



## Dihydropyrene annelated with dihydrothieno[3.4-*b*]pyrazine: synthesis and photoswitching property

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### ABSTRACT

In this study, 9,10-diacetoxy-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene annelated with a dihydrothieno[3.4-*b*]pyrazine unit (**1a**) was prepared, for the first time, from 5,13-di-*tert*-butyl-8,16-dimethyl-1,2,9,10-tetrahydroxy[2.2]metacyclophane and 3,4-diaminothiophene in two steps. The photoisomerization property of **1** was investigated by UV and <sup>1</sup>H NMR spectroscopies, and the quantitative isomerization between the more stable dihydropyrene (DHP) form and the less stable metacyclophane-diene (MCPD) form was observed. A thermally induced return reaction from the MCPD to the DHP form was examined at various temperatures, and the reaction rate was 0.0049 min<sup>-1</sup> at 45 °C, which is slower than that of the parent MCPD.

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### 1. Introduction

Photoswitching organic molecules have attracted considerable attention for applications to optical data storage devices,<sup>1</sup> molecular logic devices,<sup>2</sup> light energy conversion devices,<sup>3</sup> etc. One example of photoswitching compounds is dihydropyrene (DHP) derivatives,<sup>4</sup> which undergo wavelength-dependent reversible photoisomerization between the more stable DHP form (closed form) and the less stable [2.2]metacyclophane-1,9-diene (MCPD) (open form). DHP derivatives exhibit excellent solubility in organic solvents and undergo small changes in dimensionality when subjected to a photoswitching process.<sup>5</sup> It has been reported that benzene-annelated DHP at the [e]position (benzene-[e]annelated DHP) shows highly improved switching rates.<sup>6</sup> Further, some studies have attempted to apply benzene-[e]annelated DHPs connected with oligothiophenes to the control of conductivity.<sup>7</sup> Oligothiophenes,<sup>8</sup> which are flexible, lightweight, and do not require expensive rare metals for improving their conductivity, are promising organic conductive materials. Then, oligothiophene-[e]annelated DHPs would have high potential to control conductivity by means of photoswitching in organic electronics. While arene-[e]annelated DHPs have been reported as potential photoswitching organic devices, their applicability is limited because their synthesis involves highly complicated techniques with many steps.<sup>4,6</sup>

Previously, we reported a simple and convenient synthetic procedure<sup>9</sup> for 2,7-di-*tert*-butyl-10b,10c-dimethyl DHP and 4,5,9,10-tetraacetoxy-2,7-di-*tert*-butyl-10b,10c-dimethyl DHP from 1,2,9,10-tetrahydroxy[2.2]MCP.<sup>10</sup> In this Letter, we report the synthesis of

diacetoxy-dihydrothieno[3,4-*b*]pyrazo[e]annelated DHP **1** by the new simple synthetic procedure developed from the above-mentioned procedure and describe its photoswitching property (Fig. 1). We expect **1** to be both a novel photoswitching organic molecule and an important precursor for oligothiophene-[e]annelated DHPs.

Scheme 1 shows the synthetic route of **1a** from di-*tert*-butyl-tetrahydroxy-dimethyl[2.2]MCP **2**, which was prepared by the pinacol coupling of 4-*tert*-butyl-2,6-diformyl toluene<sup>10</sup> using aluminum powders and 20% sodium hydroxide aqueous solution.<sup>9,10</sup> The oxidation of **2** to **3** was carried out using acetic anhydride and degassed dimethyl sulfoxide (DMSO) at room temperature. It should be noted that it is necessary to carry out adequate oxygen degassing during oxidation in order to suppress producing by-products. As a result, **3** was obtained quantitatively by bubbling of nitrogen gas for 1 h before oxidation. The condensation reaction of **3** with one equivalent of 2,3-diaminothiophene and subsequent reduction using zinc powders in acetic anhydride gave a pyrazine-[e]annelated product. The chemical structure of **1a** was determined by <sup>1</sup>H NMR spectroscopy.

