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THE OXIDATION OF BENZO[*b*]THIOPHENE DERIVATIVES WITH DDQ--------PREPARATION OF π-EXTENDED HEMITHIOINDIGOID COMPOUNDS

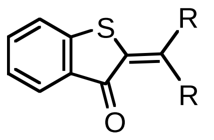
Hiroyuki Endo, Kinji Nagashima, Hidetsugu Wakabayashi,
Makoto Kanazumi, Tatsuhisa Kato, and Keiji Kobayashi*

Department of Chemistry, Graduate School of Material Science, Josai University, Sakado, Saitama 350-0295, Japan

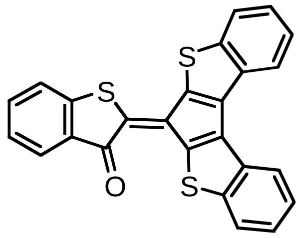
Abstract – Hemithioindigoid compounds, e. g., 2-(6*H*-cyclopenta[1,2-*b*:4,3-*b*']-bis[1]benzothiophen-6-ylidene)benzo[*b*]thiophene-3(2*H*)-one (**1**), were synthesized in good yields by the oxidation of benzo[*b*]thiophene derivatives such as 9-(2-benzo[*b*]thienyl)fluorene with DDQ in the presence of acid and under atmospheric oxygen. Under nitrogen, on the other hand, the reaction of **3** with DDQ resulted in an oxidative dimerization, the product of which was revealed to be equilibrated with radical species.

INTRODUCTION

In a previous paper, we showed that a novel hemithioindigoid compound (**1**) undergoes a color change in the solid state from red to black owing to mechanical shearing, and that the color is recovered by either heat or solvent treatment.[1] This novel piezochromic behavior has been interpreted in terms of excitonic interactions between transition dipoles on the basis of reorganized molecular arrangement caused by mechanical shearing. Besides this piezochromic property illustrated by our finding, hemithioindigoid compounds show interesting properties as thioindigo-like dyes[2] and photochromic compounds.[3]



hemithioindigos



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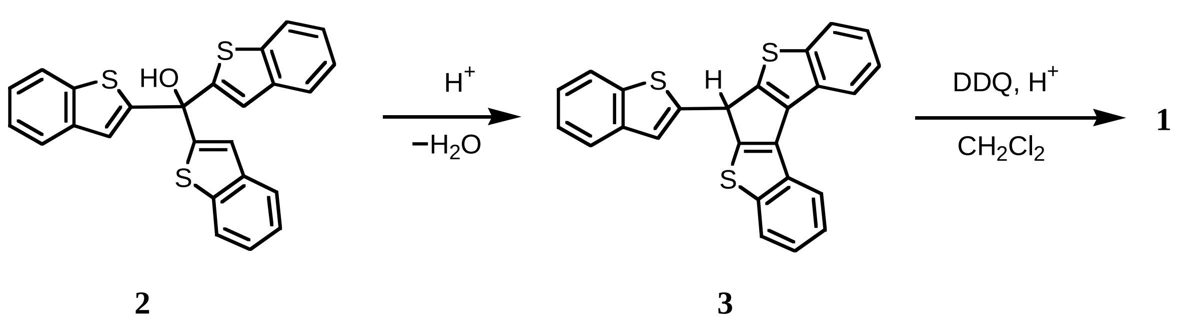
Despite such potential uses of hemithioindigoid compounds for new chromic materials, their synthetic methods are considerably limited.[4] The reaction employed for the preparation of **1** introduces a new synthetic methodology for π-extended hemithioindigo derivatives. We did not describe the details of the preparation of **1** in our previous report.[1,5] Here, we demonstrate an extension of our approach for the preparation of π-extended hemithioindigoid compounds.

