

Photochromism of Hemithioindigo Derivatives. I. Preparation and Photochromic Properties in Organic Solvents

Takeo YAMAGUCHI,[†] Takahiro SEKI,* Takashi TAMAKI, and Kunihiro ICHIMURA*,^{††}

Research Institute for Polymers and Textiles, 1-1-4 Higashi, Tsukuba, Ibaraki 305

Toyo Ink Mfg., Tsukuba Research Laboratory, 27 Wadai, Tsukuba, Ibaraki 300-42

^{††} Research Laboratory of Resources Utilization, Tokyo Institute of Technology,

4259 Nagatsuta, Midori-ku, Yokohama 227

(Received August 26, 1991)

Thirteen hemithioindigo (HT) derivatives bearing alkyl chains are newly synthesized and their photochromism and emission properties are investigated. The *Z/E* photoisomerisms of these compounds in organic solvents are essentially in agreement with data reported by Mostoslavskii and Izmail'skii (*J. Gen. Chem. USSR, Engl. Transl.*), 31, 21 (1961), and subsequent papers). At 77 K both the *E* and *Z* isomers of HT chromophore emit fluorescence of comparable intensities, whereas at room temperature very weak fluorescence is observed only from the *Z* isomer. Examination of repeatable numbers of *Z/E* photoisomerization reveals that the HT chromophore possesses remarkable inherent photofatigue resistance.

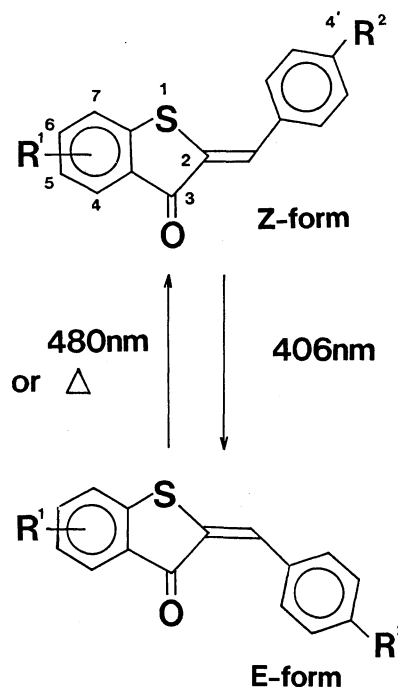
Photochromic materials have attracted much attention in recent years due to their potential applicability to high density photon-mode recording media, fabrication of new types of displaying devices, transducers of light information etc.¹⁾ Among them photochromic reactions that involve rotation about a double bond have been occupied a central position of research on photochromism.²⁾ Typical and well-investigated photochromic chromophores in this category mostly have symmetrical structures, for example, indigos, thioindigos, azobenzenes, and stilbenes.

Since 1961 Mostoslavskii and Izmail'skii have extensively studied the photochromic properties of a family of unsymmetrical chromophores, i.e., hemithioindigos (HT).³⁻⁶⁾ The fundamental skeleton of this chromophore is 2-(arylmethylene)benzo[*b*]thiophen-3(2*H*)-one; the half part of thioindigo is connected with that of stilbene. In 1977 Reamonn and O'Sullivan⁷⁾ conducted an NMR study for structural justification of the two photoisomers of HT, and confirmed that the *Z*-form (vide infra) is thermally stable. Through these studies fundamental knowledge on this chromophore itself has been accumulated. However, no attempt has been made so far to observe the photochromism of HT in solid and semisolid matrices such as polymer films and molecular assemblies, which is of critical importance toward the practical applications stated above.¹⁾ On a strategy to observe environmental effects within such matrices, it is essential, at the initial step, to prepare HT derivatives having alkyl chain(s) to improve compatibility to the matrices.

In this context, this paper reports synthetic procedures for introduction of alkyl chain(s) into the skeleton of HT, and photochromic behaviors and emission properties of these compounds in organic solvents. In spite of accumulated absorption spectral data,³⁻⁶⁾ other important characteristics such as photofatigues and emission properties are not given in earlier works. Environmental effects on the photochromic behaviors of

HT derivatives are examined in bilayer membranes, and results in this regard will be presented elsewhere.⁸⁾

The general structure of HT compounds prepared in this work and the photochromism are indicated in Scheme 1. Upon irradiation of 406 nm light, the thermally stable *Z* form (λ_{max} =ca. 440 nm) is converted to the *E* form (λ_{max} =ca. 470 nm). The *E* isomer is reverted to the *Z* upon 480 nm light irradiation or thermally (Δ).⁹⁾



Scheme 1.

Results and Discussion

Preparation of HT Derivatives. Synthesis routes for HT compounds employed in this work are shown in Scheme 2, and synthesized HT derivatives are summarized in Table 1.

Alkyl substitution at both 5-, and 4'-positions provides

a) Measured in chloroform because of very low solubility in benzene. b) A transition from crystal to liquid crystal phase followed by a transition to isotropic phase at ca. 180 °C.

rod like molecules, which is expected to favor effective incorporation into anisotropic media. Introduction of hexyl group at 5-position of HT moiety **1**—**9** was achieved starting either from hexylbenzene or 4-hexylaniline (Scheme 2a). Preparation of 4-hexylbenzenethiol from hexylbenzene involved the sulfonation of hexylbenzene using sulfuric acid followed by reduction of the sulfonyl chloride with zinc powder.¹⁰⁾ 4-Hexylbenzenethiol was then reacted with bromoacetic acid to form thioether (**14**). One batch synthesis for **14** is to start from 4-hexylaniline.¹¹⁾ Diazonium salt from 4-hexylaniline was reacted with 2-mercaptoacetic acid under alkaline conditions to give **14**. Acid chloride derivative of **14** was cyclized to give 5-hexylbenzo[*b*]thiophene-3(2*H*)-one (**15**) by way of Friedel–Crafts acylation. Condensation of **15** with 4-hydroxybenzaldehyde in benzene in the presence of base yielded the photochromic HT moiety (**1**). The key compound **1** was derived to a variety of HT derivatives (**2**—**8**). Compound **1** was also reacted with 4-(dimethylamino)-benzaldehyde to obtain **9** which absorbed lights at longer wavelengths (vide infra). A trimethylammonio group was introduced to two of them (**6** and **8**) to add hydrophilicity.