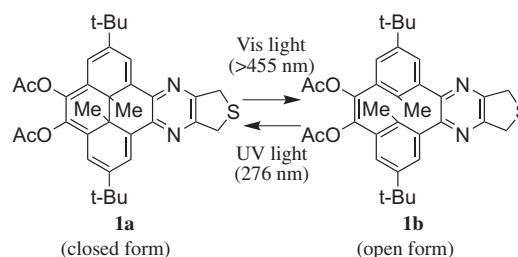
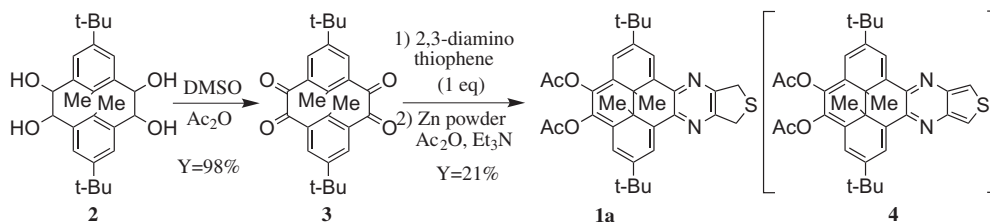


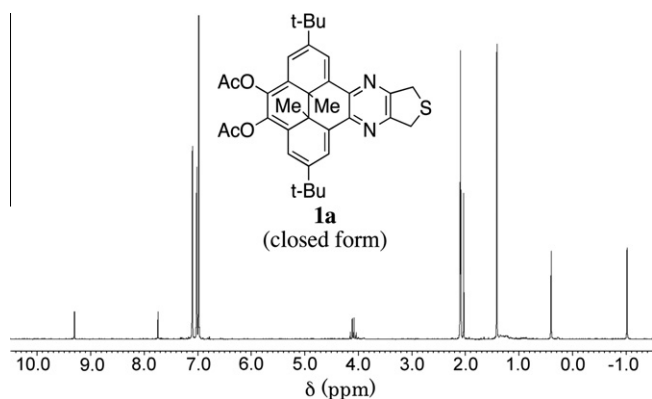
Figure 1. Photoisomerization of **1a** and **1b**.

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Scheme 1.

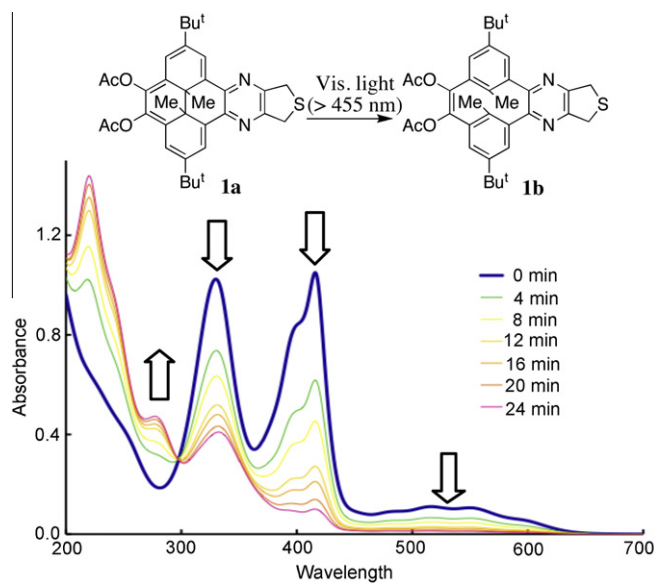
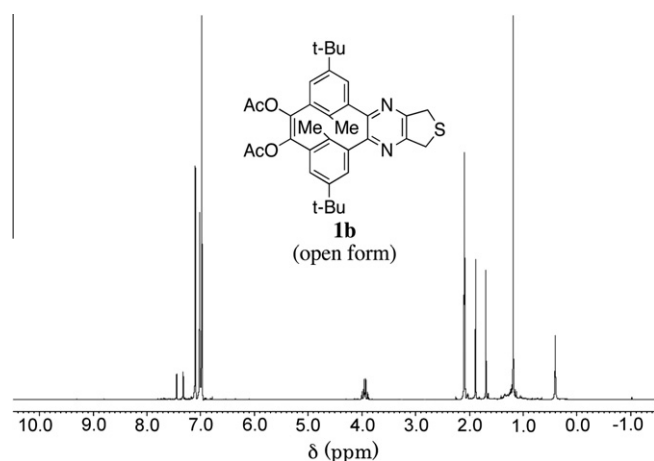
Figure 2.  $^1\text{H}$  NMR spectrum of **1a** in toluene- $d_8$ .

