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STRUCTURAL ASPECTS OF IODINE-PROMOTED ONE-POT CYCLIZATION OF *O*-BIS(METHYLTHIO)STILBENES TO THIENO[3,2-*b*]THIOPHENE DERIVATIVES: SYNTHETIC TRIALS OF TETRATHIENOACENES FROM 1,2-BIS(3-METHYLTHIOTHIOPHEN-2-YL)ETHENES

Tatsuya Yamamoto,[†,#] Eigo Miyazaki,[†] and Kazuo Takimiya[†,‡,*]

[†]Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan and [‡]Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8530, Japan, ktakimi@hiroshima-u.ac.jp

Abstract – In this paper, attempted reactions for the synthesis of tetrathienoacenes from 1,2-bis(3-methylthiothiophen-2-yl)ethenes by the iodine-promoted one-pot cyclization reaction were described. X-Ray structural analyses of the precursors indicated that the failure of reactions is closely related to the molecular structures around the reaction moiety, in particular, the bond angles defined by the aromatic ring and the neighboring carbon atom in the ethene moiety. We speculate that the larger angles in the 1,2-bis(3-methylthiothiophen-2-yl)ethenes make the intramolecular nucleophilic attack of the methylthio groups to the iodonium intermediate difficult.

INTRODUCTION

Thiophene- or selenophene- containing fused-heteroaromatic compounds, often called as heteroarenes, have been attracting current interests in view of developing novel organic semiconductors applicable to organic thin-film devices, such as organic light emitting diodes (OLEDs), organic photo-voltaic cells, or organic field-effect transistors (OFETs).[1] Among these applications, in particular, heteroarenes have been regarded as promising candidates for new organic semiconductors suitable for active materials in high-performance OFETs, owing to their structural resemblance to hydrocarbon-based fused-aromatics such as pentacene showing superior FET characteristics. Therefore, many research groups have applied various heteroarenes to the active semiconducting layer in OFET devices, for example, anthradithiophenes,[2] tetracenothiophenes,[3] oligothienoacenes,[4] and other benzene-thiophene annulated compounds (Figure 1).[5,6]

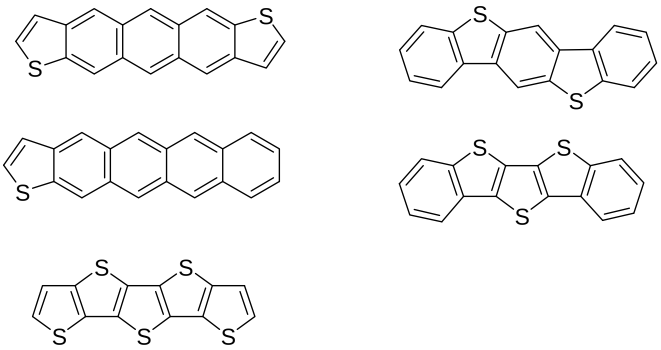
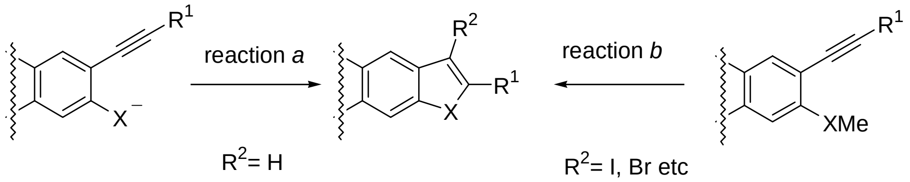


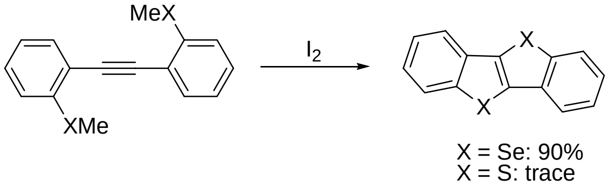
Figure 1. Representative examples of heteroarenes examined as an active semiconductor in OFET devices

Along with the prevailing interests to the heteroarenes, new synthetic approaches rather than conventional multi-step syntheses have been innovated recently. In particular, skilful uses of arylacetylene-based precursors in cyclization reactions affording fused-thiophene or selenophene moieties have been developed. In these reactions, a nucleophilic attack of *o*-thiolate or selenolate anion, generally prepared from the corresponding halogen derivative by a reaction with organometallic reagents at low temperature followed by an addition of elemental sulfur or selenium, to acetylene moieties plays a key role (Scheme 1, reaction a).[7]