For the other series of HT compounds, in which alkoxy-carbonyl group is introduced at 7 position, 2,2'-dithiodibenzoic acid is the starting material (Scheme 2b). 2,3-Dihydro-3-oxobenzo[*b*]thiophene-7-carbonyl chloride (**16**) was obtained in the method described by Badger et al.¹²⁾ and Irie et al.¹³⁾ Successive condensation of **16** with 4-substituted aldehydes at 2 position and esterification at 7 position were simultaneously achieved

in alcoholic solvents to obtain HT products of **10**—**13**.

Photochromic Behaviors of HT Derivatives. Figure 1 shows typical absorption spectrum changes of HT in organic solvents before and after 406 nm light illumination. Solvent effects on the photochromism were examined using **4** and the spectroscopic data were listed in Table 2. For other 5-hexyl HT derivatives, variation of introduced group at 4' did not affect the spectral properties, except for dimethylamino-substitution (**9**). For **9** $\lambda_{\max}$ of Z-form in benzene was 483 nm, which is shifted to longer wavelength by ca. 40 nm than that of alkoxy-substituted compounds. Among various organic media, hydrocarbon solvents such as hexane and methylcyclohexane are specific in giving a clear peak at longer wavelength in the E forms at the photostationary state (Fig. 1a). In other solvents, on the other hand, spectral changes are characterized by increase of absorbance or appearance of a shoulder at longer wavelengths (Fig. 1b). These observations are consistent with data of Mostoslavskii and Izmail'skii.³⁾ The band peaks ($\lambda_{\max}$) of Z- and E-forms in hexane were 438 and 466 nm, respectively, which closely agree with a reported analogous compound, 4'-methoxy HT ($\lambda_{\max}(Z)$ =435 nm and $\lambda_{\max}(E)$ =460 nm).³⁾ Appreciable correlation between $\lambda_{\max}(Z)$ and solvent polarity was not obtained. Also alkoxy-carbonyl substitution at 7 position made no effect on the absorption spectrum and photochromic behaviors: $\lambda_{\max}(Z)$ =435 nm and $\lambda_{\max}(E)$ =465 nm for **10**—**13** in hexane.

Figure 2 shows the absorption spectra of the two pure Z and E isomers of **4** separated by means of HPLC. Under the conditions described in Experimental Section,

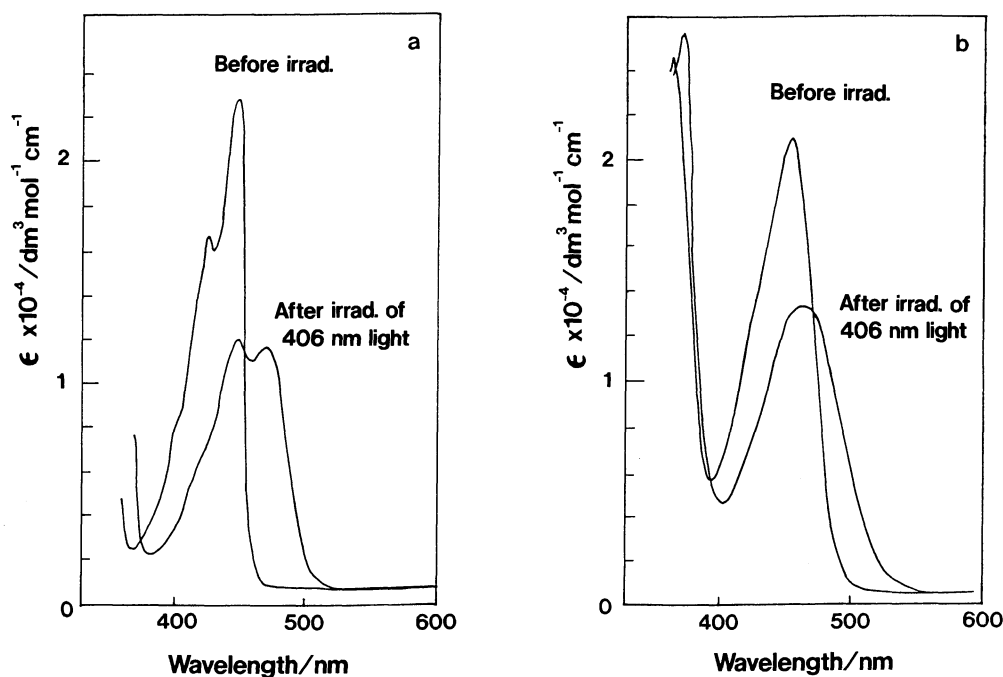


Fig. 1. Typical spectral changes of a HT compound **4** upon 406 nm illumination in hexane (part a) and ethanol (part b) at room temperature.

the *E* isomer, first eluted and successively the *Z* isomer. Thus, conversion to the *E* form at the photostationary state upon illumination of 406 nm light (C_E) in benzene could be determined by HPLC experiments. Due to very slow *E* to *Z* thermal reaction C_E values could be obtained in good accuracy by the chromatographic separation. For other solvents C_E was determined as follows. Solutions of **4**, the concentration being 1×10^{-3} mol dm $^{-3}$, was at first prepared, irradiated with 406 nm light until the photostationary state was reached, diluted with benzene to 20 folds by volume, and then injected to the HPLC system. C_E 's obtained this way are also listed in Table 2. C_E was mostly constant to give ca. 80% with an exception of hexane (=95%).