RESULTS AND DISCUSSION

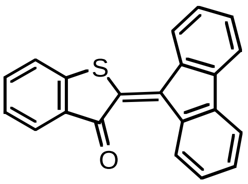
We first found the formation of **1** in a trace amount serendipitously when a triarylmethyl type of *tert*-alcohol **2** was irradiated in acetonitrile.[6,7] We envisioned that a carbocation would be produced photochemically and the electron transfer to this carbocation from photoexcited **2** would lead to the formation of the cation radical of **2**.[8] Therefore, with the intention of promoting this oxidation reaction thermally, we carried out the reaction of **2** with DDQ, which is considered to exert activity as an electron acceptor to produce a cation radical. As was presumed, compound **1** was obtained although the yield was as low as 12 %. It is noteworthy that two benzo[*b*]thiophene rings of **2** undergo the condensation to a five-membered ring during this reaction. Thus, our second presumption was that cyclopentadiene derivative **3** is involved as an intermediate, which would be readily formed by the dehydration of **2** via a Nazarov cyclization-like mechanism.[9] In fact, **3** was readily obtained in 89 % yield by treatment of **2** with hydrochloric acid. Then, we carried out the reaction of the ring-closed compound **3** with DDQ and realized the formation of **1**.



Scheme 1

In a typical experiment where the maximum yield of **1** was achieved, **3** was refluxed with an equiv. molar amount of DDQ in the presence of a drop of hydrochloric acid in dichloromethane for 5 h. The products mixture was chromatographed on a silica gel to give **1** in 89 % yield. The effect of hydrochloric acid on the oxidation reaction of **3** is significant; without hydrochloric acid the yield was 12 % at most. Under similar reaction conditions the hemithioindigoid compounds illustrated as **4**, **5**, and **6**, were prepared from the corresponding precursor benzo[*b*]thiophene compound.

The structure of the hemithioindigoid products was confirmed on the basis of the spectral properties. For **1** X-ray crystal analysis was performed.[10] A characteristic feature of the ^{1}H-NMR spectra of **4** and **6** is the downfield shift (below 9 ppm) of the aromatic proton, which is situated closely facing the carbonyl group, being attributed to the magnetic anisotropic effect of the carbonyl group. Compound **6** was obtained as a mixture of *Z*- and *E*-isomers and those could not be separated.[11] However, the isomeric ratio of 3:4 for *Z* and *E* could be deduced from the ^{1}H-NMR spectrum by considering that the aromatic proton proximate to the carbonyl group is a doublet for the *Z*-isomer, whereas it is a singlet for the *E*-isomer, both occurring characteristically in a low field. Contrary to our expectations, among the π-extended hemithioindigoid compounds prepared here, no new piezochromic compounds were found, except for **1**.



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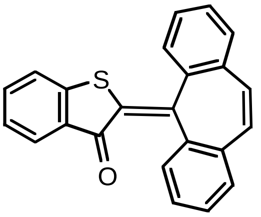

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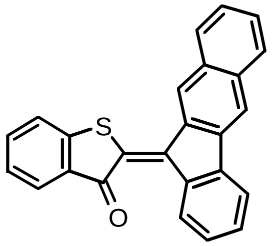
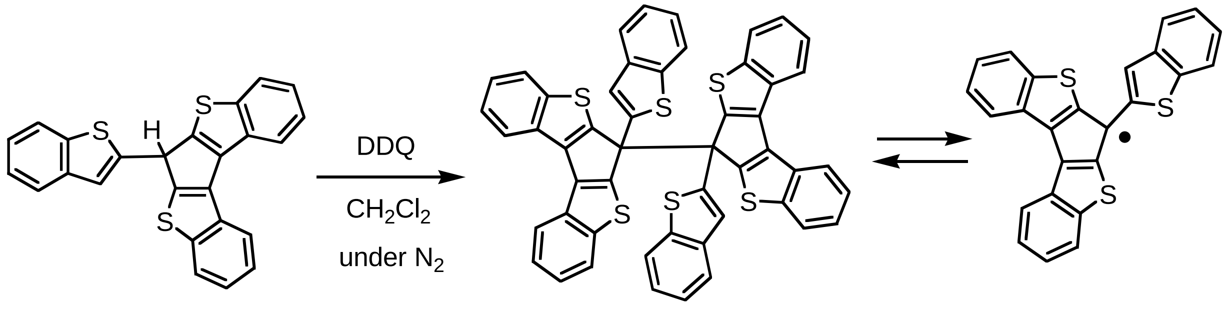


