Novel Photochromic Behavior of Benzoylhemithioindigo Based on Photodimerization

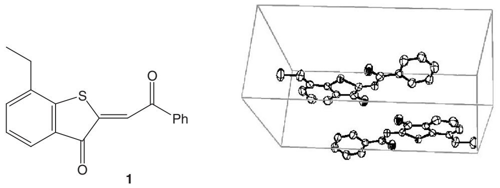
Kiyoshi Tanaka,* Kazuto Taguchi, Satoru Iwata, and Takayuki Irie
Laboratory of Molecular Control, Faculty of Engineering, Seikei University, Musahino-shi, Tokyo 180-8633

(Received April 20, 2004; CL-040443)

Benzoyl-substituted hemithioindigo **1** has a novel type of photochromic behavior based on the formation of the photoinduced [2+4] cycloadduct; that is, irradiation of **1** produces the cycloadduct **2** with all *trans*-configurations between the adjacent carbonyl moieties; this is completely dissociated back to **1** on heating.

Photochromic molecules provide a tool, with which one can manipulate the ability to recognize a binding site.[1] Typical photochromic molecules, such as azobenzenes,[2] stilbenes,[3] diarylethenes,[4] spiropyrans,[5] and thioindigos,[6] play an important role as molecular switches based on such recognition performance. Although it is reported that aryl-substituted hemithioindigos have the photochromic properties based on the *E-Z* isomerization and also that the *E-Z* repeatability is good under the basic conditions, they have been relatively little studied and their applications are limited to the shape-control of lipid membranes.[7] Benzoyl-substituted hemithioindigos are expected to be available as molecular switches because they have two carbonyl moieties, which are good acceptors for the hydrogen bonding in molecular recognition performance. Here we wish to demonstrate a novel photochromic behavior caused by the photodimerization, instead of the usual *E-Z* isomerization, of 2-benzoylmethylene-7-ethylbenzo[*b*]thiophen-3(2*H*)-one (**1**).

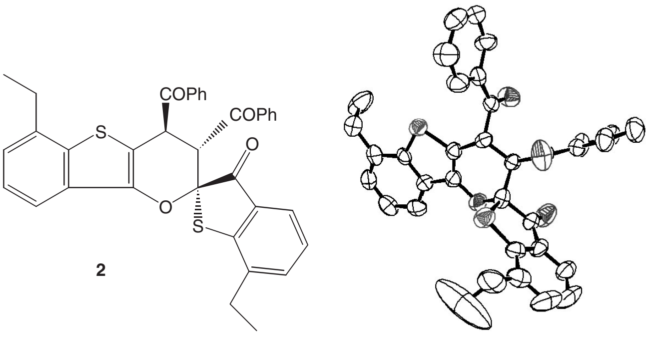
Benzoylhemithioindigo **1** was synthesized in 46% yield by the reaction of 7-ethylbenzo[*b*]thiophen-3(2*H*)-one with phenylglyoxal in toluene.[8] From the reaction mixture, only *Z* isomer was isolated and the formation of the other isomer was not detected. The *Z*-configuration of the product was determined by the deshielded olefinic proton (δ8.11) in ^{1}H NMR spectra and by X-ray analysis. The ORTEP view also shows that the π-stacking is with the reverse direction and its separation distance is 3.59 Å (Figure 1).[8]



1

Figure 1. ORTEP view of **1**.

A toluene solution of **1** is yellow and absorbs at λ_{max} of 463 nm in UV–vis spectra. When irradiated with 463 nm light, **1** keeps emitting brilliant red fluorescence (λ_{em} 599 nm) in the solid state. However, irradiation of its toluene solution brought about photobleaching. The resulting product was easily isolated; its ^{1}H NMR analysis supports the head to head dimerization and the *trans*-configuration of two benzoyl groups. Further analysis by X-ray crystallography shows that the product is not the [2+2] cycloadduct but the [2+4] type of the cycloadduct **2**, which is a diastereoisomer with all *trans*-configurations between the adjacent carbonyl moieties (Figure 2).[8]



2

Figure 2. ORTEP view of **2**.