Quantum yield of *Z* to *E* and *E* to *Z* photoisomerization in benzene was estimated to be 0.012 and 0.019 for **4**, and 0.026 and 0.030 for **13**. These values are by several folds lower than those of symmetrical indigo dyes.^{14,15)}

The first-order rate constants (k/s^{-1}) are listed also in

Table 2. As indicated the *E* to *Z* thermal isomerization in organic solvents was very slow. Rate constants k at 25 °C ranged 3×10^{-9} – $1 \times 10^{-7} s^{-1}$, approximately 10^3 times smaller than those for symmetrical acylindigo¹⁴⁾ and thioindigo¹⁵⁾ dyes.

Emission Properties. To our knowledge no data on emission properties of HT have been reported so far. HT chromophore showed only very weak emission at room temperature in organic solvents, which is in marked contrast to thioindigoes and acylindigoes.¹⁵⁾ At 77 K fluorescence intensity was enhanced by ca. 3000 folds. Figure 3 presents uncorrected fluorescence spectra of **4** in methylcyclohexane at room temperature and 77 K. At room temperature only the *Z* isomer was fluorescent as has been observed for the *trans* isomer of indigo dyes.¹⁵⁾ The fluorescence spectrum bore two peaks at 463 and 494 nm. Interestingly the fluorescence at 77 K was observed with comparable intensity for the both *Z* and *E* isomers. At 77 K the emission peaks were at 510–

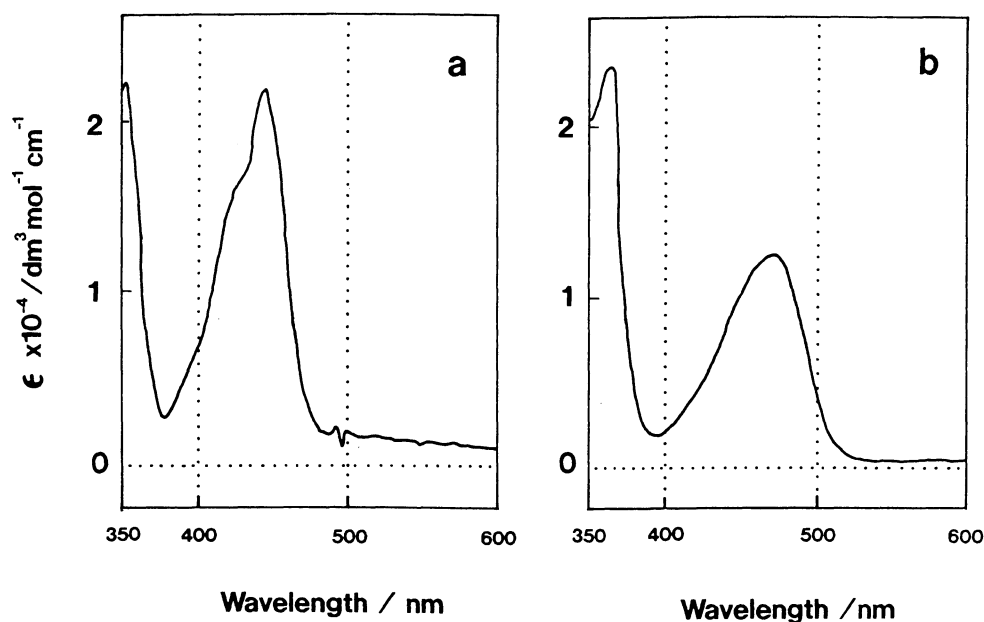


Fig. 2. Absorption spectra of pure *Z* (part a) and *E* (part b) isomers of **4** separated on HPLC in benzene at room temperatures.

Table 2. Photochromic Properties of **4** in Various Organic Solvents

Solvent	$\lambda_{\max}/\text{nm} (/10^4)$		$C_E^a)$ %	$k^b)$ at 25 °C s^{-1}
	<i>Z</i> -	<i>E</i> -		
Hexane	438 (2.3)	466 ^{d)}	95	3×10^{-8}
Benzene ^{c)}	445 (2.2)	474 (1.3)	80	3×10^{-9}
1,4-Dioxane	442 (2.4)	468 ^{e)}	83	2×10^{-8}
Ethyl acetate	440 (2.4)	469 ^{e)}	83	
Acetonitrile	440 (2.3)	465 ^{e)}	80	4×10^{-8}
Ethanol	441 (2.1)	478 ^{e)}	79	1×10^{-7}

a) Conversion to the *E* isomer at the photostationary state under 406 nm light illumination. See text for determination. b) First order rate constant. c) Spectroscopic data were obtained after HPLC separation. d) Determined at the photostationary state under 406 nm light illumination. e) Estimated by subtracting the contribution of the *Z* isomer from the spectrum of the photostationary state.

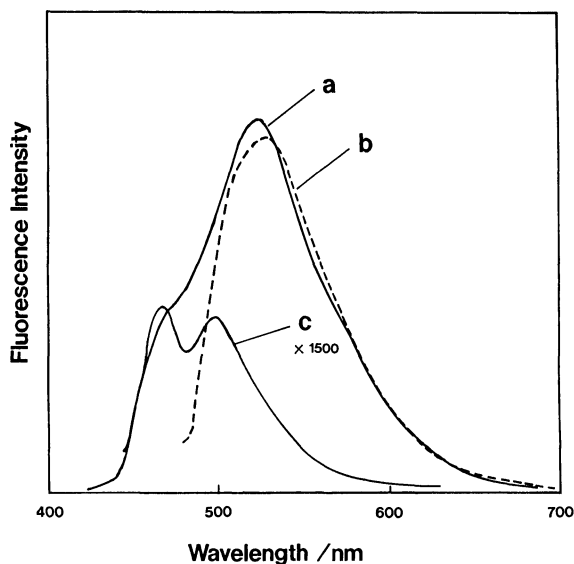


Fig. 3. Fluorescence spectra of **4** in methylcyclohexane: curves a and b indicate spectra of the *Z* and *E* (80% conversion) isomers, respectively, measured at 77 K on 438 nm excitation; curve c is the spectrum measured at room temperature on 450 nm excitation. Slit width was 5 nm for both excitation and emission monochrometers.