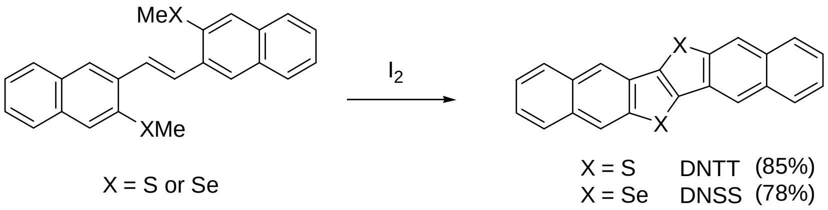
Scheme 1. Key reactions affording benzo[*b*]chalcogenophene moiety

On the other hand, *o*-methylthio- or methylseleno- groups were proved to be useful chalcogen source in related cyclization reactions by Larock and his coworkers (Scheme 1, reaction b).[8] We also found that similar double cyclization reactions of *o*-bis(methylseleno)diphenylacetylenes can be readily take place to give corresponding selenophenoselenophene derivatives,[9] though the corresponding methylthio derivative did not afford the thienothiophene derivatives (Scheme 2).[10]



Scheme 2. Facile synthesis of [1]benzoselenopheno[3,2-*b*]selenophene derivatives

In sharp contrast, we recently found that *o*-bis(methylthio)- or *o*-bis(methylseleno)-stilbenes can be easily converted into extended thienothiophenes, i.e. [1]benzothieno[3,2-*b*]thiophene or [1]benzoselenopheno-[3,2-*b*]selenophene, respectively, by an action of iodine: this new finding allowed us to synthesize highly π-extended novel heteroarenes, dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene (DNTT) and its selenium counterpart (DNSS) (Scheme 3), one of the best organic semiconductors affording high-performance OFET devices with improved stability.[11]

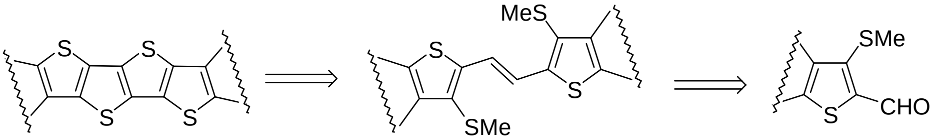


Scheme 3. Iodine-promoted one-pot cyclization of *o*-bis(methylthio)- or *o*-bis(methylseleno)-stilbenes to π-extended heteroarenes

Synthetic advantages of the cyclization from *o*-bis(methylthio)stilbene precursors are not only the high yields of the desired thieno[3,2-*b*]thiophene derivatives but also the applicability to both the thiophene and selenophene analogues. In addition, the stilbene precursors can be easily prepared from appropriate aldehydes by the low-valent titanium-mediated coupling reaction. For these reasons, we expected that the iodine-promoted one-pot cyclization of *o*-bis(methylthio)stilbenes can be a versatile reaction for the development of new heteroarenes consisting of the thieno[3,2-*b*]thiophene substructure. We thus examined application of the present method to the synthesis of tetrathienoacenes (Scheme 4), since the synthetic methods for the oligothienoacenes with even fused-thiophene rings generally required multi-step reactions.[12,13] In this paper, we report synthetic trials for the tetrathienoacene derivatives by the iodine-promoted one-pot cyclization of bis(3-methylthiothiophen-2-yl)ethenes and structural requirements of the substrates applicable to the reaction by means of single crystal X-ray analyses.

RESULTS AND DISCUSSION

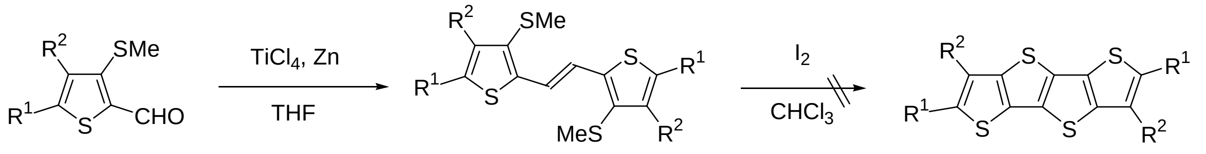
Employing the iodine-promoted one-pot cyclization of *o*-bis(methylthio)stilbenes, we suggested a straightforward synthetic route for tetrathienoacenes from readily available 3-methythio-2-thiophene aldehyde derivatives (Scheme 4).