6 (*Z*)

It should be noted that the reaction was also induced upon the solid-state cogrinding of **3** and DDQ in a mortar with a pestle to afford **1** in 80 % yield.[1]

We do not know the reaction mechanism at this stage, including the role of acid. However, we are certain that oxygen in the air participates in this oxidation reaction. When the reaction was carried out under nitrogen atmosphere, no hemithioindigoid compound was obtained. Thus, a dichloromethane solution of **3** was refluxed with DDQ under nitrogen for 4 h to give a dark red mixture. TLC of this product mixture showed several spots, but there was clearly one dominant product, which was isolated by silica-gel chromatography to give a red oil. This compound gave a molecular ion peak at *m*/*z* 816+1 in FAB-MAS along with an abundant fragment ion peak at *m*/*z* 408+1 (Figure 1), indicating that the product is caused by oxidative dimerization of **3**, that is, compound **7**.



3 **7**

Scheme 2

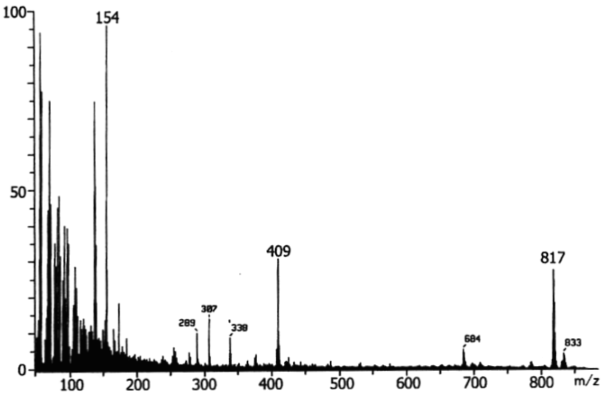


Figure 1. FAB-MAS of **7**, measured by using 3-nitrobenzyl alcohol as a matrix material.

On the other hand, we observed a peculiar ^{1}H-NMR spectrum for **7**; all the signals at ambient temperature were remarkably broad and became broader at higher temperatures. These observations are readily interpreted in terms of the intervention of radical species, which should enhance spin-lattice relaxation to bring about a broadening of NMR signals. We assume that compound **7** is equilibrated with the triarylmethyl-type radical formed by the dissociation of the central C-C bond. This is in analogy with the triphenylmethyl radical,[12] which had been well known as Gomberg's radical and was later corrected in its structure. Thus, we could not establish an accurate structure of **7** in solution because of the broad NMR spectrum; it remains ambiguous at this stage whether the radical reverts to structure **7** or undergoes reconnection at the aromatic ring.

The involvement of the radical species was supported by the occurrence of an ESR signal for a toluene solution of **7** and an increase in its intensities with an increase in temperature (Figure 2). The doublet signal (a= 0.61 mT) implies that an unpaired electron is coupled with the proton on the thiophene ring of the benzo[*b*]thiophene moiety.

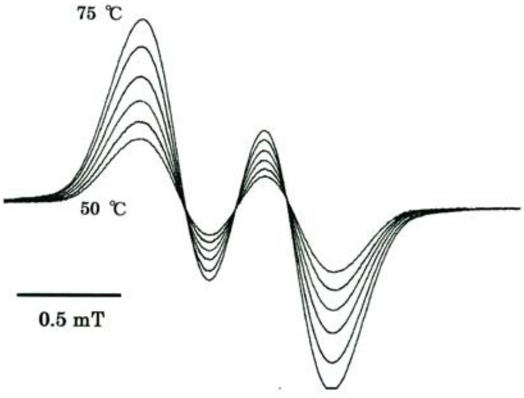


Figure 2. Temperature dependence of the ESR spectra of a solution of **7** in toluene (for each 5 degrees rise from 50 ℃ to 75 ℃)

In summary, we have demonstrated two different types of reaction induced in benzo[*b*]thiophene derivatives by treatment with DDQ. When the reaction was carried out in the presence of acid and oxygen, π-conjugated hemithioindigoid compounds were obtained, which are expected to have potential applications for chromic materials. On the other hand, when carried out the reaction under nitrogen atmosphere, oxidative dimerization took place. The dimer is equilibrated with the radical species. Further investigations to clarify the reaction mechanism and characterize the radical species are now in progress in our laboratories.

