Tetrahedron Letters 54 (2013) 4049-4053

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet



Synthesis and basic properties of tetrathieno [2,3-a:3',2'-c:2",3"-f:3"',2"'-h]naphthalene: a new π -conjugated system obtained by photoinduced electrocyclization– dehydrogenation reactions of tetra(3-thienyl)ethene



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ARTICLE INFO

Article history: Received 22 April 2013 Revised 16 May 2013 Accepted 20 May 2013 Available online 24 May 2013

Keywords: Thiophene-fused aromatics 6π-Electrocyclization Photoreaction Single electron transfer reaction

ABSTRACT

A method for the synthesis of tetrathieno [2,3-a:3',2'-c:2'',3''-f:3''',2'''-h] naphthalene (3), utilizing photoinduced electrocyclization-dehydrogenation reactions of tetra(3-thienyl)ethene (1), was developed. Photoirradiation of a toluene or $CHCl_3$ solution of 1, containing a small amount of I_2 , leads to modestly efficient production of **3**. In contrast to the UV-vis absorption property of the typical p-type organic transistor material pentacene, that of **3** does not experience a time-dependent change under aerated conditions, indicating that 3 has high stability against molecular oxygen. The results of X-ray crystallographic analysis demonstrate that **3** possesses a columnar crystalline structure in which molecules are aligned in a face-to-face manner with a high degree of the π - π overlap between adjacent molecules. This phenomenon should result in efficient charge-carrier transport properties of the crystalline form of this substance

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Introduction

Materials used in organic field-effect transistors (OFETs) need to be readily prepared and durable. Pentacene, a common material employed in OFETs,^{1,2} suffers from problems associated with its relatively short lifetime, especially when molecular oxygen is present in its environment.³ One strategy developed to circumvent the problem associated with the instability of fused aromatic hydrocarbons in air, involves the use of annulated thiophenes in OFETs. Owing to their relatively low reactivity with molecular oxygen, thiophene-fused aromatic compounds are widely used as organic optoelectronic materials. For example, 2,7-diphenyl[1]benzothieno[3,2-*b*][1]benzothiophene (DPh-BTBT, Chart 1)^{4,5} and dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene (DNTT),⁶⁻⁸ both prepared by Takimiya, have attracted great attention as organic transistor materials as a consequence of (1) high charge carrier mobilities of them comparable to that of pentacene and (2) stabilities against molecular oxygen of them much higher than that of pentacene.

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Among many of the developed approaches, a 6π -electrocyclization process followed by oxidative dehydrogenation of the photoproduct is a unique strategy for the synthesis of thiophene-fused π -conjugated systems. Applications of this process are exemplified by the synthesis of tetrathieno[3,2-*a*:2',3'-*c*:3",2"-*f*:2"',3"'-*h*]naphthalene devised by Harrit.9 Recently, Osuga employed this approach to prepare new substances that have potential applications as organic electroluminescence materials.¹⁰

Inspired by Harrit's early effort leading to the preparation of the uniquely π -conjugated tetrathienonaphthalene, and ensuing studies of derivatives of this substance by Yamaguchi and co-workers.¹¹ we developed a plan for the synthesis of the regioisomeric tetrathieno[2,3-a:3',2'-c:2",3"-f:3"",2"'-h]naphthalene substance.



Chart 1. Structures of DPh-BTBT and DNTT.



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Table



Scheme 1. Syntheses of **2** and **3** using a photoinduced electrocyclization-dehydrogenation sequence starting with 1.

(3, Scheme 1) from tetra(3-thienyl)ethene (1). We also envisaged that 3 would have ideal optoelectronic properties and stabilities against molecular oxygen. Owing to these predicted properties, 3 along with its ring-opened counterpart, 5,6-di(3-thienyl)dithieno[2,3-a:3',2'-c] benzene (2), should be novel OFET materials. The results of studies guided by these expectations show that **3** has a small HOMO-LUMO gap, a low reactivity with molecular oxygen, and a columnar-ordered crystalline structure that possesses a large degree of intermolecular π - π overlap, and consequently that **3** is a potential charge-carrier transport material.

Results and discussion

Preparation of 1

Tetrathienylethene 1, employed as a key synthetic intermediate in the route for preparation of polycyclic thiophenes 2 and 3, was generated using a sequence that is initiated by conversion of commercially available 3-bromothiophene (4) to di(3-thienyl)methanol (5) promoted by treatment with *n*-BuLi and methyl formate (Scheme 2). Reaction of alcohol 5 under pyridinium chlorochromate oxidation conditions¹² yields di(3-thienyl) ketone (6), which is then subjected to McMurry coupling¹³ using TiCl₄ and Zn to produce 1 as colorless needles.