Scheme 4. Proposed synthetic route to tetrathienoacene derivatives

3-Methythio-2-thiophene aldehyde (**1a**)[14] and 3-methythio-2-formylbenzo[*b*]thiophene (**1b**)[15] were easily prepared, and their spectroscopic data agreed with reported ones. The aldehydes (**1a** and **1b**) could be readily converted into the corresponding 1,2-bis(2-thienyl)ethene derivatives (**2a** and **2b**) by the coupling reaction mediated by the low-valent titanium conveniently *in situ* generated from titanium tetrachloride and zinc powder in THF (Scheme 5).[16] Owing to the presence of methylthio substituents, **2a** and **2b** were easily soluble to various organic solvents, which makes them readily purified by column chromatography and recrystallization.

Using the precursors **2a** and **2b** we tried to synthesize tetrathienoacenes by the iodine-promoted cyclization reaction. Out of our expectations, however, reaction of **2a** with excess iodine (32 eq.) in refluxing chloroform for 3 h did not afford the desired tetrathienoacene (**3a**), instead only black tar, which could not be identified, was obtained. Control of the amount of iodine in the reaction did not make any difference. The vacant α-position on the terminal thiophene rings may react with iodine to form polymer-like intractable material, and thus an α-blocked precursor, *trans*-1,2-bis(5-bromo-3-methylthiothiophen-2-yl)ethene (R^1 = Br, R^2 = H, **2a′**) was synthesized and examined.[17] However, the reaction gave a similar unidentified black tar. These results implied that iodine reacts first with the thiophene moiety rather than with bis(methylthio)stilbene moiety (*vide infra*). In sharp contrast, **2b** possessing annulated benzene rings did not react with iodine at all even applying longer reaction time (15 h): the substrate **2b** was recovered quantitatively.



1a: $R^1 = R^2 = H$
1b: R^1, R^2 = CH=CH-CH=CH

2a: $R^1 = R^2 = H$
2a': R^1 = Br, R^2 = H
2b: R^1, R^2 = CH=CH-CH=CH

3a: $R^1 = R^2 = H$
3a': R^1 = Br, R^2 = H
3b: R^1, R^2 = CH=CH-CH=CH

Scheme 5. Synthesis of *trans*-1,2-bis(3-methylthiothiophen-2-yl)ethene precursors (**2**) and trials to convert to tetrathienoacenes

Poor reactivity of **2b** as well as different reactivity of **2a** from those of *o*-bis(methylthio)stilbenes implies the structural difference in the reaction focal part between 1,2-bis(3-methylthiothiophen-2-yl)ethenes and *o*-bis(methylthio)stilbenes. In order to get insight into the structural aspects of the bis(methylthio)stilbene substrates, X-ray crystal structure analyses of **2a** and **2b** were carried out. For comparison, the molecular structure of *trans*-1,2-bis(3-methylthionaphthalen-2-yl)ethene (**4**), which successfully afforded the ring-closed product (Scheme 3), was also elucidated (Figure 2 and Table 1). All **2a**, **2b**, and **4** have the planer, conjugated backbones, and the sulfur atoms in the methylthio groups are also in the same planes, though orientations of the methyl groups are different. Regardless of the aromatic parts or the orientation of the methylthio groups, the bond lengths (l^4, 1.32~1.33 Å) and angles (ϕ^3, ~126°) around the ethene moieties are quite similar to one another. Among them, fairly large ϕ^2s (> 127°), defined by the aromatic C=C bond and the neighboring carbon atom in the ethene moiety is noticeable, when compared with the corresponding angle in *trans*-1,2-bis(3-methylthionaphthalen-2-yl)ethene (120.2°). In contrast, ϕ1s in three compounds are close to 120°, indicating that no significant differences are present in the aromatic-methylthio connecting part.