520 nm for both isomers, but the spectrum of the *E* isomer was somewhat sharpened compared to that of the *Z*-form. Phosphorescence was not detectable both at room temperature and 77 K.

Repeatability of Photoisomerization.¹⁶⁾ Stability in terms of durability against photofatigue is one of the most required properties in photochromic compounds from the standpoint of technological applications.¹⁾ Absorption recoveries of the *Z* form after repeated photoisomerization upon alternate exposure of 406 and 480 nm light are shown in Fig. 4. As seen in the figure, sufficient absorption intensity recovered even after the alternate light exposure was repeated in the order of 10^4 times. Presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) in the solution apparently improved the photofatigue resistance both for **4** and **13**. In particular, **13** in the presence of DABCO practically retained the initial level even after 4×10^4 cycle numbers.

According to Kawauchi et al.¹⁷⁾ the repeatable numbers to 50% recovery of well-known photochromic compounds, spirobenzopyran, flugide, azobenzene, and spironaphthoxazine were ca. 3×10^2 , 5×10^2 , 1×10^3 , and 5×10^3 (for spironaphthoxazine estimation by extrapolating from their data), respectively. Lo¹⁹⁾ have found that the photochromic cycle due to tautomerism of an *N*-salicylideneaniline crystal is repeatable up to 5×10^4 times with no obvious fatigue. Recently Irie¹⁸⁾ reported that diarylethene type compounds, whose photochromism involves the ring closure/open reaction, possess good fatigue resistance comparable to the HT chromophore. Repeatable number depends on the experimental

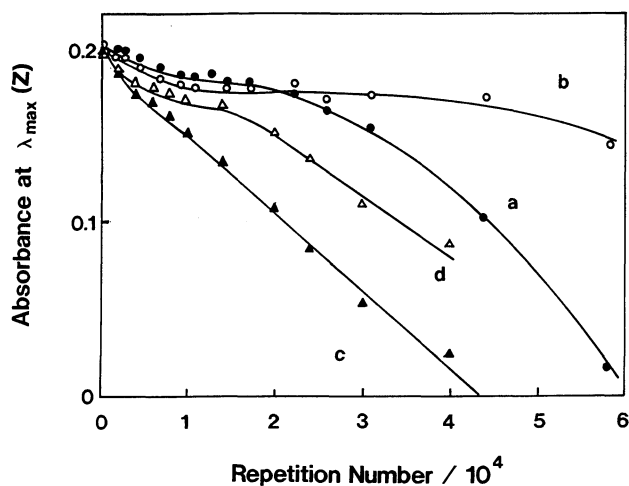


Fig. 4. Photofatigue resistance of **13** (curves a and b) and **4** (curves c and d) on alternate exposure of 406 and 480 nm lights under air conditions. Curves b and d are data in the presence of 5-fold molar excess of DABCO.

conditions and therefore, direct comparisons of the numbers obtained by different research groups may often be misleading. However, it is stressed that, as solution systems in which photochromic molecules are readily susceptible to oxidation and other side reactions, the HT derivatives and diarylethene compounds of Irie's group¹⁸⁾ possess exceptional inherent photostability as organic photochromic materials. The improving effect of DABCO may be due to the quenching of $^1\text{O}_2$ generated photochemically in a manner described in the case of thioindigos.²⁰⁾ The related stability increase in the presence of DABCO was also observed for spirobenzopyrans.²¹⁾

Experimental

Preparation of HT Compounds. Starting materials for syntheses were obtained from Tokyo Kasei Kogyo Co. ^1H NMR spectra were obtained on a Nicolet NMC 1280 (360 MHz) spectrometer. FD-mass spectra were taken with a Hitachi M-2000 mass spectrometer.

Hexylbenzene was converted to hexylbenzenethiol according to Nerbert et al.¹⁰⁾ or Truce et al.¹¹⁾

Potassium 4-Hexylbenzenesulfonate. Hexylbenzene (10 g, 61.6 mmol) in concentrated sulfuric acid (18 ml) was heated to 70°C for 1 h. The solution turned orange in color. The reaction mixture was poured into cold water (80 ml), and the organic substances were first taken up with chloroform, and then extracted with water to remove hexylbenzene. To the water layer was added aqueous potassium hydroxide until pH 10. The water was in part evaporated and cooled to obtained precipitates. This potassium salt was recrystallized from water (13.3 g, 77%); mp 300°C .

4-Hexylbenzenesulfonyl Chloride. The mixture of potassium 4-hexylbenzenesulfonate (18 g, 64.2 mmol) and phosphoryl chloride (14 g, 91.3 mmol) was stirred at 170°C for 1 h. 1,2-Dichloroethane was then added to the cooled mixture

(60 °C) and refluxed for 30 min. After being poured into water, the sulfonyl chloride was extracted with chloroform, washed with aqueous NaCl solution, and dried (16.0 g, 61.4 mmol, 96%); $\delta_{\text{H}}(\text{CDCl}_3)=0.89$ (3H, t, CH_3), 1.32 (6H, m, $\text{MeCH}_2\text{CH}_2\text{CH}_2$), 1.61–1.70 (2H, m, CH_2), 2.73 (2H, t, CH_2Ar), 7.41 (2H, d, ArH), 7.94 (2H, d, ArH).

