doi:10.1246/cl.2010.300

Pentaleno[1,2-*c*:4,5-*c*′]dithiophene Derivatives: First Synthesis, Properties, and a Molecular Structure

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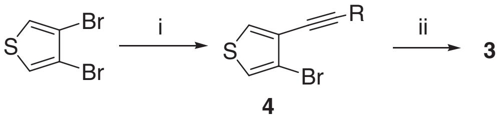
(Received December 28, 2009; CL-091160; E-mail: kawase@eng.u-hyogo.ac.jp)

New π-extended pentalene derivatives bearing two thiophene rings are synthesized from 3-bromo-4-ethynylthiopenes as stable orange crystals by using a nickel complex. The observed electronic properties and molecular structure clearly indicate low contribution of the pentalene π system as predicted by the TD-DFT calculations.

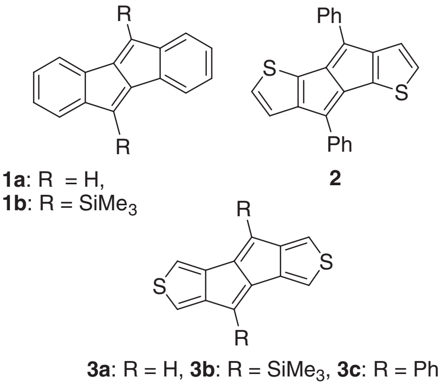
Although various dibenzopentalene derivatives **1** have been known to date, few pentalene derivatives bearing heteroaromatic rings in place of benzene rings have been prepared, probably due to the lack of appropriate synthetic methods.[1] Recently we have found a novel reaction yielding dibenzopentalene derivatives from readily available *o*-bromoethynylbenzenes using commercially available nickel complexes.[2] Independently, Levi and Don Tilley also reported a new pentalene synthesis from 1-bromo(or -iodo)-2-ethynylethylenes using a Pd(0) complex.[3] In the paper, they described the synthesis of a di-(2,3)-thiophene fused pentalene derivative **2**; however, a di-(3,4)-thiophene fused derivative **3** is still elusive (Chart 1). In the course of our study, we synthesized the new π-extended pentalene **3** from 3-bromo-4-ethynylthiophenes using a Ni(0) complex. Their electronic and structural properties are rather different from those of **1**. We here discuss the physical and structural properties of the π-extended pentalenes **3** together with their theoretical studies.

Partial Sonogashira couplings of 3,4-dibromothiophene afforded corresponding 3-bromo-4-ethynylthiophenes, **4a** and **4b**, as reported procedures.[4] Treatments of **4** with a Ni(0) complex, generated from $NiCl_2(PPh_3)_2$ and zinc dust in toluene, furnished the corresponding dithienopentalenes **3b** and **3c** in 18 and 21% yields, respectively (Scheme 1). Neither DME (1,2-dimethoxyethane) nor THF are employed for the solvent. The reactions in these solvents gave complex mixtures. Taking into account that three C–C bonds form in one reaction, the yields would be tolerable.



Scheme 1. Reagents and conditions; i) R–C≡C–H, 5 mol % $PdCl_2(PPh_3)_2$, CuI, NEt_3, reflux for 7 h; **4a**; R = $SiMe_3$, 18%, **4b**; R = Ph, 51%. ii) 1.0 equiv $NiCl_2(PPh_3)_2$, 1.5 equiv Zn, toluene, 110 °C, 12 h; **3b**; R = $SiMe_3$ 18%, **3c**; R = Ph 21%.