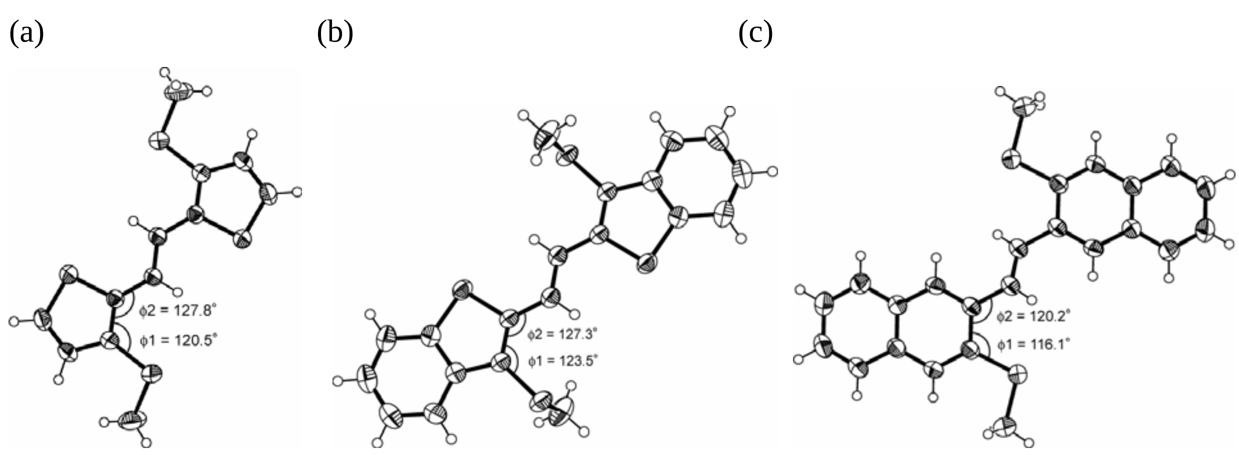
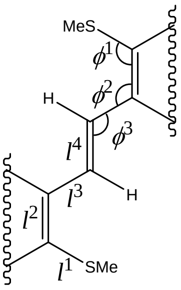


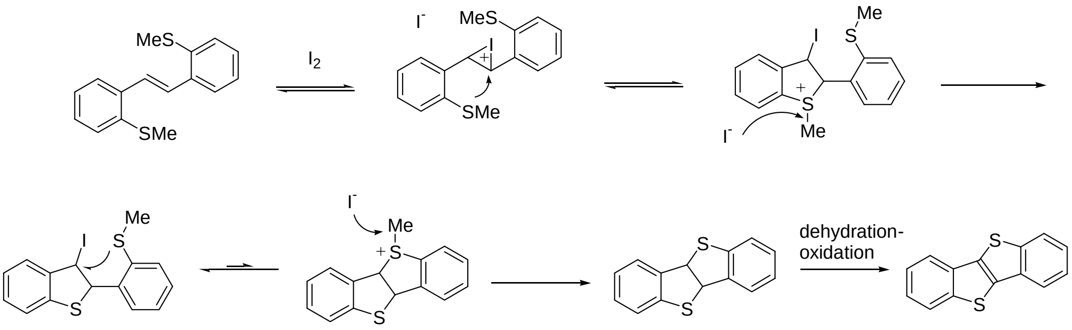
Figure 2. ORTEP drawings of **2a** (a), **2b** (b) and *trans*-1,2-bis(3-methylthionaphthalen-2-yl)ethene (**4**) (c)

Table 1. Selected bond lengths and bond angles of **2a**, **2b**, and *trans*-1,2-bis(3-methylthionaphthalen-2-yl)ethene (**4**)



	l^1 / Å	l^2 / Å	l^3 / Å	l^4 / Å	ϕ^1 / °	ϕ^2 / °	ϕ^3 / °
2a	1.762(2)	1.377(3)	1.440(3)	1.337(4)	120.5(2)	127.8(2)	126.4(2)
2b	1.7583(14)	1.3673(19)	1.4408(18)	1.332(3)	123.51(10)	127.29(12)	125.78(16)
4	1.7747(14)	1.4360(18)	1.4790(17)	1.320(3)	116.08(10)	120.20(12)	125.76(15)