4-Hexylbenzenethiol. To a stirred mixture of 4-hexylbenzenesulfonyl chloride (5.3 g, 20.3 mmol) in water (50 ml) and concentrated sulfuric acid (6 ml) was slowly added zinc powder (7 g), and the mixture was heated at 100 °C for 2 h and cooled. After the insoluble materials being filtered off, the mixture was poured into cold water and extracted with ether. The ether layer was washed with aqueous NaCl solution, and the solvent was evaporated to give oil of 4-hexylbenzenethiol (3.5 g, 88%); $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH_3), 1.29 (6H, m, $\text{MeCH}_2\text{CH}_2\text{CH}_2$), 1.80 (1H, s, SH), 2.54 (2H, t, CH_2 , Ar), 7.05 (2H, d, ArH), 7.20 (2H, d, ArH).

(4-Hexylphenylthio)acetic Acid (14). A mixture of 4-hexylbenzenethiol (1.1 g, 5.6 mmol) in acetone (30 ml), potassium carbonate (2.0 g, 14.5 mmol), and bromoacetic acid (0.9 g, 6.5 mmol) was refluxed for 2 h. The solvent was removed, and to the residue was added diluted aqueous hydrochloric acid to pH 2. The precipitate of **14** was recrystallized from ethanol–water (1.2 g, 4.8 mmol, 84%); mp 67–68 °C.

5-Hexylbenzo[*b*]thiophen-3(2*H*)-one (15). A mixture of **14** (3.9 g, 15.5 mmol), thionyl chloride (20 ml), and two drops of *N,N*-dimethylformamide was stirred for 1 h at room temperature. Thionyl chloride was removed under vacuum, and to the residue was added freshly distilled 1,2-dichloroethane over calcium hydride (100 ml). After cooling down to 5 °C, crashed anhydrous aluminum chloride (3 g, 22.5 mmol) was added slowly to the mixture. The mixture was stirred at room temperature for 1 h, and poured into crashed ice-water. After addition of dichloromethane (100 ml) to the aqueous mixture, insoluble substances were filtered off and washed with dichloromethane. The organic layer was washed with aqueous NaCl solution, dried over MgSO_4 , and the solvent was evaporated to obtain crude product of **15** (4.0 g). Indoxyl skeleton could be simply confirmed by blue emission on a silica gel TLC plate, which changed to red emission on heating under air atmosphere due to thioindigo formation. $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH_3), 1.28 (6H, m, $\text{MeCH}_2\text{CH}_2\text{CH}_2$), 1.60 (2H, m, CH_2), 2.62 (2H, t, CH_2Ar), 3.80 (2H, s, COCH_2S), 7.32–7.40 (2H, m, ArH), 7.59 (1H, s, ArH).

2-(4-Hydroxyphenylmethylene)-5-hexylbenzo[*b*]thiophen-3(2*H*)-one (1). Crude **15** (4.0 g, 17.1 mmol), 1.8 g 4-hydroxybenzaldehyde (1.8 g, 14.7 mmol), and two drops of piperidine were dissolved in benzene (50 ml) under nitrogen and refluxed for 1 h. Unreacted aldehyde was first removed off with aqueous sodium hydrogensulfite solution, insoluble by-product of thioindigo was filtered off, and finally the residue was purified on a silica-gel column using benzene as eluent. The crude product of **1** was recrystallized from toluene (4.4 g, 13.0 mmol, 88% from starting aldehyde); mp 134–136 °C; $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH_3), 1.31 (6H, m, $\text{MeCH}_2\text{CH}_2\text{CH}_2$), 1.63 (2H, m, CH_2), 2.66 (2H, t, CH_2Ar), 6.95 (2H, d, ArH), 7.41 (2H, s, ArH), 7.64 (2H, d, ArH), 7.76 (1H, s, ArH), 7.92 (1H, s, $\text{C}=\text{CHAr}$). FD-MS: $m/z=338$. Found: C, 74.3; H, 6.5%. Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{S}$: C, 74.52; H, 6.55%.

2-[4-(4-Bromobutoxy)phenylmethylene]-5-hexylbenzo[*b*]thiophen-3(2*H*)-one (5). A mixture of **1** (0.5 g, 1.48 mmol),

potassium carbonate (0.24 g, 1.74 mmol), and 1,4-dibromobutane (0.95 g, 1.48 mmol) in acetone (15 ml) was stirred at 70 °C for overnight. The solvent was removed, and the residue was washed with ether and water. The crude product of **5** was recrystallized from ethyl acetate (0.26 g, 0.55 mmol, 37%); mp 103–107 °C. $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH_3), 1.31 (6H, m, $\text{MeCH}_2\text{CH}_2\text{CH}_2$), 1.59–1.67 (2H, m, CH_2), 1.95–2.05 (2H, m, CH_2), 2.05–2.13 (2H, m, CH_2), 2.66 (2H, t, CH_2Ar), 3.50 (2H, t, CH_2Br), 4.07 (2H, t, OCH_2), 6.98 (2H, d, ArH), 7.41 (2H, s, ArH), 7.67 (2H, d, ArH), 7.76 (1H, s, ArH), 7.93 (1H, s, $\text{C}=\text{CHAr}$). After UV-visible spectroscopic measurements, the total amount of this product was converted to **6**.

5-Hexyl-2-[4-[4-(trimethylammonio)butoxy]phenylmethylene]benzo[*b*]thiophen-3(2*H*)-one Bromide (6). Compound **5** (0.25 g, 0.53 mmol) was dissolved in tetrahydrofuran (25 ml). To the solution was added large excess of trimethylamine gas, and stirred at room temperature for 1 day. The precipitated ammonium salt (**6**) was collected and dried to obtain yellow powder (0.24 g, 0.45 mmol, 85%); mp 178–180 °C. $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH_3), 1.33 (6H, m, $\text{MeCH}_2\text{CH}_2\text{CH}_2$), 1.64 (2H, m, CH_2), 1.99–2.03 (4H, m, CH_2CH_2), 2.66 (2H, t, CH_2Ar), 3.44 (9H, s, $(\text{CH}_3)_3$), 3.78–3.82 (4H, m, CH_2N^+), 4.12 (2H, t, OCH_2), 7.00 (2H, d, ArH), 7.41 (2H, s, ArH), 7.67 (2H, d, ArH), 7.76 (2H, s, ArH), 7.91 (1H, s, $\text{C}=\text{CHAr}$). FD-MS: m/z 452. Found: C, 63.4; H, 7.1; N, 3.0%. Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_2\text{N}_1\text{S}_1\text{Br}_1$: C, 63.14; H, 7.19; N, 2.62%.

