-3-yl)-2-phenylthiazole (1a): A 200 mL four-necked flask was charged with 4,4,5,5-tetramethyl-2-(2-methylbenzo[*b*]thiophen-3-yl)-1,3,2-dioxaborolane (**8**, 170 mg, 0.64 mmol), 4-bromo-5-(2-ethoxybenzo[*b*]-thiophen-3-yl)-2-phenylthiazole (**7**, 270 mg, 0.64 mmol), triphenylphosphane (83 mg, 0.32 mmol), $Pd(PPh_3)_4$ (36 mg, 0.032 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (25 mL/50 mL) solution. The mixture was then stirred at 110 °C under N_2. After stirring for 2 d, the reaction mixture was extracted with EtOAc, and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/EtOAc, 20:1) and reverse-phase HPLC (MeOH) afforded **1a** (52 mg, 17%) as a colorless solid. ^{1}H NMR (300 MHz, [D$_6$]acetone/TMS): δ = 1.02–1.28 (t, J = 7 Hz, 3 H), 4.02–4.04 (q, J = 7 Hz, 2 H), 7.23–7.26 (m, 2 H), 7.37–7.45 (m, 4 H), 7.55–7.60 (m, 3 H), 7.78–7.79 (m, 1 H), 7.92–7.93 (m, 1 H), 8.13–8.14 (m, 2 H), 8.32–8.33 (m, 1 H) ppm. EI-HRMS: calcd. for $C_{27}H_{19}NOS_3^+$ $[M]^+$ 469.6409; found 469.0630.

5-(2-Ethoxybenzo[*b*]thiophen-3-yl)-4-(2-methylbenzo[*b*]thiophen-3-yl)-2-phenylthiazole (2a): A 300 mL four-necked flask was charged with 4,4,5,5-tetramethyl-2-(2-methylbenzo[*b*]thiophen-3-yl)-1,3,2-dioxaborolane (**9**, 990 mg, 3.6 mmol), 4-bromo-5-(2-ethoxybenzo-[*b*]thiophen-3-yl)-2-phenylthiazole (**7**, 1.5 g, 3.6 mmol), triphenylphosphane (940 mg, 3.6 mmol), $Pd(PPh_3)_4$ (939 mg, 3.6 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (100 mL/200 mL) solution. The mixture was then stirred at 110 °C under N_2. After stirring for 12 h, the reaction mixture was extracted with EtOAc, and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/EtOAc, 20:1) followed by recrystallization from hexane afforded **2a** (1.2 g, 69%) as a colorless solid. ^{1}H NMR (300 MHz, CD_2Cl_2/TMS): δ = 0.85–0.89 (t, J = 7 Hz, 3 H), 2.1 (s, 3 H), 3.81 (s, 2 H), 7.12–7.18 (m, 2 H), 7.25–7.28 (m, 2 H), 7.48–7.52 (m, 4 H), 7.62–7.65 (m, 1 H), 7.72–7.75 (m, 2 H), 8.06–8.09 (m, 2 H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2/TMS): δ = 14.40, 14.93, 71.32, 105.82, 121.21, 121.98, 122.57, 123.39, 123.59, 124.07, 124.44, 125.41, 126.79, 127.15, 128.42, 129.41, 130.45, 131.14, 134.30, 137.59, 138.35, 139.36, 140.49, 148.62, 161.78, 167.14 ppm. ESI-HRMS: calcd. for $C_{28}H_{22}NOS_3^+$ $[M + H]^+$ 484.0858; found 484.0856. $C_{28}H_{21}NOS_3$ (483.66): calcd. C 69.53, H 4.38, N 2.90; found C 69.55, H 4.18, N 3.08.

