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A convenient synthesis of isothianaphthene oligomers and their electrochemical studies

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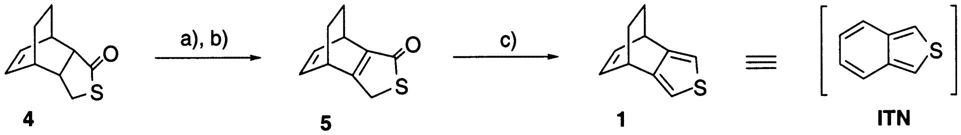
Abstract—Bi- and tri-isothianaphthene-α,ω-dicarbaldehydes were easily synthesized by using 4,7-dihydro-4,7-ethano-2-benzo[*c*]thiophene as a useful synthon of 1,3-unsubstituted isothianaphthene. The UV–vis absorptions of oligo-isothianaphthene derivatives exhibit a considerable bathochromic shift compared to the cases of other oligo-thiophene analogs, and their cyclic voltammetry shows narrowed HOMO–LUMO gaps of the isothianaphthene derivatives. This indicates high efficiency of π-electron delocalization in the oligo-isothianaphthenes along the conjugated backbone. © 2002 Elsevier Science Ltd. All rights reserved.

Since the first synthesis of polyisothianaphthene as a low-band-gap conducting polymer,[1] the subsequent investigations are mainly focused both on improved methods of their preparation and on their physical and chemical studies.[2] Benzo[*c*]thiophene, generally called isothianaphthene (**ITN**), was easily prepared by dehydration of 1,3-dihydrobenzo[*c*]thiophene 2-oxide (Cava's method),[3] and variously substituted analogs of poly(**ITN**) were obtained by oxidative polymerization of the corresponding **ITN** derivatives.[2] Several stable **ITN** derivatives bearing aryl, alkyl, or 2-thienyl groups at 1- and 3-positions could be prepared by the direct ring-forming reactions,[4,5] and Cava and his co-workers have synthesized a mixture of α,ω-bis-TBS **ITN** oligomers by the oxidative coupling reaction of 1,3-bis-TBS **ITN**.[6] However, construction of oligo-**ITN** derivatives is still quite difficult due to the instability of 1,3-unsubstituted **ITN** derivatives. In order to investigate the electrochemical behavior of poly(**ITN**)s at the molecular level, an efficient preparation method for well-defined **ITN** oligomers is necessary. In this paper we report a new method for the preparation of well-defined **ITN** oligomers by using retro Diels–Alder reaction from the oligothiophenes annelated with bicyclo[2.2.2]octadiene (BCOD) rings. As expected from our recent synthesis of isoindole derivatives,[7] BCOD-annelated thiophene **1**, namely 4,7-dihydro-4,7-ethano-2-benzo[*c*]thiophene, was also a useful synthon of 1,3-unsubstituted **ITN**. The electronic properties of a series of α,ω-dialdehyde-capped **ITN** oligomers have also been studied.

Synthesis of the thiophene **1** is summarized in Scheme 1. The Diels–Alder reaction of 2-hydroxythiophene with 1,3-cyclohexadiene gave *endo*-4-thiatricyclo[5.2.2.0^{2,6}]undec-8-en-3-one **4**.[8] The enone **5** was prepared from **4** by selenenylation followed by selenoxide elimination.[9] Reduction with diisobutylaluminium hydride (DIBAL) followed by spontaneous dehydration gave the targeted thiophene **1** in good yield.[10]



Scheme 1. *Reagents and conditions*: (a) LDA, THF, −78°C, 20 min, then PhSeBr, 91%; (b) *m*-CPBA, CH_2Cl_2, −20°C, 2 h, 80%; (c) DIBAL, CH_2Cl_2, −10°C, 30 min, 82%.

Keywords: bicyclo[2.2.2]octadiene; isothianaphthene; retro Diels–Alder reaction.

