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Novel photoinduced cyclization of pentafluorophenylhemithioindigo

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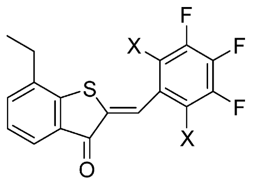
Abstract

Photoirradiation of the pentafluorophenyl-substituted *Z*-hemithioindigo **1** causes a novel type of photoinduced cyclization, to produce the intramolecularly cyclized alcohol **2** and its dehydrated ether **3**. For this photoinduced cyclization, the *o*-fluorine atoms of the phenyl group of **1** are found to be crucial.

Keywords: Photochromism; Hemithioindigo; Fluoroaromatics; Photoinduced cyclization

1. Introduction

Reversible molecular systems caused by the photoinduced *E*, *Z* isomerizations provide a tool to manipulate the recognizing ability of a binding site [1,2]. For example, azobenzenes [3], stilbenes [4], and thioindigos [5] play an important role as molecular switches based on the *E*, *Z* isomerizations. Hemithioindigos have a potential for use of molecular switches, because aryl-substituted hemithioindigos are well known to have a good repeatability of *E*, *Z* isomerization and high stability of both *E* and *Z* isomers [6]. In our previous papers, we reported that irradiation of benzoyl-substituted hemithioindigo produced, instead of an usual *Z–E* isomerization product, the photoinduced cycloadduct that could be thermally dissociated to the original hemithioindigo, and that the reversible interconversion was applied to the molecular switch for the porphyrin-quinone recognition [7,8]. On the other hand, perfluoroaromatics have been widely utilized for the derivatization due to their facile nucleophilic substitutions [9]. So it is important to study the photoinduced behaviors of pentafluorophenyl-substituted hemithioindigo from the viewpoints of the developments of hemithioindigos as functionalized molecular devices. Here, we wish to report that irradiation of *Z*-2-pentafluorophenylmethylene-7-ethylbenzo[*b*]thiophen-3(2*H*)-one (**1**) results in the novel photoinduced cyclization, instead of the usual *Z–E* isomerization.



1 (X = F); **4** (X = H)

2. Results and discussion

Pentafluorophenylhemithioindigo **1** was synthesized in 43% yield by the reaction of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one with pentafluorobenzaldehyde in toluene. From the reaction mixture, only *Z* isomer was isolated and the formation of the other isomer was not detected. The *Z*-configuration of the product was determined by the deshielded olefinic proton (δ 7.75) in ^{1}H NMR spectra [7,8].

A toluene solution of **1** is yellow (λ_{max} = 432 nm). Exposing the anhydrous toluene solution to the sunlight or irradiation with 390 nm light did not cause red-shifted absorption due to the *E* isomer but did cause disappearance of the absorption (Fig. 1), which suggests that photoproducts other than the *E* isomer are formed under the photoirradiation. The identifications of the products could not be done because of the formations of many unstable products. However, one product was isolated from the photoirradiation with 390 nm light of a

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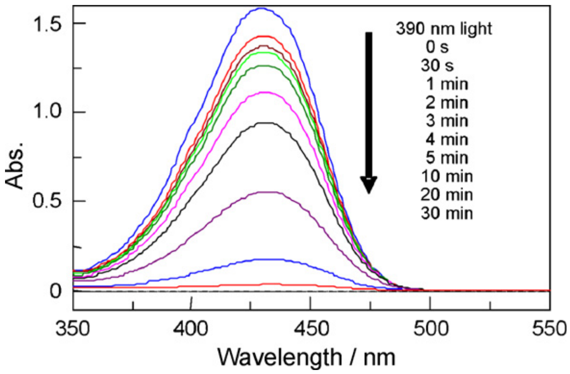


Fig. 1. UV–vis spectra change of **1** by irradiation with 390 nm light. [**1**] = 3.2 × 10^{-4} M in anhydrous toluene.

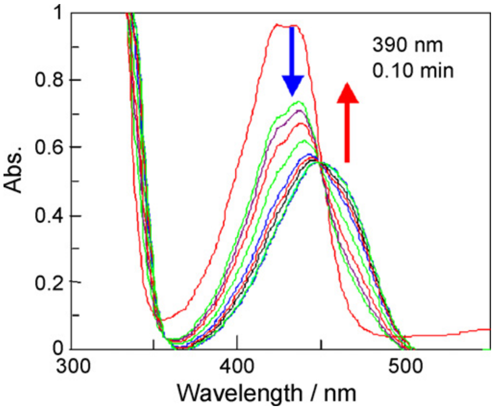
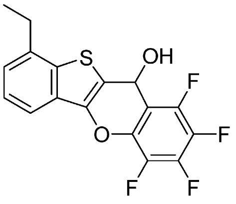