As shown in Figure 2, the signal at 2.04 ppm was assigned to acetoxy protons. The signals at 9.31 and 7.75 ppm were assigned to aromatic protons on the DHP periphery. No other aromatic protons were observed, which indicated that there were no thiophene protons. Generally, the signals appeared at 7.00–7.60 ppm.<sup>11</sup> On the other hand, two doublet signals were detected at 4.56 and 4.49 ppm with a coupling constant of 14.6 Hz, and these signals were assigned to the geminal protons at the 1 and 3 positions of the thieno[3,4-*b*]pyrazine unit, thereby supporting a dihydrothieno[3,4-*b*]pyrazine structure. In addition, the signal at –1.03 ppm was assigned to internal methyl protons. The high magnetic field shift is due to the shielding effect by the ring current of  $\pi$ -electrons on the DHP periphery. Therefore, a closed form is expected to be preferred over an open form. The calculation showed that the closed form is more stable than the open form:  $\Delta H_f$  (open-closed forms) is calculated as 0.029 kcal mol<sup>-1</sup> by the semi-empirical method (AM1) using GAUSSIAN09.<sup>12</sup> These results indicate that the pyridine-*e*]annulated product is **1a**. This unexpected preparation of **1a** instead of **4** suggests that the thiophene moiety is reduced by zinc powders.

The photoisomerization of **1a** was examined by UV–vis and  $^1\text{H}$  NMR spectroscopies. Figure 3 shows the UV–vis spectral change of **1a** through visible light irradiation of >455 nm by using 110 V/500 W halogen light equipped with a long-pass glass filter I (Schott GG455). The absorption peaks at 339, 416, and 550 nm decreased with irradiation, with the appearance of an isosbestic point at 298 nm. Finally, the red-purple cyclohexane solution of **1a** was almost bleached in 24 min of irradiation.

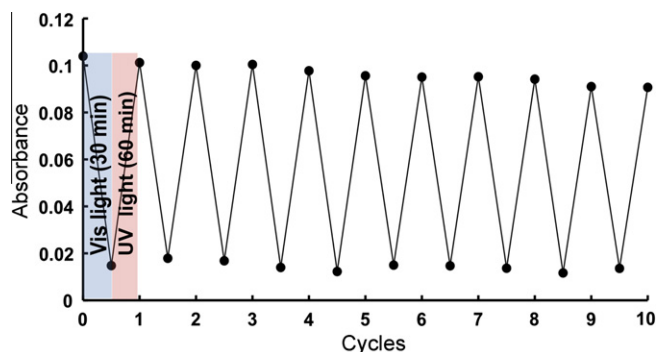
Figure 4 shows the  $^1\text{H}$  NMR spectrum of the resulting compound obtained after visible light irradiation for 1 h. Chemical shift of the internal methyl protons of **1b** was detected at 1.69 ppm, and the peak at –1.03 ppm, which was assigned to the internal methyl protons of **1a**, almost disappeared. This result indicates that photoisomerization from **1a** (closed form) to **1b** (open form) was induced quantitatively by irradiation in different solvents and higher concentration than UV–vis spectroscopy.