If we consider molecular orbital interactions, we find that concerted [2+2] cycloadditions are permitted in photocycloadditions of olefins. But in an exceptional case such as enones, photocycloadditions are reported to proceed via biradical intermediates.[9] Therefore, in this case, the formation of the [2+4] cycloadduct **2** is speculated to be via the biradical species that is directly formed at the primary step or via the cleavage of the once-formed [2+2] cycloadduct. One reason why the *Z-E* isomerization is not observed in the case of **1** is ascribed to the relative instability of the *E* isomer or to the relative stability of the *Z* isomer. The calculated difference in total energy between the *E* and *Z* isomers is rather large ($\Delta E = 14.11\ \mathrm{kcal\,mol^{-1}}$, based on the calculation at B3LYP/6-31G* level) for **1**, which is in sharp contrast to $\Delta E = 3.93\ \mathrm{kcal\,mol^{-1}}$ for the analogous 4-methoxyphenylmethylenehemithioindigo that performs the usual *E-Z* isomerization.[10] The *trans*-configuration between the adjacent carbonyl moieties of **2** is thought to arise from the electrostatic and steric repulsions between the carbonyl groups.

A toluene solution of **2** does not absorb visible light and so is stable to the visible light. **2** is also thermally stable and remains unchanged for more than 2 days at room temperature. However, heating at 70 °C accelerates the dissociation to **1**; the time-dependent change of the dissociation could be traced by the ^{1}H NMR analysis. The results follow a first-order reaction; the rate constant was estimated to be $k = 0.22\ \mathrm{h^{-1}}$ (70 °C) on the basis of the *k*-plot. Heating at 100 °C for 10 min completely recovered **1**. Reversible interconversion between the photodimerization of **1** and the thermal dissociation of **2** was monitored several times using a $C_6D_5CD_3$ solution of 1×10^{-2} M. The results are summarized in Figure 3; they show good repeatability between **1** and **2**.

Thus, irradiation of the benzoyl-substituted hemithioindigo **1** produced the [2+4] type of cycloadduct **2**, instead of the [2+2] cycloadduct and the *E-Z* isomerized product. Cycload-

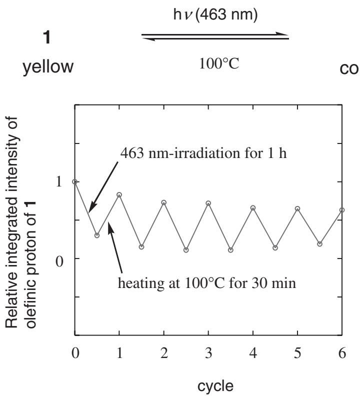


Figure 3. Repeatability between **1** and **2**. [**1**] = **1** × **10^{-2}** M in $C_6D_5CD_3$.

duct **2** is stable at room temperature but is completely dissociated to **1** on heating. This reversible photochromic property based on the photodimerization of benzoylhemithioindigo **1** can be applied to molecular switches. The role of **1** as a photoswitch in the porphyrin-quinone recognition will be reported elsewhere.[11]

We thank Dr. T. Tsukuda and Professor T. Tsubomura for the measurements of X-ray crystallography and for their helpful discussions.

References and Notes

1 I. Willner and S. Rubin, *Angew. Chem., Int. Ed. Engl.*, **35**, 367 (1996).

2 F. Vogtle, "Supramolecular Chemistry," Wiley, Chichester (1991), Chap. 7.

3 a) H. Sugimoto, K. Kuramoto, and S. Inoue, *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1826. b) M. V. Alfimov, S. P. Gromov, Yu. V. Fedorov, O. A. Fedorova, A. I. Vedernikov, A. V. Churakov, L. G. Kuz'mina, J. A. K. Howard, S. Bossmann, A. Braun, M. Woerner, D. F. Sears, Jr., and J. Saltiel, *J. Am. Chem. Soc.*, **121**, 4992 (1999). c) I. K. Lednev, R. E. Hester, and J. N. Moore, *J. Am. Chem. Soc.*, **119**, 3456 (1997).

4 a) M. Takeshita, K. Uchida, and M. Irie, *Chem. Commun.*, **1996**, 1807. b) J.-P. Malval, I. Gosse, J.-P. Morand, and R. Lapouyade, *J. Am. Chem. Soc.*, **124**, 904 (2002).

5 a) M. Tanaka, M. Nakamura, M. A. A. Salhin, T. Ikeda, K. Kamada, H. Ando, Y. Shibutani, and K. Kimura, *J. Org. Chem.*, **66**, 1534 (2001). b) M. Inouye, Y. Noguchi, and K. Isagawa, *Angew. Chem., Int. Ed. Engl.*, **33**, 1163 (1994).