Dithienopentalenes **3b** and **3c** are obtained as fairly stable orange crystals, while a dibenzopentalene **1b** is dark red. Bis(trimethylsilyl) derivative **3b** is fairly soluble in low polar organic solvents such as toluene and dichloromethane; however, diphenyl derivative **3c** is rather insoluble in common organic solvents. Then, ^{13}C NMR spectrum of **3c** was not observed clearly. Figure 1 shows their absorption spectra in CH_2Cl_2. The third and second longest absorption bands of **3b** (250–350 and 350–450 nm) are almost identical to those of **1b**. The spectrum of **3c** shows ca. 20 nm of bathochromic shift. The substituent effect is relatively small. On the other hand, the first longest absorption band of **3b** is observed as a shoulder band at about 500 nm, and the band of **3c** would be submerged with the intense second absorption band. The difference of colors is due to the hypsochromism of the longest absorption bands. In contrast to dibenzopentalene derivatives, **3b** shows fluorescence (λ_{max} = 605 nm, Figure S9[6]), but the intensity is considerably weak. On the other hand, **3c** shows no fluorescence.



1a: R = H,
1b: R = $SiMe_3$

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3a: R = H, **3b**: R = $SiMe_3$, **3c**: R = Ph

Chart 1.

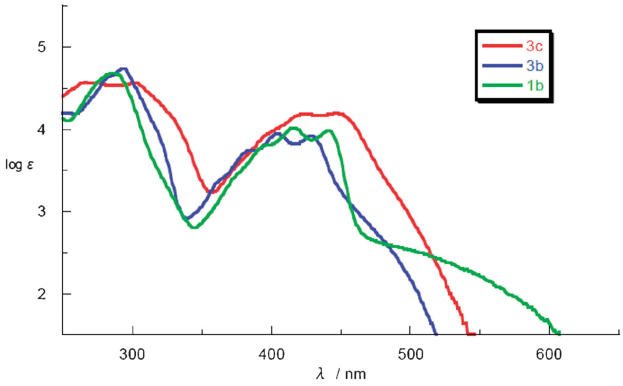

Figure 1. Absorption spectra of **3b**, **3c**, and **1b** in CH_2Cl_2.

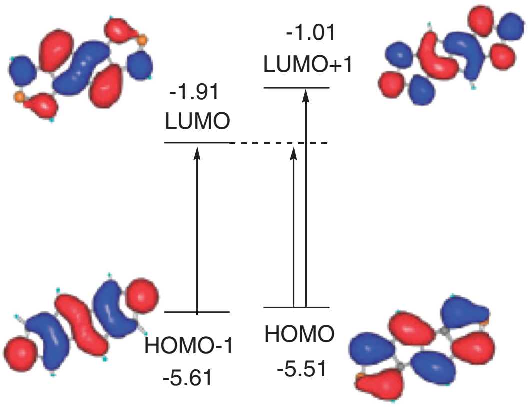

Figure 2. Calculated molecular orbitals and energy diagrams (eV) of **3a**.

The electronic properties of unsubstituted **3a** are calculated with the TD-DFT (RB3LYP/6-31G**) calculation.[5,6] The molecular orbitals and energy diagrams are shown in Figure 2. The TD calculation shows that the longest absorption band of **3a** (S0 → S1 band) is attributable to a HOMO−1 → LUMO transition, which is symmetry-forbidden as a typical character of $4n\pi$ electron systems. An allowed HOMO → LUMO transition occurs at higher energy, and proximity in energy of HOMO−1 and HOMO would lead to near overlap of the both transitions (Figure S1[6]); consistent with the observed absorption spectrum of **3b**. The HOMO–LUMO gap of **1a**[2] (3.13 eV) is considerably smaller than that of **3a** (3.60 eV). The result also agrees with the observation.

Good single crystals of **3b** were collected from an ethanol solution. An ORTEP drawing reveals a planar π-skeleton of **3b**.[7] Two independent molecules exist in the crystal and the molecules have a C_i symmetry. The selected averaged bond lengths are listed in Figure 3. **3b** shows the large bond alternation in the pentalene skeleton and *exo*-butadiene conjugations with regard to the pentalene skeleton. The features are analogous to **1b**, and the degree is largely enhanced. The averaged bond length of the thiophene:pentalene ring fusion of **3b** (1.443 Å) is obviously longer than that of 5:6 ring fusion of **1b** (1.425 Å).[1f] The bond lengths of the thiophene ring are common as 3,4-substituted thiophene derivatives (Figure S3).[6,8] The counterbalance between aromatic stabilization of the thiophene ring and destabilization of the pentalene π system would determine the bond alternation.