Syntheses of 2 and 3

Studies were carried out to uncover the best conditions for the syntheses of the polycyclic thiophenes 2 and 3 using tandem photoinduced electrocyclization-dehydrogenation reactions of 1 (Table 1). Irradiation of a toluene (TOL) solution of 1 (4.7 \times 10^{-2} M) and a small amount of I₂ using a high-pressure mercury lamp (313 nm, 500 W) for 24 h results in formations of 2 and 3 in 20% and 1%, respectively. In contrast, when a TOL solution of 1 and a small amount of I₂ are irradiated with Ravonet lamps (350 nm, 70 W) for 18 h, 3 is generated predominantly (20%) along with only a trace quantity of **2**. Photoreactions of **1** in CHCl₃ containing I₂ generate **2** and **3** in 19% and 7%, respective yields when a high-pressure mercury lamp is used as the light source, and **3** is produced nearly exclusively (23% and trace of 2) when Rayonet lamps are employed. The structures of 2 and 3 were elucidated on



Scheme 2. Preparation of 1.

Table 1	
Photoinduced electrocyclization-dehydrogenation reactions of	1 ^a

Solvent ^b	$\lambda_{\rm EX} ({\rm nm})$	Time (h)	Conv. (%)	Yields (%)	
				2	3
TOL	313 ^c	24	100	20	1
	350 ^d	18	94	Trace	20
CHCl ₃	313 ^c	24	100	19	7
	350 ^d	18	94	Trace	23

^a Compound **1**, 2.8 mmol; I₂, 0.2 μmol (0.07 equiv).

^b 6 mL.

High-pressure mercury lamp (500 W) with Pyrex cut filter.

^d Rayonet lamps (70 W).



Scheme 3. Plausible reaction pathway for generation of 2 and 3 by photoinduced electrocyclization-dehydrogenation of 1 and potential reaction pathway for formation of 9 and 10 by photoinduced dyotropic rearrangement from 7 and 8, respectively

the basis of their characteristic spectroscopic data and demonstrated unambiguously using X-ray crystallographic analysis.

The photochemical transformation from **1** to **3** via **2** most likely takes place through a stepwise pathway involving 7 and 8 as key intermediates (Scheme 3). However, no direct evidence for the existence of 7 and 8 in this pathway was obtained by monitoring the reaction of **1** using UV-vis absorption and NMR spectroscopy. This is probably due to the occurrence of efficient dehydrogenation reactions from 7 to 8. The only moderate yields of 2 and 3 in these processes might be a consequence of the formation of side products 9 and 10, which could arise by secondary photoinduced dyotropic rearrangement¹⁴ of **7** and **8**, respectively. However, no direct evidence for the existence of 9 and 10 was also obtained in the experiment.

The possibility of promoting the electrocyclization-dehydrogenation reactions of 1 to form 2 and 3, by utilizing single electrontransfer (SET) conditions and the oxidants, was explored (Table 2).

le 2					
-initiated e	electrocyclization-dehydrogenation reactions	of 1	in	CH_2C	l_2

Tab

SET

Oxidant	T (°C)	Time (h)	Conv. (%)	Yields (%)	
				2	3
$(p-BrC_6H_4)_3N^+SbCl_6^{-a}$	25	6	100	48	6
$(n-Bu_4N)_2[Ce(NO_3)_6]^b$	25	1	100	27	0
FeCl ₃ ^c	0	1	100	41	3

^a Compound **1**, 0.1 mmol; (*p*-BrC₆H₄)₃N⁺SbCl₆⁻, 0.1 mmol (1.0 equiv); CH₂Cl₂, 20 mL

Compound 1, 0.2 mmol; (n-Bu₄N)₂[Ce(NO₃)₆], 0.3 mmol (1.5 equiv); CH₂Cl₂, 50 mL

Compound 1, 0.3 mmol; anhydrous FeCl₃, 1.5 mmol (5.0 equiv); CH₂Cl₂, 30 mL.

Indeed, treatment of a CH₂Cl₂ solution of **1** with tris(*p*-bromophenyl)aminium hexachloroantimonate $[(p-BrC_6H_4)_3N^+SbCl_6^-]$ promotes electrocyclization-dehydrogenation reactions to give 2 and **3** in 48% and 6% yields, respectively. The use of $FeCl_3^{18-21}$ to promote these reactions leads to nearly the same yields of these products, while (n-Bu₄N)₂[Ce(NO₃)₆]^{22,23} is less effective. Radical cations 7^{+} and 8^{+} must serve as intermediates in the mechanistic routes for these SET reactions. In addition, the low yields of **3** might be a consequence of either the high oxidation potential of **1** compared to **2** or some unexpected decompositions of 7^{+} and 8^{+} .