EXPERIMENTAL

All melting points were determined using a Yanaco MS-500V apparatus and are uncorrected. The IR spectra were obtained using a Shimadzu FT-IR 8200PC spectrometer. The UV spectra were recorded by Shimadzu FTUV-2200PC. The ^{1}H-NMR (500 MHz) spectra were recorded by a JEOL α-500 spectrometer. Chemical shifts are given in δ values (ppm) using TMS as the internal standard. The Mass spectra were taken on Shimadzu GCMS-QP5050A and JEOL JNM-700 mass spectrometers. Elementary combustion analyses were performed using a Yanaco CHN CORDER MT-6 analyzer. All reactions were monitored by TCL employing a 0.25 mm silica gel plate (Merck 60F 254). Column chromatography was carried out on silica gel (Merck 60N spherical). The ESR spectra were recorded on a JEOL RE2X X-band spectrometer, in which the temperature was controlled by a JEOL DVT3 variable-temperature unit. Before measurements were taken, the sample in toluene was degassed and sealed in an ESR tube.

Dehydration of tribenzo[*b*]thienylmethylalcohol (2) ----- Preparation of 6-Benzo[*b*]thien-2-yl-6*H* -cyclopenta[1,2-*b*:4,3-*b*']bis[1]benzothiophene (3).

To a solution of tris(benzo[*b*]thieny)lmethylalcohol (**2**) (428 mg, 1.0 mmol) in MeCN (50 mL) was added hydrochloric acid (1 mL). Immediately after the addition the solution showed coloration in deep violet. The reaction mixture was stirred for 2 h, while the solution turned to a suspension. The solids were filtered and recrystallized from $CHCl_3$ to give **3** (364 mg, 89%) as colorless solids.[7]

3: mp 228-229 ºC. ^{1}H-NMR ($CDCl_3$) δ 8.48 (2H, d, *J*=8.0 Hz), 7.92 (2H, d, *J*=8.0 Hz), 7.74 (1H, d, *J*=8.0 Hz), 7.50 (1H, d, *J*=7.5 Hz), 7.57 (2H, dd, *J*=8.0, 7.5 Hz), 7.39 (2H, dd, *J*=8.0, 7.5), 7.35 (1H, s), 7.33 (1H, dd, *J*=8.0, 7.5 Hz), 7.28 (1H, dd, *J*=8.0, 7.5 Hz), 5.63 (1H, s). MS (*m*/*z*) 410. UV/Vis 450 nm (log ε =3.55). *Anal.* Calcd for $C_{25}H_{14}S_3$: C, 73.13; H, 3.44. Found: C, 72.88; H, 3.62.

General procedure for the oxidation to the hemithioindigos.

To a stirred solution of DDQ (25.0 mg, 0.11 mmol) in CH_2Cl_2 (20 mL) was added **3** (41.0 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) and a drop of hydrochloric acid. The mixture was refluxed for 5 h and was allowed to cool. The reaction mixture was poured into water and extracted with CH_2Cl_2. The extract was dried over sodium sulfate and evaporated. The residue was chromatographed on silica gel column with CH_2Cl_2 to give **1** (36.0 g, 85 %) as red solid.

In a similar manner, hemithioindigoid compounds **4**, **5**, and **6** were prepared from 9-benzo[*b*]thienylfluorene, 5-benzo[*b*]thieny-5*H*-dibenzo[*a*,*d*]cycloheptene, and 11-benzo[*b*]thienyl-11*H*-benzo[*b*]fluorene, respectively.

2-(6*H*-Cyclopenta[1,2-*b*:4,3-*b*']bis[1]benzothiophen-6-ylidene)benzo[*b*]thiophene-3(2*H*)-one (1).