4-Bromo-5-(2-methylbenzo[*b*]thiophen-3-yl)-2-phenylthiazole (10): A 300 mL four-necked flask was charged with 4,4,5,5-tetramethyl-2-(2-methylbenzo[*b*]thiophen-3-yl)-1,3,2-dioxaborolane (**9**, 570 mg, 2.1 mmol), 4,5-dibromo-2-phenylthiazole (**6**, 660 mg, 2.1 mmol), triphenylphosphane (270 mg, 1.0 mmol), $Pd(PPh_3)_4$ (120 mg, 0.1 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (70 mL/150 mL) solution. The mixture was then stirred at 110 °C under N_2. After stirring for 12 h, the reaction mixture was extracted with EtOAc, and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Recrystallization from hexane afforded **10** (570 mg, 71%) as a colorless solid. ^{1}H NMR (300 MHz, [D$_6$]acetone/TMS): δ = 2.58 (s, 3 H), 7.42–7.57 (m, 6 H), 7.96–8.06 (m, 3 H) ppm.

4-(2-Ethoxybenzo[*b*]thiophen-3-yl)-5-(2-methylbenzo[*b*]thiophen-3-yl)-2-phenylthiazole (3a): A 200 mL four-necked flask was charged with 2-(2-ethoxybenzo[*b*]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**, 360 mg, 1.2 mmol), 4-bromo-5-(2-methylbenzo[*b*]thiophen-3-yl)-2-phenylthiazole (**10**, 570 mg, 1.2 mmol), triphenylphosphane (150 mg, 0.59 mmol), $Pd(PPh_3)_4$ (69 mg,

0.060 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (70 mL/150 mL) solution. The mixture was then stirred at 110 °C under N_2. After stirring for 12 h, the reaction mixture was extracted with EtOAc, and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/EtOAc, 20:1) and recrystallization from hexane afforded **3a** (320 mg, 57%) as a colorless solid. ^{1}H NMR (300 MHz, CD_2Cl_2/TMS): δ = 0.59–0.64 (t, J = 7 Hz, 3 H), 2.10 (s, 3 H), 3.43–3.48 (dq, J = 9, 6 Hz, 1 H), 3.70–3.75 (dq, J = 9, 6 Hz, 1 H), 7.21–7.37 (m, 4 H), 7.48–7.53 (m, 3 H), 7.64–7.69 (m, 2 H), 7.75–7.78 (m, 1 H), 7.87–7.90 (d, J = 8 Hz, 1 H), 8.07–8.10 (m, 2 H) ppm. ESI-HRMS: calcd. for $C_{28}H_{21}NNaOS_3^+$ $[M + Na]^+$ 506.0683; found: 506.0709. $C_{28}H_{21}NOS_3$ (483.66): calcd. C 69.53, H 4.38, N 2.90; found C 69.41, H 4.19, N 2.86.

4,5-Bis(2-ethoxybenzo[*b*]thiophen-3-yl)-2-phenylthiazole (4a): A 500 mL four-necked flask was charged with 2-(2-ethoxybenzo[*b*]-thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**, 0.94 g, 3.1 mmol), 4,5-dibromo-2-phenylthiazole (**6**, 0.45 g, 1.4 mmol), triphenylphosphane (0.39 g, 1.5 mmol), $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (150 mL/300 mL) solution. The mixture was then stirred at 110 °C under N_2. After stirring for 20 h, the reaction mixture was extracted with EtOAc, and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/EtOAc, 20:1) and recrystallization from hexane afforded **4a** (0.44 g, 61%) as a colorless solid. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 0.54–0.59 (t, J = 7 Hz, 3 H), 0.68–0.75 (t, J = 7 Hz, 3 H), 3.49–3.56 (q, J = 7 Hz, 2 H), 3.72–3.79 (q, J = 7 Hz, 2 H), 7.11–7.16 (m, 3 H), 7.21–7.26 (m, 1 H), 7.40–7.47 (m, 4 H), 7.61–7.68 (m, 2 H), 7.77–7.80 (d, J = 8 Hz, 1 H), 7.97–8.00 (m, 2 H) ppm. $C_{29}H_{23}NO_2S_3$ (513.69): calcd. C 67.81, H 4.51, N 2.73; found C 67.73, H 4.32, N 2.70.