6 a) M. Irie and M. Kato, *J. Am. Chem. Soc.*, **107**, 1024 (1985). b) S. M. F. Rahman and K. Fukunishi, *J. Chem. Soc., Chem. Commun.*, **1994**, 917.

7 a) P. Friedlaender, *Monatsh.*, **30**, 347 (1909). b) M. A. Mostoslavskii and V. A. Izmail'skii, *J. Gen. Chem. USSR*, **35**, 519 (1965). c) L. S. S. Reamonn and W. I. O'Sullivan, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1009. d) T. Seki, T. Tamaki, T. Yamaguchi, and K. Ichimura, *Bull. Chem. Soc. Jpn.*, **65**, 657 (1992). e) K. Eggers, T. M. Fyles, and P. J. M.-Pelaez, *J. Org. Chem.*, **66**, 2966 (2001).

8 Selected data for **1**, mp 125–126 °C, FT/IR (CCl_4): 1686 cm^{-1} (C=O), UV–vis (toluene): λ_{max} ($\log \varepsilon$/dm^3 mol^{-1} cm^{-1}) 463 nm (3.84), ^{1}H NMR (CCl_4:CD_3CN = 5:1, 400 MHz): δ1.36 (t, $J = 7.6$ Hz, 3H), 2.78 (q, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 2H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 1H), 8.11 (s, 1H), 8.12 (d, $J = 7.6$ Hz, 2H), Anal. Calcd. for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79%. Found : C, 73.67; H, 4.76%. A solution of **1** in hexane–acetone was irradiated with a Xenon lamp using a filter (UV39) for 2 h. The solution was allowed to stand in the dark to give crystals of **2** in 80% yield. The crystals melt in a range of 117–126.5 °C to give red oil because of the dissociation; **2**, pale yellow crystals, FT/IR (CCl_4): 1678 cm^{-1} (C=O), ^{1}H NMR (CCl_4:CD_3CN = 5:1, 400 MHz): δ1.27 (t, $J = 7.6$ Hz, 6H), 2.60 (q, $J = 7.6$ Hz, 2H), 2.70 (q, $J = 7.6$ Hz, 2H), 5.29 (d, $J = 10.5$ Hz, 1H), 5.82 (d, $J = 10.5$ Hz, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 7.06 (dd, $J = 7.6$ and 1.7 Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.39 (dd, $J = 7.6$ and 1.7 Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.60 (d, $J = 7.3$ Hz, 2H), 7.63 (t, $J = 7.3$ Hz, 2H), 7.75 (t, $J = 7.3$ Hz, 1H), 8.17 (d, $J = 7.3$ Hz, 2H), Anal. Calcd for $C_{36}H_{28}O_4S_2$: C, 73.44; H, 4.79. Found: C, 73.09; H, 4.45%. *Crystal data for* **1**: $C_{18}H_{14}O_2S$, $M = 294.37$, monoclinic, space group $P2_1/a$, $a = 7.288(2)$, $b = 15.455(3)$, $c = 13.091(2)$ Å, $\beta = 103.54(2)°$, $V = 1433.6(5)$ Å^3, $T = 296$ K, $Z = 4$, $D_c = 1.364$ g cm^{-3}, $\lambda = 0.71069$ Å, 3684 reflections measured, 3294 unique ($R_{int} = 0.067$). $R_1 = 0.070$, and $R_w = 0.160$; Compound **2**: $C_{72}H_{56}O_8S_4$, $M = 1177.47$, triclinic, space group P−1, $a = 16.186(3)$, $b = 23.200(5)$, $c = 8.1493(8)$ Å, $\alpha = 90.08(2)°$, $\beta = 100.668(10)°$, $\gamma = 81.64(2)°$, $V = 2974.4(9)$ Å^3, $T = 296$ K, $Z = 2$, $D_c = 1.315$ g cm^{-3}, $\lambda = 0.71069$ Å, 14151 reflections measured, 13665 unique ($R_{int} = 0.071$). $R_1 = 0.091$, and $R_w = 0.266$.

9 A. C. Weedon, in "Synthetic Organic Photochemistry," ed. by W. M. Horspool, Plenum Press, New York (1984), Chap. 2.

10 SPARTAN '02 Windows (Wavefunction, Inc. 18401 Von Karman Ave., Suite 370, Irvine, CA 92612 U.S.A.).

11 a) K. Tanaka, Y. Yamamoto, I. Machida, and S. Iwata, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 285. b) K. Tanaka, Y. Yamamoto, H. Obara, and S. Iwata, *Supramol. Chem.*, **14**, 347 (2002).