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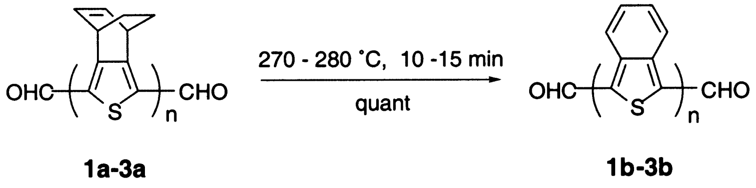
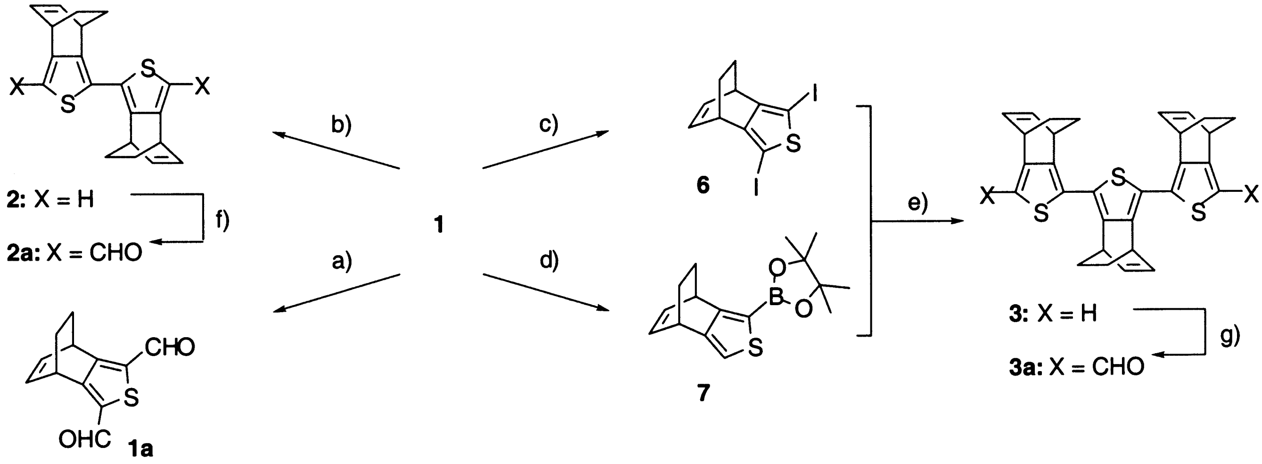
The thiophene **1** is stable at room temperature, and can be easily functionalized at the 1,3-position and oligomerized by various coupling reactions (Scheme 2). Dimer **2** was prepared by oxidative dimerization of lithiated **1** with $CuCl_2$. Trimer **3** was obtained by Pd-catalyzed Suzuki coupling reaction of **6** and **7**. Successive treatment of these oligomers with *n*-butyllithium in the presence of TMEDA and with DMF afforded the corresponding dialdehyde **1a**–**3a**.[11]

Optimum conditions of the thermal decomposition of **1a**–**3a** into the corresponding **ITN** derivatives **1b**–**3b** were investigated. Contrary to the cases of BCOD-annelated pyrrole derivatives,[7] the retro Diels–Alder reaction of **1a**–**3a** proceeded very slowly even at 200°C for 3 h, and most of the starting materials was recovered. When the reaction was carried out at an elevated temperature (270–280°C) for 10–15 min in vacuo (2 mmHg), the retro Diels–Alder reaction occurred smoothly and the color of the reacting materials dramatically changed during the reaction. The **ITN** dimer **2b** and trimer **3b** were obtained in quantitative yields. In the case of **1a**, the reaction was carried out under an inert atmosphere due to its volatility to give **1b** in a quantitative yield. Products **1b**–**3b** are pure enough and they gave satisfactory spectroscopic and analytical data without further purification.[12] The spectroscopic data for **1b** are in good agreement with those previously reported.[13]

The absorption maxima (λ_{max}), the redox potentials and the estimated HOMO–LUMO gaps (ΔE) of **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** are summarized in Table 1. As shown in Table 1, the increasing of the **ITN** units leads to a





Scheme 2. *Reagents and conditions*: (a) *n*-BuLi, TMEDA, *n*-hexane, reflux, 30 min, then DMF, THF, 75%; (b) *n*-BuLi, THF, −10°C, 30 min, then $CuCl_2$, 62%; (c) LDA, THF, 0°C, 30 min, then I_2, 85%; (d) *n*-BuLi, THF, −10°C, 30 min, then pinacol boronate, 70%; (e) $Pd(PPh_3)_4$, K_3PO_4, DMF, 110°C, 24 h, 60%; (f) *n*-BuLi, TMEDA, THF, rt, 30 min, then DMF, 72%; (g) *n*-BuLi, TMEDA, THF, 0°C, 1 h, then DMF, 60%.