Then, a photoinduced return reaction from **1b** to **1a** was carried out by photoirradiation using UV light (276 nm, 150-W xenon

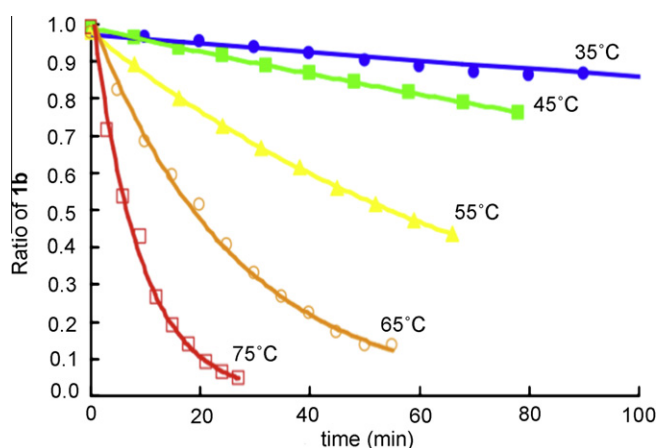
Figure 3. Structure and UV–vis spectra of **1a** under irradiation by >455 nm light in cyclohexane.Figure 4.  $^1\text{H}$  NMR spectra of **1b** isomerized from **1a** after photoirradiation (>455 nm) for 1 h in toluene- $d_8$ .

lamp equipped with a concave grating spectrograph).<sup>13</sup> UV light irradiation for 1 h caused **1b** to transform to **1a** quantitatively.

The repeatability of photoisomerization between **1a** and **1b** was also examined. As shown in Figure 5, the photoisomerization between **1a** and **1b** was repeated at least 10 times. This result indicates that **1a** can be photoswitched more than 100 times in organic solutions; these results obtained from the prediction of the decrease in intensity over 10 cycles.



**Figure 5.** Repeatability of photoisomerization between **1a** and **1b** determined by UV–vis spectroscopy (at 516 nm, in cyclohexane).



**Figure 6.** Thermally induced return reactions of **1b** to **1a** at various temperatures, examined by  $^1\text{H}$  NMR spectroscopy in toluene- $d_8$ .

**Table 1**  
Thermodynamic parameters of thermal return reaction in **1** and **5**

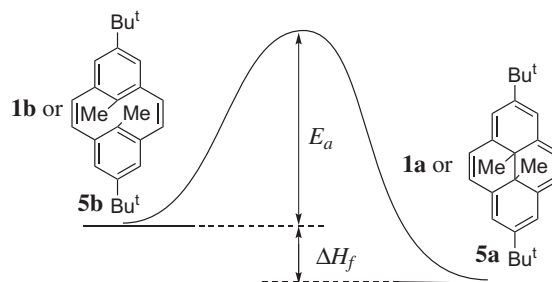
	$E_a$ (kcal mol $^{-1}$ )	$\Delta H$ (kcal mol $^{-1}$ )	$\Delta S$ (cal K $^{-1}$ mol $^{-1}$ )	$\Delta H_f^a$ (kcal mol $^{-1}$ )
<b>1</b>	23.3	22.6	1.58	0.029
<b>5</b>	24.0	23.2	4.30	3.71

<sup>a</sup> GAUSSIAN09, semi-empirical method, AM1.<sup>12</sup>

The thermally induced return reaction of **1b** to **1a** was examined by  $^1\text{H}$  NMR spectroscopy in toluene- $d_8$  at various temperatures (Fig. 6). The thermodynamic parameters of **1b** and 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCPD (**5b**),<sup>4,6,9</sup> which was investigated as a reference, are listed in Table 1. The return reactions of **1b** and **5b** were found to be facilitated at higher temperatures; the reaction rate of **1b** and **5b** were determined to be 0.0049 min $^{-1}$  and 0.0061 min $^{-1}$  at 45 °C, respectively (Fig. 7).