Fig. 2. UV–vis spectra change of **4** by irradiation with 390 nm light. [**4**] = 1 × 10^{-4} M in toluene.

highly dilute acetone solution of **1** in the presence of a small amount of water. The product was determined to be the intramolecularly cyclized alcohol **2** from the disappearance of the carbonyl group in the IR spectra and from the ^{1}H NMR and ^{19}F NMR spectra, the MS spectra, and elemental analysis. In particular, the position of hydroxy group was determined by the observation that two doublets of the OH and CH protons with the same coupling constants are changed to one singlet by the coexistence of D_2O in the ^{1}H NMR spectra, which indicates that the OH and CH protons are adjacent to each other. When a carbon tetrachloride solution of **1** was irradiated in the presence of a small amount of water, another product was isolated and its structure was determined to be **3**, the dehydrated ether of **2**, based on the spectral data and the elemental analysis.



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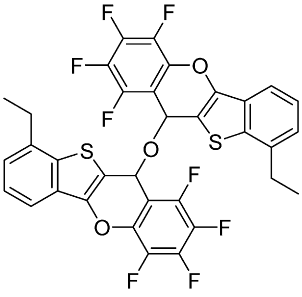

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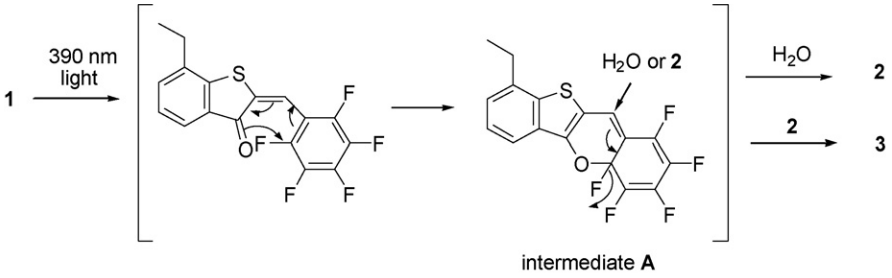
The reaction mechanism for the formations of **2** and **3** is speculated to be as follows: pericyclic reaction of the photoinduced *E*-hemithioindigo affords the intermediate **A** [10], which undergoes a nucleophilic substitution with water or with the formed **2** in a S_N2' manner, to produce **2** or **3**, respectively (Scheme 1). The fact that **3** was isolated in the case of irradiation under a moderate concentration of **1** is ascribed to the relatively high concentration of **2** in the reaction mixture.

As shown in the proposed mechanism for the formations of **2** and **3**, the *o*-fluorine atoms of the phenyl group are expected to play an important role for the photoinduced cyclization. This is supported by the following observations: irradiation of 3,4,5-trifluorophenyl-substituted *Z*-hemithioindigo **4** under the same conditions leads to the usual *Z*, *E*-isomerization; irradiation with 390 nm light caused a red-shifted absorption due to the *E* isomer and subsequent irradiation with 490 nm light returned it to the original absorption (Fig. 2). Reversible interconversion between *Z* and *E* isomers was monitored several times using UV–vis spectra. The results are summarized in Fig. 3, showing good repeatability.

We assume the following reasons to explain why, in the case of **1**, *E* isomer is not isolated but the photocyclized products **2** and **3** are formed. The B3LYP/6-31G*-optimized structure of *E*-**1** and charges of the selected atoms are collected in Fig. 4, together with those of the *E*-**4** [11]. The benzothiophenone and phenyl rings of *E*-**4** lie on the same plane, whereas these rings of *E*-**1** are twisted with respect to each other. The twisted structure of *E*-**1** may be ascribed to electronic repulsion between the *o*-fluorine atom and the carbonyl oxygen atom. Meanwhile, the electron-deficient *o*-carbon atom of the pentafluorophenyl group of *E*-**1** may cause the attack of the carbonyl oxygen atom, giving rise to the intermediate **A**.

Thus, photoirradiation of the pentafluorophenyl-substituted *Z*-hemithioindigo **1** causes novel type of photoinduced



Scheme 1.

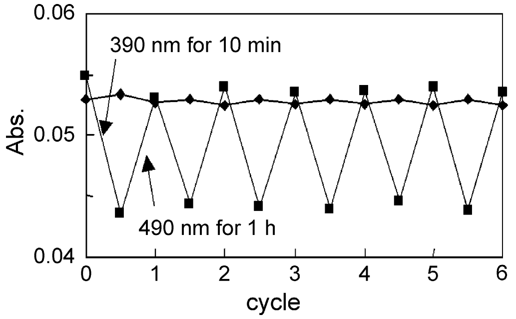
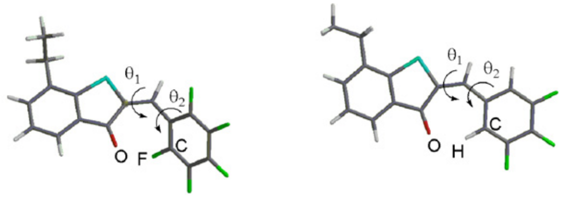


Fig. 3. Change in absorbance of **4** by irradiations of 390 nm light and of 490 nm light. [**4**] = 1 × 10^{-5} M in toluene. (◆): 434 nm (λ_{max} of Z-**4**), (■): 441.5 nm (λ_{max} of *E*-**4**).