2-[4-(10-Bromodecyloxy)phenylmethylene]-5-hexylbenzo[*b*]thiophen-3(2*H*)-one (7) was prepared in similar ways to the synthesis of **5** and recrystallized from ethyl acetate in 25% yield; mp 130–133 °C. After UV-visible spectroscopic measurements, the total amount of this product converted to **8**.

5-Hexyl-2-[4-(10-(trimethylammonio)decyloxy)phenylmethylene]benzo[*b*]thiophen-3(2*H*)-one Bromide (8) was prepared in similar ways to the synthesis of **6** in 68% yield; mp 135–137 °C. FD-MS: m/z 536. Found: C, 66.6; H, 8.0; N, 2.7%. Calcd for $\text{C}_{34}\text{H}_{50}\text{O}_2\text{N}_1\text{S}_1\text{Br}_1$: C, 66.21; H, 8.17; N, 2.27%.

5-Hexyl-2-[4-(hexyloxy)phenylmethylene]benzo[*b*]thiophen-3(2*H*)-one (4). Reaction of **1** (0.5 g, 1.48 mmol) with 1-bromohexane (0.26 g, 1.58 mmol) in a similar method described for the synthesis of **5** yielded **4** (0.35 g, 0.83 mmol, 56%); mp 90–95 °C. $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH_3), 0.92 (3H, t, CH_3), 1.31 (6H, m, $\text{MeCH}_2\text{CH}_2\text{CH}_2$), 1.35 (4H, m, MeCH_2CH_2), 1.44–1.50 (2H, m, CH_2), 1.59–1.66 (2H, m, CH_2), 1.77–1.85 (2H, m, CH_2), 2.66 (2H, t, CH_2Ar), 4.03 (2H, t, OCH_2), 6.99 (2H, d, ArH), 7.29 (2H, s, ArH), 7.67 (2H, d, ArH), 7.76 (1H, s, ArH), 7.93 (1H, s, $\text{C}=\text{CHAr}$). FD-MS: m/z 422. Found: C, 77.2; H, 8.0%. Calcd for $\text{C}_{27}\text{H}_{34}\text{O}_2\text{S}_1$: C, 76.73; H, 8.11%.

2-[4-(Ethoxycarbonylmethoxy)phenylmethylene]-5-hexylbenzo[*b*]thiophen-3(2*H*)-one (2). A mixture of **1** (1.25 g, 3.0 mmol), ethyl bromoacetate (1.65 g, 9.8 mmol), and anhydrous potassium carbonate (1.1 g, 8.0 mmol) was stirred at 70 °C for overnight. After acetone was evaporated off, benzene and water were added. The organic layer was washed with aqueous NaCl solution, dried over anhydrous MgSO_4 . After the solvent was partially removed, the products were chromatographically purified on a silica gel column using benzene as eluent (2.1 g, 5.0 mmol, 67%); mp 104–106 °C. $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH_3), 1.32 (9H, m, $\text{MeCH}_2\text{CH}_2\text{CH}_2+\text{ethoxy-CH}_3$), 1.60–1.66 (2H, m, CH_2), 2.66

(2H, t, CH₂Ar), 4.29 (2H, q, COOCH₂Me), 4.69 (2H, s, OCH₂COO), 7.01 (2H, d, ArH), 7.41 (2H, s, ArH), 7.68 (2H, d, ArH), 7.76 (1H, s, ArH), 7.92 (1H, s, C=CHAr). FD-MS: *m/z* 424. Found: C, 70.7; H, 6.6%. Calcd for C₂₅H₂₈O₄S₁: C, 70.73; H, 6.65%.

2-[4-(Carboxymethoxy)phenylmethylene]-5-hexylbenzo[b]thiophen-3(2H)-one (3). To a solution of **2** (2.0 g, 4.7 mmol) in 1,4-dioxane (20 ml) was added 6 M hydrochloric acid (10 ml) and stirred at 70 °C for 3 h (1M=1 mol dm⁻³). The solvent was removed and the residue was recrystallized from *o*-dichlorobenzene (1.4 g, 3.5 mmol, 75%); mp 221–223 °C. $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH₃), 1.31 (6H, m, MeCH₂CH₂CH₂), 1.59–1.67 (2H, m, CH₂), 2.66 (2H, t, CH₂Ar), 4.76 (2H, s, OCH₂COO), 7.04 (2H, d, ArH), 7.41 (2H, s, ArH), 7.71 (2H, d, ArH), 7.76 (1H, s, ArH), 7.92 (1H, s, C=CHAr). FD-MS: *m/z* 396. Found: C, 69.6; H, 6.1%. Calcd for C₂₃H₂₇O₄N₁S₁: C, 69.67; H, 6.10%.

2-[4-(Dimethylamino)phenylmethylene]-5-hexylbenzo[b]thiophen-3(2H)-one (9) was synthesized as described for **4** from **1** and 4-(dimethylamino)benzaldehyde and purified on a silica gel column using benzene–hexane as eluent in 32% yield; mp 88–91 °C. $\delta_{\text{H}}(\text{CDCl}_3)=0.88$ (3H, t, CH₃), 1.33 (6H, m, MeCH₂CH₂CH₂), 1.62 (2H, m, CH₂), 2.65 (2H, t, CH₂Ar), 3.08 (6H, s, N(CH₃)₂), 6.78 (2H, d, ArH), 7.36–7.43 (2H, m, ArH), 7.64 (2H, d, ArH), 7.76 (1H, s, ArH), 7.94 (1H, s, C=CHAr). FD-MS: *m/z* 365. Found: C, 74.5; H, 7.5; N, 3.8%. Calcd for C₂₃H₂₇O₁N₁S₁: C, 75.57; H, 7.44; N, 3.83%.