These results suggest that **1b** is more thermally stable than **5b**, their entropy parameters also support this result. Although it is not clear as to whether the thieno[3,4-*b*]pyrazyl unit or acetoxy groups are more effective in stabilizing **1b** than **5b**, the electron-withdrawing property of the acetoxy group and/or electron localization at the [e]position by pyrazyl ring will improve the thermal stability of **1b**. This better thermal stability would be useful in a photoswitching device.

In conclusion, we successfully developed a simple and convenient synthetic method of pyrazine-[e]annulated DHPs and applied



**Figure 7.** Thermally induced return reaction of **1b** and **5b**.

it for the synthesis of diacetoxy-dihydrothieno[3,4-*b*]pyrazine-[e]annulated DHP **1a**. In this study, we could not obtain thiophene-[e]annulated DHP **4**, but the above-mentioned method can be modified to synthesize oligothiophene-[e]annulated DHPs, which are promising as molecular photoswitching devices in organic electronics. We experimentally confirmed the repeatability of photoisomerization between the closed (**1a**) and open (**1b**) forms, which correspond to long and short  $\pi$ -conjugating isomers, respectively. This repeatability and the slow thermally induced return reaction of **1b** indicate that **1** (**1a** and **1b**) can be a promising photoswitching material. Further investigations are being conducted to acquire knowledge about the functionalization of **1** and its application as a photoswitching material.

## 2. Experimental

### 2.1. Preparation of *tert*-butyl-dimethyl-hydrothieno[3,4-*b*]pyrazo[e]annulated DHP **1a**

Commercially available 3,4-diaminothiophene (29 mg, 0.25 mmol) was added to a suspension of [2.2]MCP tetraone **3** (100 mg, 0.25 mmol) in ethanol (20 ml), and the mixture was stirred for 3 h and the solvent was evaporated in vacuo.  $\text{Ac}_2\text{O}$  (0.5 ml, 5.0 mmol) and  $\text{Et}_3\text{N}$  (1.0 ml, 7.5 mmol) were added to a suspension of the reaction mixture and Zn powder (322 mg, 5.0 mmol) in dry  $\text{CH}_2\text{Cl}_2$  and stirred for 5 h under nitrogen atmosphere at rt and then filtered through Celite. The filtrate was washed with 10 wt % aq HCl (50 ml  $\times$  2) and saturated aq.  $\text{NaHCO}_3$  (50 ml  $\times$  2). The organic layer was dried over  $\text{MgSO}_4$ , evaporated in vacuo, and purified by TLC (eluent: hexane/ethyl acetate, 5/1) to afford **1a** (30 mg, 21%) as a red powder. **1a**: red powder: mp 198.6–199.1 °C; FT-IR (KBr) 2980, 2927, 2869, 1774, 1362, 1204  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (25 °C, toluene- $d_8$ )  $\delta$  9.31 (br s, 2H), 7.75 (br s, 2H), 4.14 (d,  $J = 14.6$  Hz, 2H), 4.07 (d,  $J = 14.6$  Hz, 2H), 2.04 (s, 6H), 1.41 (s, 18H),  $-1.03$  (s, 6H);  $^{13}\text{C}$  NMR (25 °C,  $\text{CDCl}_3$ )  $\delta$  169.1, 152.7, 147.1, 137.5, 134.9, 133.6, 125.8, 121.3, 114.0, 35.9, 35.2, 34.9, 30.5, 20.4, 17.5; HRMS (FAB) calcd for  $\text{C}_{34}\text{H}_{38}\text{N}_2\text{O}_4\text{S}$ : 570.2552, found: 570.2552 ( $\text{M}^+$ ).

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### Supplementary data

Supplementary data (experimental details about preparation,  $^1\text{H}$  NMR spectra, photoisomerization, and thermally induced return reaction) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.05.092.

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13. See [Supplementary data](#).