E-**1**

O; -0.484, C; 0.328, F; -0.264
θ_1; 10.93 degree, θ_2; 47.47 degree

E-**4**

O; -0.490, C; -0.274, H; 0.230
θ_1; 0.0 degree, θ_2; 0.0 degree

Fig. 4. B3LYP/6-31G*-optimized structures of *E*-**1** and *E*-**4**, net charges of the selected atoms based on Mulliken population analysis, and dihedral angle (θ).

cyclization, to produce the intramolecularly cyclized alcohol **2** and its dehydrated ether **3**. The similar photo-irradiation of the 3,4,5-trifluorophenyl-substituted *Z*-hemithioindigo **4** leads to the usual *Z*–*E* isomerization. These results support the conclusion that the *o*-fluorine atoms of the phenyl group of **1** are important for the photoinduced cyclization.

3. Experimental

The FT-IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer and samples were run in a CCl_4 solution or as potassium bromide pellets. The UV–vis spectra were recorded with a JASCO V-530 spectrophotometer and measured in toluene of the highest quality for spectroscopy (KOKUSAN Chemical Co.) without further purification. The ^{1}H NMR and ^{19}F NMR spectra were recorded with a JEOL JNM-LA400 spectrometer (400 MHz for ^{1}H NMR spectra and 376 MHz for ^{19}F NMR spectra). The chemical shifts are given in δ (ppm) downfield from tetramethylsilane as an internal standard for ^{1}H NMR spectra and from trifluoroacetic acid as an external standard for ^{19}F NMR spectra, respectively; *J* values are given in Hz. The MS spectra were taken with a HITACHI M-80B mass spectrometer. The elemental analyses were measured with a Perkin-Elmer 2400 II CHN Analyzer.

7-Ethylbenzo[*b*]thiophen-3(2*H*)-one was prepared by the reactions of 2-ethylbenzenethiol with bromoacetic acid and then with thionyl chloride, as previously reported [6b].

3.1. *Z-2-Pentafluorophenylmethylene-7-ethylbenzo[b]thiophen-3(2H)-one (**1**)*

A solution of 7-ethylbenzo[*b*]thiophen-3(2H)-one (1.85 g, 10.4 mmol) and pentafluorobenzaldehyde (1.53 g, 7.8 mmol) in 35 mL of toluene was stirred at 50 °C for 3 h in the dark under an argon atmosphere. The reaction mixture was washed with 20% aqueous sodium hydrogen sulfite solution to remove the unreacted aldehyde, and then with water and brine. The mixture was dried over magnesium sulfate and evaporated. The resulting solid was chromatographed on silica gel (toluene) to give 1.20 g (43% yield) of **1**. Recrystallization from hexane–acetone was carried out in the dark to give yellow crystals of **1**: mp 131–132 °C; FT-IR (KBr) ν 3019, 2979, 1690, cm^{-1}; UV–vis (toluene) λ_{max} (log ε (L mol^{-1} cm^{-1})) 432 nm (3.69); ^{1}H NMR ($CDCl_3$) δ 1.28 (3H, t, *J* = 7.6 Hz), 2.65 (2H, q, *J* = 7.6 Hz), 7.23 (1H, dd, *J* = 7.6, 7.3 Hz), 7.45 (1H, d, *J* = 7.3 Hz), 7.75 (1H, s), 7.78 (1H, d, *J* = 7.6 Hz); ^{19}F NMR ($CDCl_3$) δ −83.4 (2F, m), −73.4 (1F, t, *J* = 20.4 Hz), −57.8 (2F, m). Anal. Calcd for $C_{17}H_9F_5OS$: C, 57.30; H, 2.55. Found: C, 57.63; H, 2.92.