The structural difference at the reaction part, in particular the large value of ϕ^2s is expected to affect the iodine-promoted cyclization reactions. A plausible reaction pathway of the cyclization reactions is depicted in Scheme 6. We expected that the initial step of the reaction is addition of iodine to the ethene part to form the iodonium-like ionic species, and then the intramolecular nucleophilic substitution by the sulfur atom in the methylthio group takes place to give the sulfonium intermediate, the methyl group of which is then liberated by nucleophilic attack by iodide anion to give 2,3-dihydro-3-iodobenzothiophene intermediate. Successive intramolecular nucleophilic substitution on the C3 atom in the 2,3-dihydrobenzothiophene intermediate followed by demethylation and oxidation will complete the cyclization. In these reaction steps, the intramolecular nucleophilic attack by the methylthio groups to form the five-membered ring plays a key role. For this reason, the bond angle ϕ^2s will be the important structural factor for the cyclization reaction. Therefore the larger ϕ^2s in **2** (~127°) than that in *trans*-1,2-bis(3-methylthionaphthalen-2-yl)ethene (120°) makes the intramolecular nucleophilic attack in **2** unfavorable, resulting in totally different reactivity in the iodine-promoted cyclization reaction.



Scheme 6. A plausible reaction path for the iodine-promoted cyclizaition

CONCLUSIONS

We tried to apply the iodine-promoted cyclizaition reaction of *o*-bis(methylthio)stilbenes to the synthesis of tetrathienoacene derivatives using *trans*-1,2-bis(3-methylthiothiophen-2-yl)ethene precursors (**2**) as substrates. However, the desired reaction did not proceed, and no tetrathienoacenes were obtained at all. To investigate the reasons for the failure reactions, we focused on the structural factors of *trans*-1,2-bis(3-methylthiothiophen-2-yl)ethenes (**2**). X-Ray crystallographic analysis clearly indicated that the bond angle defined by the neighboring carbon atom in the ethene moiety and the thiophene α,β bond is quite larger in **2** (~127°) than that in *trans*-1,2-bis(3-methylthionaphthalen-2-yl)ethene (~120°). From the viewpoint of the reaction pathway, the bond angles in question will be a key structural factor, because the intramolecular nucleophlic attack of the methylthio group will be a crucial step in the reaction. Therefore, it can be concluded that the scope of the iodine-promoted cyclizaition reaction would be limited within *o*-bis(methylthio)stilbene analogues where aromatic rings should be six-membered, not five-membered rings such as thiophene and the related heteroaromatics.

EXPERIMENTAL

SYNTHESIS OF PRECURSOR: All chemicals and solvents are of reagent grade unless otherwise indicated. THF was distilled from sodium benzophenone ketyl prior to use. Nuclear magnetic resonance spectra were obtained in deuterated chloroform with a JEOL Lambda 400 spectrometer operating at 400 MHz for ^{1}H with TMS as internal reference; chemical shifts (δ) are reported in parts per million. EI-MS spectra were obtained on a Shimadzu QP-5050A spectrometer using an electron impact ionization procedure (70 eV). The molecular ion peaks of the sulfur-containing compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ^{32}S, unless otherwise stated.

Synthesis of 3-methylthio-2-thiophenealdehyde (1a)[14] To a solution of 3-methylthiothiophene (2.605 g, 20.0 mmol) in anhydrous DMF (5 mL, 72.4 mmol) was slowly added phosphorus oxychloride (1.825 mL, 20.0 mmol) over a period of 5 min. After the mixture was stirred for 10.5 h at rt, and then cooling to 0 °C, a solution of saturated aqueous sodium chloride solution (20 mL) was added over a period of 5 min. The resulting mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluted with $CHCl_3$ (*Rf* = 0.7) to give 3-methylthio-2-thiophenealdehyde as yellow oil (2.421 g, 15.30 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H, CH_3), 7.11 (d, 1H, *J* = 5.2 Hz, thiophene-H_4), 7.74 (dd, 1H, *J* = 5.2, 0.9 Hz, thiophene-H_5), 10.04 (d, 1H, *J* = 0.9 Hz, CHO); EIMS (70 eV) *m/z* = 158 (M^+).