Photophysical and electrochemical studies of 2 and 3

The results of a photophysical investigation showed that 2 and **3** in CH₂Cl₂ have respective UV-vis absorption maxima at λ_{AB} = 338 and 364 nm, and that they exhibit very weak fluorescence ($\Phi_{\rm FI}$ <0.01) with emission maxima at λ_{FL} = 366 and 390 nm, respectively (Table 3). The UV-vis absorption spectra of 2 and 3 remain unchanged when aerated CH₂Cl₂ solutions containing these substances are allowed to stand in the dark for 48 h at room temperature (Fig. 1a and b). This result shows that 2 and 3 have higher stabilities against molecular oxygen than pentacene whose

Table 3

UV-vis absorption and fluorescence maxima (λ_{AB} and λ_{FL}), fluorescence quantum yield (Φ_{FL}), anodic peak potentials (E_{AP}), energy levels of the HOMO (E_{H}), and differences in energy level between the HOMO and LUMO (E_{H-L}) for pentacene, DPh-BTBT, DNTT, and 1-3

	λ_{AB} (nm)	λ _{FL} (nm)	$arPsi_{ ext{FL}}$	E _{AP} (V versus SCE)	$E_{\rm H} ({\rm eV})$	E _{H-L} (eV)
Pentacene DPh-BTBT DNTT 1 2 3	$578^{a,b}$ $336^{g,h}$ $400^{a,k}$ 324^{a} 338^{a} 364^{a}	582 ^{a,b} ^c ¹ 366 ^a 390 ^a	_c _c _l 0.006 ^{a,o} 0.008 ^{a,o}	$\begin{array}{l} +0.51^{a,b,d} \\ +1.32^{d,h,i} \\ +1.03^{d,i,k} \\ +1.11^{a,m} \\ +1.41^{a,m} \\ +1.35^{a,m} \end{array}$	$-^{c}$ -5.41 ^{h,j} -5.19 ^{j,k} -5.24 ⁿ -5.66 ⁿ -5.44 ⁿ	$\begin{array}{c} 2.21^{\rm e,f} \\ 3.89^{\rm h,j} \\ 3.38^{\rm j,k} \\ 3.94^{\rm n} \\ 4.59^{\rm n} \\ 4.01^{\rm n} \end{array}$

^a In CH₂Cl₂.

b See Ref. 24

Not available.

d Obtained by assuming the following empirical relationship, EAP (in V versus SCE) = E_{AP} (in V versus Fc/Fc⁺) +0.41 V.

- See Ref 3
- f Calculated using B3LYP/6-31+G(d).
- g In THF.
- h See Ref. 4.
- In benzonitrile.
- Calculated using B3LYP/6-31G(d). k
- See Ref. 6. 1
- No attempt.

m The first E_{AP} versus SCE. For the detail, see Fig. 2.

- n Calculated using B3LYP/6-31G(d,p).
- Determined using an integrating sphere system.



Figure 1. Time course of the UV-vis absorption spectra of (a) $2(1 \times 10^{-5} \text{ M})$ and (b) $\mathbf{3}$ (1 × 10⁻⁵ M) in aerated CH₂Cl₂ for 48 h.



Figure 2. Cyclic voltammograms of 1 (red, E_{AP} = +1.11 and +1.42 V), 2 (green, E_{AP} = +1.41 V), and **3** (blue, E_{AP} = +1.35 V) in CH₂Cl₂ containing 0.1 M *n*-Bu₄N⁺ClO₄⁻. Scan rate, 0.1 V s⁻¹; reference electrode, SCE; working and counter electrodes, Pt.



Figure 3. Energy levels of the HOMOs and LUMOs of 1-3 calculated using B3LYP/6-31G(d,p).

UV-vis absorption spectrum in aerated CH₂Cl₂ drastically changes upon standing for 24 h at room temperature.⁶

Observations made in electrochemical studies show that the cyclic voltammogram of 1 contains irreversible anodic peaks at the potential E_{AP} = +1.11 and +1.42 V versus SCE, and that of **2** contains one irreversible peak at +1.41 V versus SCE (Fig. 2 and Table 3). The poor electrochemical reversibilities indicate that radical cations 1^{+} and 2^{+} , arising by SET oxidation of 1 and 2, as expected, undergo rapid chemical reactions. The voltage similarity (+1.42 vs +1.41 V) between the second anodic peak of 1 and the first peak of **2** is likely caused by the generation of **2** from 1^{+} . In addition, the anodic peak of cyclization product 3 appears at a lower potential (E_{AP} = +1.35 V) than that of **2**.