3.2. *Z-2-(3,4,5-Trifluorophenyl)methylene-7-ethylbenzo[b]thiophen-3(2H)-one (**4**)*

A solution of 7-ethylbenzo[*b*]thiophen-3(2H)-one (280 mg, 1.6 mmol), 3,4,5-trifluorobenzaldehyde (200 mg, 1.25 mmol), and a drop of piperidine in 5 mL of toluene was stirred at 90 °C for 1 h and then refluxed for 1 h under an argon atmosphere. The reaction mixture was washed with 20% aqueous sodium hydrogen sulfite solution to remove the unreacted aldehyde, and then with water and brine. The mixture was dried over magnesium sulfate and evaporated. The resulting solid was chromatographed on silica gel (toluene) to give 270 mg (68% yield) of **4**. Recrystallization from hexane–acetone was carried out to give yellow crystals of **4**: mp 202-203 °C; FT-IR (KBr) ν 3068, 2975, 1680 cm^{-1}; UV–vis (chloroform) λ_{max} (log ε (L mol^{-1} cm^{-1})) 424 (3.88), 434 nm (3.91); ^{1}H NMR ($CDCl_3$) δ 1.33 (3H, t, *J* = 7.6 Hz), 2.73 (2H, q, *J* = 7.6 Hz), 7.26 (1H, t, *J* = 7.6 Hz), 7.36 (2H, dd, *J* = 8.1, 6.8 Hz), 7.47 (1H, d, *J* = 7.6 Hz), 7.75 (1H, s), 7.81 (1H, d, *J* = 7.6 Hz); ^{19}F NMR ($CDCl_3$) δ −56.3 (2F, dd, *J* = 19.9, 8.1 Hz), −79.7 (1F, tt, *J* = 19.9, 6.8 Hz). Anal. Calcd for $C_{17}H_{11}F_3OS$: C, 63.74; H, 3.46. Found: C, 63.68; H, 3.36.

3.3. *Photoinduced cyclization of **1** in highly dilute acetone solution*

A mixture of **1** (10 mg, 0.03 mmol) and 1 mL of water in 50 mL of acetone was irradiated with a xenon lamp using a filter (UV-D35, transmittance: 0.75) at room temperature for 1 h. The reaction mixture was evaporated in the dark. The resulting solid was collected on a glass filter and washed with hexane and then dried to give 4.7 mg (47% yield) of **2**. Recrystallization from hexane–chloroform was carried out in the dark to give white powder of **2**: mp 110–111 °C (dec.);

FT-IR (CCl_4) ν 3437, 2976, 1658, 1391, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (3H, t, $J = 7.3$ Hz), 2.65 (1H, d, $J = 7.6$ Hz), 2.88 (2H, q, $J = 7.3$ Hz), 6.38 (1H, d, $J = 7.6$ Hz), 7.31 (1H, d, $J = 7.3$ Hz), 7.44 (1H, dd, $J = 7.6$, 7.3 Hz), 7.84 (1H, d, $J = 7.6$ Hz); ^{19}F NMR ($CDCl_3$) δ −86.9 (1F, t, $J = 20.4$ Hz), −83.7 (1F, dd, $J = 20.4$, 10.2 Hz), −78.9 (1F, t, $J = 20.4$ Hz), −68.2 (1F, dd, $J = 20.4$, 10.2 Hz); MS *m/z* (relative intensity) 354 (M^+, 2.5), 353 ($M^+{-}H$, 3.4), 337 ($M^+{-}OH$, 100), 322 ($M^+{-}OH{-}CH_3$, 24). Anal. Calcd for $C_{17}H_{10}F_4O_2S$: C, 57.63; H, 2.84. Found: C, 57.46; H, 2.85.

3.4. Photoinduced cyclization of **1** in carbon tetrachloride solution

A mixture of **1** (25 mg, 0.07 mmol) and 0.1 mL of water in 5 mL of carbon tetrachloride was irradiated with a xenon lamp using a filter (UV-D35, transmittance: 0.75) at room temperature for 3 h. The resulting solid was collected on a glass filter and washed with hexane and then dried to give 10.8 mg (44% yields) of **3**. Recrystallization from chloroform was carried out in the dark to give white powder of **3**: mp 201–202 °C (dec.), FT-IR (KBr) ν 2977, 2936, 1660, 1389, 1119 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (6H, t, $J = 7.6$ Hz), 2.80 (4H, q, $J = 7.6$ Hz), 6.58 (1H, s), 7.30 (2H, d, $J = 7.8$ Hz), 7.42 (2H, dd, $J = 7.8$, 7.3 Hz), 7.82 (2H, d, $J = 7.3$ Hz); ^{19}F NMR ($CDCl_3$) δ −85.4 (2F, t, $J = 21.5$ Hz), −82.2 (2F, dd, $J = 21.5$, 10.2 Hz), −77.2 (2F, t, $J = 21.5$ Hz), −64.4 (2F, dd, $J = 21.5$, 10.2 Hz); MS *m/z* (relative intensity) 690 (M^+, 0.75), 353 ($M^+{-}C_{17}H_9F_4OS$, 100), 337 ($M^+{-}C_{17}H_9F_4O_2S$, 21). Anal. Calcd for $C_{34}H_{18}F_8O_3S_2$: C, 59.13; H, 2.63. Found: C, 59.46; H, 2.43.

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