2-(Carboxymethylthio)benzoic Acid was synthesized from 2,2'-dithiosalicylic acid (76.5 g, 250 mmol) according to Badger et al.¹²⁾ Crude product was recrystallized from 2-ethoxyethyl acetate to give needles (57.2 g, 270 mmol, 54%); mp 216–217 °C (lit.¹²⁾ 214 °C).

2,3-Dihydro-3-oxobenzo[b]thiophene-7-carbonyl Chloride (16) was synthesized according to Badger et al.¹²⁾ with slight modification. This compound was isolated as carbonyl chloride instead of corresponding carboxylic acid. A mixture of 2-(carboxymethylthio)benzoic acid (10 g, 47 mmol) and thionyl chloride (30 ml) was stirred at room temperature for 1 h in the presence of one drop of *N,N*-dimethylformamide. After thionyl chloride was roughly evaporated off, small amount of dry 1,2-dichloroethane was added under nitrogen and evaporated under reduced pressure. The carbonyl chloride was dissolved in dry 1,2-dichloroethane (100 ml), to which anhydrous aluminum chloride (9 g, 67 mmol) was added gradually at 5 °C. After stirring at room temperature for 1 h, the solution was slowly poured onto crashed ice, and the organic layer was quickly separated off with additional 1,2-dichloroethane. The 1,2-dichloroethane layer was washed with aqueous NaCl solution, dried over anhydrous MgSO₄, and the solvent was evaporated to obtain crude **16** (10.9 g).

7-Ethoxycarbonyl-2-[4-(hexyloxy)phenylmethylene]benzo[b]thiophen-3(2H)-one (13). Crude **16** (2.5 g, 11.8 mmol), ethanol (2.7 g) and 4-(hexyloxy)benzaldehyde (2.7 g, 14.2 mmol), and several drops of piperidine was dissolved in benzene (20 ml) and the solution was stirred at room temperature for 1 h followed by refluxing for 1 h. After unreacted aldehyde was removed off with aqueous sodium hydrosulfite solution, the product of **13** was purified first chromatographically on a silica-gel column using benzene as eluent, and then recrystallized from ethanol–water (1.1 g, 2.4 mmol, 20%); mp 110–111 °C. $\delta_{\text{H}}(\text{CDCl}_3)=0.92$ (3H, t, CH₃), 1.33–1.37 (4H, m, MeCH₂CH₂), 1.46–1.49 (2H, m,

CH₂), 1.77–1.85 (2H, m, CH₂), 4.04 (2H, t, OCH₂), 4.50 (2H, q, OCH₂), 6.99 (2H, d, ArH), 7.39 (1H, t, ArH), 7.77 (2H, d, ArH), 7.96 (1H, s, C=CHAr), 8.13 (1H, d, ArH), 8.29 (1H, d, ArH). FD-MS: *m/z* 410. Found: C, 70.2; H, 6.2%. Calcd for C₂₄H₂₆O₄S₁: C, 70.21; H, 6.38%.

7-Hexyloxy carbonyl-2-(4-methoxyphenylmethylene)benzo[b]thiophen-3(2H)-one (10), 7-Hexyloxy carbonyl-2-(4-ethoxyphenylmethylene)benzo[b]thiophen-3(2H)-one (11), and 7-Hexyloxy carbonyl-2-(4-hexyloxyphenylmethylene)benzo[b]thiophen-3(2H)-one (12) were synthesized likewise to above procedure for **13** using hexanol and 1.1 molar excess of corresponding 4-alkoxybenzaldehyde. Mp are listed in Table 1. For **10**, FD-MS: *m/z* 396. Found: C, 69.9; H, 5.9%. Calcd for C₂₃H₂₄O₄S₁: C, 69.67; H, 6.10%. For **11**, FD-MS: *m/z* 410. Found: C, 70.4; H, 6.3%. Calcd for C₂₄H₂₆O₄S₁: C, 70.22; H, 6.38%. For **12**, FD-MS: *m/z* 467. Found: C, 72.0; H, 7.2%. Calcd for C₂₇H₃₄O₄S₁: C, 72.07; H, 7.34%.

Materials. All solvents for spectroscopic measurements were of spectroscopic grade and used as purchased.

1,4-Diazabicyclo[2.2.2]octane (DABCO, from Tokyo Kasei Co.) was recrystallized from hexane–benzene.

Methods. In general sample preparations and spectroscopic measurements were achieved under dimmed red light. In organic solutions the concentrations of HT compounds were ca. 1×10⁻⁵ mol dm⁻³.

Absorption spectra in the dark were measured on a Shimadzu UV-220 spectrophotometer equipped with a electrically controlling thermostated cell holder (Shimadzu SPR-5). For observations of spectral changes under crossed light illumination, a Hewlett–Packard HP8452A diode array UV-vis spectrophotometer was used with a cell holder thermostated by water circulation. The accuracy of the temperature in both photometers was within ±0.5 °C.

High-performance liquid chromatography (HPLC) experiments were carried out using a Twinkle liquid chromatography pump (Japan Spectroscopy Co.), a LiChrosorb Si-60 Column (Merck), and a diode-array photometric detector (Otsuka Elec. Co., MCPD-350). The pumping speed was 1 ml min⁻¹. Benzene (guaranteed grade) as eluent was the product of Wako Pure Chem. and used as purchased.