Red solid. mp >300 ℃ ($CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ 8.35 (1H, d, *J*=8.5 Hz), 8.30 (1H, d, *J*=8.5 Hz), 7.95 (1H, d, *J*=7.5 Hz), 7.87 (2H, dd, *J*=8.5, 8.5 Hz), 7.64 (1H, dd, *J*=7.5, 8.5 Hz), 7.58 (1H, d, *J*=8.0 Hz), 7.48 (1H, dd, *J*=7.5, 8.0 Hz), 7.45 (1H, dd, *J*=7.5, 8.0 Hz), 7.38-7.32 (3H, m). IR (KBr) 1655 cm^{-1}, MS(*m*/*z*) 424. UV/Vis 510 nm (log ε = 4.9). *Anal.* Calcd for $C_{25}H_{12}OS_3$: C, 70.72; H, 2.85. Found: C, 70.86; H, 2.95.

2-Fluorenylidenebenzo[*b*]thiophene-3(2*H*)-one (4). 72 %. Orange solid. mp 131 ℃ (benzene-EtOH). ^{1}H-NMR (CD_2Cl_2) δ 9.42 (1H, d, *J*=8.0 Hz), 8.21 (1H, d, *J*=7.5 Hz), 7.95 (1H, d, *J*=8.0 Hz), 7.66 (1H, d, *J*=7.5 Hz), 7.63 (1H, d, *J*=7.5 Hz), 7.62 (1H, dd, *J*=8.0, 7.5 Hz), 7.52 (1H, d, *J*=7.5 Hz), 7.43-7.35 (2H, m), 7.38-7.30 (3H, m). MS (*m*/*z*) 312. UV/Vis 484 nm (log ε = 3.7). IR (KBr) 1650 cm^{-1}. *Anal.* Calcd for $C_{21}H_{12}OS$: C, 80.77; H, 3.85. Found: C, 80.59; H, 3.77.

2-(5*H*-Dibenzo[*a*,*d*]cycloheptenylidene)benzo[*b*]thiophene-3(2*H*)-one (5). 63 %. Yellow solid. mp 256-257 ℃ (benzene-EtOH). ^{1}H-NMR ($CDCl_3$) δ 7.68 (1H, d, *J*=7.8 Hz), 7.63 (1H, d, *J*=8.5 Hz), 7.60 (1H, d, *J*=7.5 Hz), 7.49-7.39 (7H, m), 7.29 (1H, d, *J*=7.8 Hz), 7.17 (1H, dd, *J*=7.5, 8.5 Hz), 6.99 (1H, d, *J*=11.6 Hz), 6.92 (1H, d, *J*=11.6 Hz). IR 1675 cm^{-1}. MS (*m/z*) 338. UV/Vis 430 nm (log ε = 3.74). *Anal.* Calcd for $C_{23}H_{14}OS$: C, 81.63; H, 4.17. Found: C, 81.48; H, 4.20.

2-(Benzofuluorenylidene)benzo[*b*]thiophene-3(2*H*)-one (6). 15 %. 4:3 mixture of the *Z*- and *E*-isomers. Orange solid. mp ca. 230 °C (benzene-CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): signals due to the *E* isomer 10.69 (1H, s), 8.32 (1H, d, *J*=5.3 Hz), 7.75 (1H, s), 7.94 (1H, d, *J*=7.9 Hz), 7.93 (1H, d, *J*=7.6 Hz), 7.74 (1H, d, *J*=6.0 Hz); signals due to the *Z* isomer: 10.05 (1H, d, *J*=7.9 Hz), 8.75 (1H, s), 7.76 (1H, s), 7.87 (1H, d, *J*=7.6 Hz), 7.61(1H, d, *J*=8.2 Hz), 7.58 (1H, d, *J*=8.3 Hz). Other signals are overlapped at higher field above 7.5 ppm and could not be distinguished. MS (*m/z*) 362. UV/Vis 494 nm (log ε = 4.20). *Anal.* Calcd for $C_{25}H_{14}OS$: C, 82.85; H, 3.89. Found: C, 83.03; H, 3.96.

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