Synthesis of 2-formyl-3-methylthiobenzo[*b*]thiophene (1b)[15] To a solution of 3-methylthiobenzo[*b*]thiophene (1.803 g, 10.00 mmol) in anhydrous DMF (3 mL, 38.77 mmol) was slowly added phosphorus oxychloride (1.004 mL, 11.00 mmol) over a period of 20 min. After the mixture was stirred for 20.5 h at rt, and then cooling to 0 °C, a solution of saturated aqueous sodium chloride solution (20 mL) was added. The resulting mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluted with CH_2Cl_2 (*Rf* = 0.8) to give 2-formyl-3-methylthiobenzo[*b*]thiophene (**1b**) as off-white solid (1.007 g, 4.83 mmol, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 3H, CH_3), 7.51 (ddd, 1H, *J* = 7.3, 7.3, 1.2 Hz, ArH), 7.56 (ddd, 1H, *J* = 7.3, 7.3, 1.2 Hz, ArH), 7.91 (dd, 1H, *J* = 7.3, 1.2 Hz, ArH), 8.17 (dd, 1H, *J* = 7.3, 1.2 Hz, ArH), 10.57 (s, 1H, CHO); EIMS (70 eV) *m/z* = 208 (M^+).

Synthesis of *trans*-1,2-bis(3-methylthiothiophen-2-yl)ethane (2a) To an ice-cooled suspension of zinc powder (3.683 g, 56.33 mmol) in THF (90 mL), titanium tetrachloride (6.204 mL, 56.33 mmol) was slowly added, and anhydrous pyridine (0.506 mL, 6.258 mmol) was added. The resulting mixture was refluxed for 1.5 h, after cooling to rt, a solution of 3-methylthio-2-thiophenealdehyde (**1a**, 2.971 g, 18.78 mmol) in THF (36 mL) was slowly added to the mixture, and the mixture was then refluxed for 5 h. After cooling to rt, the mixture was diluted with saturated aqueous $NaHCO_3$ solution (10 mL), saturated aqueous sodium hydrogen sulfite (10 mL) and saturated aqueous Na_2CO_3(10 mL) and stirred for 12 h. The mixture was filtered through a filter paper, and the filtrate was separated into an organic and an aqueous layers. The aqueous layer was extracted with CH_2Cl_2 (30 mL × 3), and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The resulting reside was purified by passing through a silica gel pad eluted with CH_2Cl_2, column chromatography on silica gel eluted with hexane-EtOAc (9:1, v/v, *Rf* = 0.5), and recrystallization from hexane/CH_2Cl_2 to give *trans*-1,2-bis(3-methylthiothiophen-2-yl)ethane (**2a**) as yellow crystal (1.457 g, 5,122 mmol, 55%). mp 102.0-103.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 6H, Me), 7.02 (d, 2H, *J* = 5.1 Hz, thiophene-H5), 7.20 (d, 2H, *J* = 4.8 Hz, thiophene-H4), 7.31 (s, 2H, HC=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 120.3, 123.7, 130.3, 132.1, 139.5; IR (KBr) ν 627, 695, 923, 1505 cm^{-1}; EIMS (70 eV) *m/z* = 284 (M^+); Anal. Calcd for $C_{12}H_{12}S_4$: C, 50.66; H, 4.25. Found: C, 50.52; H, 4.34%.

Synthesis of *trans*-1,2-bis(3-methylthiobenzo[4,5]thiophen-2-yl)ethene (2b) To an ice-cooled suspension of zinc powder (0.637 g, 9.74 mmol) in THF (15 mL), titanium tetrachloride (1.07 mL, 9.74 mmol) was slowly added, and anhydrous pyridine (0.262 mL, 3.25 mmol) was added. The resulting mixture was refluxed for 1.5 h, after cooling to rt, and a solution of 2-formyl-3-methylthiobenzo[*b*]thiophene (0.676 g, 3.25 mmol) in THF (15 mL) was slowly added to the mixture, and the mixture was then refluxed for 9.5 h. After cooling to rt, the mixture was diluted with saturated aqueous $NaHCO_3$ solution (20 mL) and stirred for 7 h. The mixture was filtered through a filter paper, and the filtrate was separated into an organic and an aqueous layers. The aqueous layer was extracted with $CHCl_3$ (30 mL × 3), and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The resulting reside was purified by passing through a silica gel pad eluted with CH_2Cl_2 to give 1,2-bis(3-methylthiobenzo[4,5]thiophen-2-yl)ethene as yellow crystal (0.596g, 1.55 mmol, 95%). mp 195.0-196.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 6H, Me), 7.39 (ddd, 2H, J = 7.5, 7.5, 1.5 Hz, ArH), 7.44 (ddd, 2H, J = 7.5, 7.5, 1.5 Hz, ArH), 7.80 (dd, 2H, J = 7.5, 1.5 Hz, ArH), 7.86 (s, 2H, HC=CH), 7.98 (dd, 2H, J = 7.5, 1.5 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 122.5, 123.1, 124.0, 124.9, 125.9, 128.0, 137.9, 141.0, 144.9; IR (KBr) ν 727, 750, 939, 1694 cm^{-1}; EIMS (70 eV) m/z = 384 (M^+); Anal. Calcd for $C_{20}H_{16}S_4$: C, 62.46; H, 4.19. Found: C, 62.23; H, 4.31%.