1c: ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 7.39–7.45 (m, 3 H), 7.49–7.70 (m, 4 H), 8.11–8.47 (m, 4 H), 8.47 (d, J = 8 Hz, 2 H) ppm. EI-HRMS: calcd. for $C_{25}H_{13}NS_3$ $[M]^+$ 423.0210; found 423.0208.

2c: ^{1}H NMR (300 MHz, CD_2Cl_2/TMS): δ = 2.10 (s, 3 H), 3.01 (s, 3 H), 7.14–7.31 (m, 3 H), 7.44–7.50 (m, 4 H), 7.55–7.58 (m, 1 H), 7.83 (m, 1 H), 7.96–7.99 (m, 3 H), 8.16–8.19 (d, J = 8 Hz, 1 H) ppm. EI-HRMS: calcd. for $C_{27}H_{19}NOS_3$ $[M]^+$ 469.063; found 469.063.

3c: ^{1}H NMR (300 MHz, CD_2Cl_2/TMS): δ = 2.07 (s, 3 H), 3.05 (s, 3 H), 7.15–7.18 (m, 1 H), 7.23–7.33 (m, 2 H), 7.42–7.62 (m, 7 H), 7.92–7.95 (d, J = 8 Hz, 1 H), 8.07–8.10 (m, 2 H) ppm. ESI-HRMS: calcd. for $C_{27}H_{19}NOS_3$ $[M + H]^+$ 470.071; found 470.070.

Supporting Information (see footnote on the first page of this article): Analytical HPLC details, full-range ^{1}H NMR spectra of **2b**, **2c**, **3b**, and DFT calculations of carbocation intermediates.

Acknowledgments

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[15] Crystallographic data for **2c**: $C_{17}H_{19}NOS_3$, a = 10.3731(2), b = 15.0793(3), c = 14.9232(4) Å, β = 107.8331(7)°, monoclinic, space group $P2_1/n$ (#14), Z = 4, V = 2222.17(8) Å^3, $\rho_{calcd.}$ = 1.404 g cm^{-3}. Of 21818 reflections measured up to 2θ = 55.0°, 5090 were independent (R_{int} = 0.018). The structure was solved

by direct methods and refined with a full matrix against all F^2 data. Hydrogen atoms were calculated in riding positions. wR = 0.0882, R = 0.0334. Crystallographic data for **3c**: $C_{17}H_{19}NOS_3$, a = 9.7515(3), b = 10.8079(4), c = 20.4930(7) Å, β = 95.7083(9)°, monoclinic, space group $P2_1/n$ (#14), Z = 4, V = 2149.1(2) Å^3, $\rho_{calcd.}$ = 1.451 g cm^{-3}. Of 20613 reflections measured up to 2θ = 54.9°, 4903 were independent (R_{int} = 0.0143). The structure was solved by direct methods and refined with a full matrix against all F^2 data. Hydrogen atoms were calculated in riding positions. wR = 0.0931, R = 0.0480. CCDC-875531 (for **2c**) and -875532 (for **3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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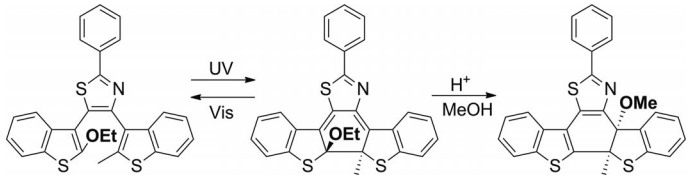
Photochromism



Subsequent chemical reactions are demonstrated for photoproducts of 4,5-dibenzothienylthiazoles possessing leaving groups at the 2-position of benzothienyl rings. Closed-ring isomers of 4,5-dibenzothienylthiazoles having an ethoxy group underwent an alcoholysis reaction under acidic conditions accompanying rearrangement of carbocation intermediates.

Keywords: Terarylene / Photochromic compound / Elimination / Heterocycles / Photochromism / Dibenzothienylthiazoles / Alcoholysis