The order of the electrochemically determined E_{AP} values of 1–3 agrees well with the energy level of the HOMOs $(E_{\rm H})$ for these substances obtained by using density functional theory (DFT) calculations (Table 3 and Fig. 3). In spite of the less planar structure of 1, the $E_{\rm H}$ of **1** is significantly higher than those of **2** and **3**. This noteworthy difference is a unique feature of tetrathienylethene frameworks and is responsible for the ease with which 1 undergoes photo- and electrochemical electrocyclization-dehydrogenation reactions.^{17,23,25-27} The results of DFT calculations also demonstrate that the difference in energy level between the HOMO and LUMO $(E_{H-L} = E_L - E_H)$ for **3** is nearly equal to that of DPh-BTBT (Chart 1 and Table 3),⁵ suggesting that **3** has a high potential for use as an OFET material.



Figure 4. ORTEP plots of structural data of (a) **1**; (b) **2**; and (c) **3** obtained by using X-ray crystallographic analysis showing 30%-probability thermal ellipsoids for **1**, **2** (T = 296 K) and 50%-probability ones for **3** (T = 93 K); (d) a columnar ordering of **3** in the crystalline state.

X-ray crystallographic analyses of 1-3

Inspection of the ¹H NMR spectrum of **1** shows that its four thienyl moieties are magnetically equivalent, suggesting that these groups are rapidly rotating in solution at ambient temperature. In the X-ray structure of **1**,²⁸ several disorders are observed in the orientations of the thienyl moieties (Fig. 4a). Similarly, the molecular structure of **2** in the crystalline state is comprised of a mixture of disordered parallel and anti-parallel conformers (Fig. 4b), in which the two thienyl moieties are oriented in the same and opposite directions, respectively. The results of X-ray crystallographic analysis show that **3** has a planar structure that the molecules adopt a columnar order with a face-to-face manner, a large degree of overlap and short π - π spacing distance of 3.45 Å between heteroarene rings of adjacent molecules (Fig. 4c and d). This structural feature should enable **3** to have ideal charge-carrier transport properties. More generally, observations in this study indicate that electrocyclization-dehydrogenation reactions, which produce products that contain thiophene moieties annulated within aromatic systems, represent a promising methodology to produce substances that meet the requirements for OFET materials.

Conclusion

The effort described above has resulted in the synthesis of 3 utilizing a route that features key photoirradiation promoted electrocyclization-dehydrogenation reactions of 1 followed by an I2induced oxidative dehydrogenation process. In addition, although an electrocyclization reaction of 1 takes place under SET conditions, the process affords mainly the monocyclization product 2. Although moderately yielding of new π -conjugated systems, these synthetic processes only require filtration through a short column with silica gel. Moreover, the current studies demonstrate that the hexacyclic heteroarene 3 has high stability against molecular oxygen comparable to DPh-BTBT and DNTT and that 3 has the $E_{\rm H-L}$ value nearly equal to those of them, especially DPh-BTBT.⁵ Finally, owing to the fact that its crystalline structure is columnar in a face-to-face manner, 3 should have a high charge-carrier transportability. Unfortunately, it was turned out that similar ability is not expected for 2, probably due to a poor ordering (a lack of repeating overlap and long π - π spacing distance) in the crystalline state (for the detail, see the Supplementary data). From these points of view, development of **3** as an OFET material is an intriguing subject now being probed in our laboratory.

Acknowledgments

A.Y. gratefully acknowledges financial support (No. 25-304) by the Sasakawa Scientific Research Grant from the Japan Science Society. E.O. acknowledges financial support in the form of a Grant-in-Aid for Young Scientist (B) (No. 24750044) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. K.M. is grateful for financial support in the form of a Grantin-Aid for the Scientific Research (C) (No. 23550058) from the MEXT of Japan. K.M. also thanks the Cooperation for Innovative Technology and Advanced Research in Evolutional Area (Wakayama) program. H.I. gratefully acknowledges financial support in the form of a Grant-in-Aid for Scientific Research on Priority Areas 'New Frontiers in Photochromism' (Nos. 20044027 and 21021025 in the Area No. 471), Innovative Areas ' π -Space' (Nos. 21108520) and 23108718 in the Area No. 2007), and the Grant-in-Aid for Scientific Research on Innovative Areas 'Stimuli-responsive Chemical Species' (No. 24109009), the Scientific Research (B) (Nos. 20044027 and 23350023), and the Challenging Exploratory Research (Nos. 21655016 and 24655037) from the MEXT of Japan.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013. 05.090.

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