Photoirradiation was performed using a 500 W high pressure mercury lamp (Ushio 5010) and appropriate glass filters. A Corning 5-58 glass filter was used for 406 nm irradiation, and either a Kenko interference filter BP-48 or a Hoya glass Y-46 filter was used to select 480 nm light. Samples were placed at ca. 30 cm distance from the filters.

Quantum yield of *Z*⇌*E* isomerization was evaluated using a calibrated thermopile (Eppley Lab. Inc.)/microvoltmeter (Ishikawa AM-2002) system. With this instrument 1 V×1.39×10⁻² corresponded to 1 mW cm⁻². Amounts of photoisomerized HT molecules at the initial stage upon photoirradiation was determined photometrically using optical density at $\lambda_{\text{max}}(\text{Z})$. The transmittances of the solution were below 10% and ca. 50% at $\lambda_{\text{max}}(\text{Z})$ for *Z* to *E* and *E* to *Z* photoisomerization, respectively.

Kinetic measurements of *Z* to *E* thermal isomerization were carried out by monitoring absorbances at λ_{max} of *Z* form in the dark immediately after the photostationary state due to 406 light exposure was reached.

Emission spectra (uncorrected) were taken on a Hitachi MPF-4 fluorescence spectrophotometer at ambient

temperature (ca. 20 °C) and 77 K.

Photofatigue of HT compounds was evaluated with an alternating irradiator constructed with a 500-W high-pressure mercury lamp.²⁰⁾ Lights for photoisomerization was selected by the combination of the glass filters described above. This repeating procedure was automatically done with a filter exchanger, and the number of repetition was simultaneously recorded. Time intervals for light exposure was selected to be 10 and 30 s for 406 and 480 nm light, respectively. These intervals were sufficient for achieving the each photostationary state. This experiment was carried out using benzene as solvent under air atmosphere.

References

- 1) a) S. Tazuke, *Jpn. J. Appl. Phys., (Suppl. 4)*, **26**, 3 (1987).
b) K. Ichimura, "Photochromic Materials and Photoresists," in "Photochromism—Molecules and Systems," ed by H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam (1990), Chap. 26, pp. 903–918. c) A. E. J. Wilson, *Phys. Technol.*, **15**, 232 (1984). d) H. Dürr, *Angew. Chem., Int. Ed. Engl.*, **28**, 413 (1989).
 - 2) a) D. L. Ross and J. Blanc, "Photochromism by *cis-trans* Isomerization," in "Photochromism," ed by G. H. Brown, Wiley, New York (1971), Chap. 5, pp. 471–556. b) J. Saltiel and Y. -P. Sun, "*cis-trans* Isomerization of C=C Double Bonds," in "Photochromism—Materials and Systems," Chap. 3, pp. 64–164. c) H. Rau, "Azo Compounds," in "Photochromism—Materials and Systems," Chap. 4, pp. 165–192.
 - 3) M. A. Mostoslavskii and V. A. Izmail'skii, *J. Gen. Chem. USSR*, **31**, 21 (1961).
 - 4) M. A. Mostoslavskii, V. A. Izmail'skii, and Shapkina, *J. Gen. Chem. USSR*, **32**, 1731 (1962).
 - 5) M. A. Mostoslavskii and V. A. Izmail'skii, *J. Gen. Chem. USSR*, **33**, 727 (1963).
 - 6) M. A. Mostoslavskii and V. A. Izmail'skii, *J. Gen. Chem. USSR*, **35**, 519 (1965).
 - 7) L. S. S. Reamonn and W. I. O'Sullivan, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1009. Note that the term 'hemithioindigo' appeared in the review of Ross and Blanc.²⁾ These authors used the term 'thioaurone' for the identical chromophore.
 - 8) T. Seki, T. Yamaguchi, T. Tamaki, and K. Ichimura, the following paper of this issue.
 - 9) In Ref. 7, this reaction has been termed as *trans/cis* isomerization. *trans* and *cis* refer to the relative positions of the carbonyl and the side-chain aryl groups.
 - 10) M. E. Neubert, S. J. Laskos, Jr., R. F. Griffith, M. E. Stahl, and L. J. Maurer, *Mol. Cryst. Liq. Cryst.*, **54**, 221 (1979).
 - 11) W. E. Truce, D. P. Tate, and D. N. Burge, *J. Am. Chem. Soc.*, **82**, 2872 (1960).
 - 12) G. M. Badger, D. J. Clark, W. Davis, K. T. H. Farrer, and N. P. J. Kefford, *J. Chem. Soc.*, **1957**, 2624.
 - 13) M. Irie and M. Kato, *J. Am. Chem. Soc.*, **107**, 1024 (1985).
 - 14) G. R. Seely and E. R. Shaw, *J. Photochem.*, **24**, 383 (1984).
 - 15) J. Blanc and D. L. Ross, *J. Phys. Chem.*, **72**, 2817 (1968).
 - 16) The marked repeatability of the photochromic reaction of the HT chromophore described in this section has already been reported as a letter: K. Ichimura, T. Seki, T. Tamaki, and T. Yamaguchi, *Chem. Lett.*, **1990**, 1645.
 - 17) S. Kawauchi, H. Yoshida, N. Yamashina, M. Ohira, S. Saeda, and M. Irie, *Bull. Chem. Soc. Jpn.*, **63**, 267 (1990).
 - 18) M. Irie, *Jpn. J. Appl. Phys., (Suppl. 3)*, **28**, 215 (1989).
 - 19) D. S. Lo, *Appl. Opt.*, **13**, 861 (1974).
 - 20) N. Kuramoto and T. Kitao, *J. Soc. Dyers Colour.*, **95**, 257 (1979).
 - 21) M. Sakuragi, K. Aoki, T. Tamaki, and K. Ichimura, *Bull. Chem. Soc. Jpn.*, **63**, 74 (1990).
-