TRIALS TO IODINE-PROMOTED CYCLIZATION

Reaction of *trans*-1,2-bis(3-methylthiothiophene-2-yl)ethene with I_2: A solution of *trans*-1,2-bis(3-methylthiothiophene-2-yl)ethene (**2a**, 0.057 g, 0.20 mmol) and iodine (1.624 g, 6.4 mmol) in $CHCl_3$ (5 mL) was refluxed for 3 h. After cooling to rt, saturated aqueous sodium hydrogen sulfite solution (20 mL) was added, and the resulting precipitate was collected by filtration to give the insoluble black tar (0.215 g).

Reaction of *trans*-1,2-bis(3-methylthiobenzo[4,5]thiophene-2-yl)ethene with I_2: A solution of *trans*-1,2-bis-(3-methylthiobenzo[4,5]thiophene-2-yl)ethene (**2b**, 0.192 g, 0.50 mmol) and iodine (4.061 g, 16.0 mmol) in $CHCl_3$ (15 mL) was refluxed for 15 h. After cooling to rt, saturated aqueous sodium hydrogen sulfite solution (60 mL) was added, and the resulting precipitate was collected by filtration and was washed with water and $CHCl_3$. The crude product was purified by passing through a silica gel pad eluted with CH_2Cl_2 to recover substrate **2b** (0.190 g, 99%).

SINGLE CRYSTAL X-RAY ANALYSIS

Single crystals were obtained by recrystallization from $CHCl_3$. The X-ray crystal structure analysis was made on a Rigaku Rapid-S imaging plate (Mo$K\alpha$ radiation, λ = 0.71069 Å, graphite monochromator, T = 296 K, $2\theta_{max}$ = 55.0°). The structure was solved by the direct methods.[18,19] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the calculations but not refined. All calculations were performed using the crystallographic software package CrystalStructure 3.8.0.[20] or SHELXL-97[19].

Crystal data for 2a: $C_{12}H_{12}S_4$, M = 284.47, yellow block, 0.60×0.50×0.50 mm^3, *Monoclinic*, space group $P2_1/n$ (no. 14), a = 4.6911(4), b = 9.0419(7), c = 15.4825(13) Å, β = 94.461(3)°, V = 654.72(9) Å^3, Z = 2, D_{calc} = 1.443 gcm^{-3}, GOF = 1.213, R = 0.0569 for 1488 observed reflections (I > 2σ(I)) and 79 variable parameters, R_w = 0.1540 for all data.

Crystal data for 2b: $C_{20}H_{16}S_4$, M = 384.57, yellow needle, 0.50×0.30×0.20 mm^3, *Monoclinic*, space group $P2_1/n$ (no. 14), a = 10.5843(6), b = 6.6108(3), c = 13.2132(8) Å, β = 102.203(3)°, V = 903.65(9) Å^3, Z = 2, D_{calc} = 1.443 gcm^{-3}, GOF = 1.155, R = 0.0369 for 2045 observed reflections (I > 2σ(I)) and 110 variable parameters, R_w = 0.1311 for all data.

Crystal data for *trans*-1,2-bis(3-methylthionaphthalen-2-yl)ethene: $C_{24}H_{20}S_2$, M = 372.52, yellow needle, 0.25×0.25×0.10 mm^3, *Monoclinic,* space group $P2_1$/n (no. 14), a = 5.4258(6), b = 15.7015(18), c = 11.4043(8) Å, β = 97.867(3)°, V = 962.42(17) Å^3, Z = 2, D_{calc} = 1.285 gcm^{-3}, GOF = 1.145, R = 0.0371 for 1817 observed reflections (I > 2σ(I)) and 119 variable parameters, R_w = 0.1321 for all data.

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