Table 1. Electronic absorption and cyclic voltammetric data[a]

Compounds	*n*	λ_{max}/nm ($h\nu_{max}$/eV)[b]	$E_{p(ox)}$/V[c]	$E_{1/2(red)}$/V[c]	ΔE/eV[e]
1a	1	307 (4.04)	1.84[d] (i)	−1.62[d]	3.35
2a	2	361 (3.43)	1.32 (i)	−1.85	2.95
3a	3	387 (3.20)	0.94, 1.24 (i)	−2.02	2.73
1b	1	409 (3.03)	1.49 (i)	−1.26, −1.77	2.70
2b	2	478 (2.59)	0.86 (i)	−1.23, −1.43	2.18
3b	3	537 (2.31)	0.48, 0.83 (i)	−1.23	1.88

(i) Indicates the peak potential of an irreversible process.

[a] Half-wave redox potentials referenced versus Fc/Fc$^+$.

[b] In CH_2Cl_2.

[c] In PhCN, 0.1 mol dm^{-3} TBAP, ref. Ag/Ag$^+$, scan rate 100 mV s^{-1}.

[d] In CH_3CN.

[e] Estimated from the low-energy absorption edge.

considerable bathochromic shift of λ_{max} compared to the cases of the corresponding precursors **1a**–**3a** and other oligo-thiophene analogs.[5e,14] Cyclic voltammetry of the oligomers shows, as expected, that with increasing chain length in both series of compounds **a** and **b** oxidation peaks shifted to less positive potentials. It is also interesting to note that these shifts are larger than those in the alkyl-substituted thiophene oligomers.[15] In addition, the **ITN** derivatives are oxidized at much lower potentials than the corresponding precursors. This is easily understood by taking it into account that the benzo[*c*]thiophene structures of the **b** series, namely *ortho*-quinodimethane structures have the high HOMO energy level and are easy to be oxidized to form the stable radical cation, in which the benzene ring exists.[16] Trimers **3a** and **3b** show two oxidation processes (one reversible and one irreversible wave) indicating the production of both the radical cations and the dications. The reduction potentials negatively shifted as the chain increased in series of **a** compounds. This may be due to the steric bulkiness of the BCOD group, which impedes planarization of the thiophene rings and thus prevents formation of a quinoid structure in the radical anion states. In contrast, the reduction potentials of **1b**–**3b** are shifted to slightly less negative potentials and from two separated 'one-electron' waves to a 'two-electron' wave feature in **3b**. This brings to mind the 'merging wave behavior' described recently[17] and may indicate that in the more extended π-system **3b** the reduction to the radical anion is more costly and that it merges with the reduction to the dianion. The significant reduction of the ΔE values estimated from the low-energy absorption edge in the series of **ITN** derivatives provides these compounds as promising candidates for highly conductive materials.

In conclusion, we have described here a facile method for the preparation of **ITN** oligomers using **1** as a useful synthon of 1,3-unsubstituted **ITN**. This strategy has several advantages. First, introduction of the rigid bulky BCOD ring to the oligothiophenes prevents the intermolecular π–π stacking, so that the solubility is increased and the processability of higher oligothiophenes is enhanced with respect to their applications in molecularly doped organic light-emitting devices (OLEDs). Second, BCOD-annelated thiophenes are chemically stable as normal alkyl-substituted thiophenes, which can be easily oligomerized and functionalized at the 1,3-position. Third, the retro Diels–Alder reaction of these precursors produced the corresponding **ITN** derivatives in quantitative yields in the final step, which is a useful way to control the physical properties of various thiophene oligomers, and both types of oligomers would find their own applications for the optoelectronic devices. Further synthesis of new thiophene-based materials using this retro Diels–Alder strategy is now in progress in our laboratory.

Acknowledgements

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