The redox properties of **3b** and **3c** were examined by cyclic voltammetry (CV). The cyclic voltamogram of **3b** exhibits a reversible reduction wave (−2.04 V) and an irreversible oxidation wave (+0.90 V) in CH_2Cl_2 solution (Figure S5).[6] But, that of **3c** was not clear, because of low solubility. The oxidation of **3b** readily produced insoluble polymeric materials. The numerical sum of E_{ox} and E_{red} for **3b** (2.94 V) is larger than that of **1b** (2.50 V).[2] The result corresponds to the larger HOMO–LUMO gap of **3a** than that of **1a** as the theoretical prediction.

In conclusion, a nickel(0)-mediated reaction of 3-bromo-4-ethynylthiophenes afforded corresponding di-(3,4)-thienopentalene derivatives as a new π-extended pentalene derivative. Although the yields are not so high, the wide applicability of our method to produce a variety of novel π-conjugated systems with pentalene skeleton can be proven. The electronic properties and the molecular structure indicate low contribution of the pentalene π system. The features are well consistent with theoretical calculations. The measurement of FET properties of the compounds will be examined in due course.

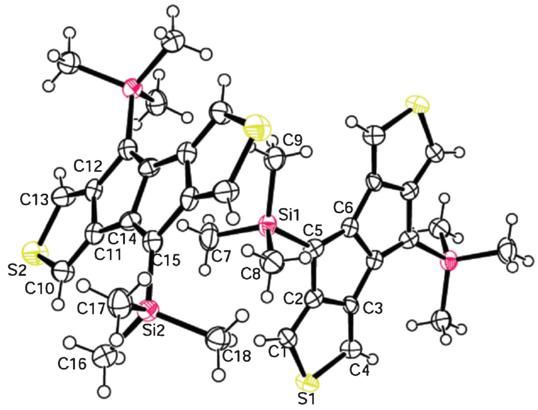

Figure 3. A molecular structure of **3b**: An ORTEP drawing with thermal ellipsoids at 50% probability level. Selected averaged bond lengths (Å) S1–C1 (S2–C13) 1.721, S1–C4 (S2–C10) 1.719, C1–C2 (C13–C12) 1.355, C2–C3 (C11–C12) 1.443, C2–C5 (C11–C14) 1.488, C3–C4 (C11–C10) 1.377, C5–C6 (C14–C15) 1.366, C6–C6′ (C14–C14′) 1.488.

T.K thanks Prof. Don Tilley (Department of Chemistry, University of California at Berkeley) for helpful discussion. This work was supported by the Naito Foundation and a Grant-in-Aid for Scientific Research on Innovative Areas (No. 21108521 A01, “pi-Space”) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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5 The theoretical calculations of **3a** were performed with the Gaussian 03 software package. The details see the Supporting Information.[6]

6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

7 Crystal data for **3b**, triclinic, $P\bar{1}$ (#2), $a = 9.496(1)$ Å, $b = 9.848(1)$ Å, $c = 11.553(2)$ Å, $\alpha = 96.470(5)°$, $\beta = 92.530(4)°$, $\gamma = 116.655(4)°$, $V = 1084.8(7)$ Å^3, Z value = 2, $\mu(\mathrm{Mo}\,K\alpha) = 3.99\ \mathrm{cm}^{-1}$, $T = 200$ K, $R1[F^2 > 2\sigma\ (F^2)] = 0.069$, $wR2$(all data) = 0.209, $S = 1.05$, Refl./param. = 2115/199. CCDC number 761503.

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