ORGANIC
LETTERS

2009
Vol. 11, No. 18
4104−4106

Tetradehydrodinaphtho[10]annulene: A Hitherto Unknown Dehydroannulene and a Viable Precursor to Stable Zethrene Derivatives

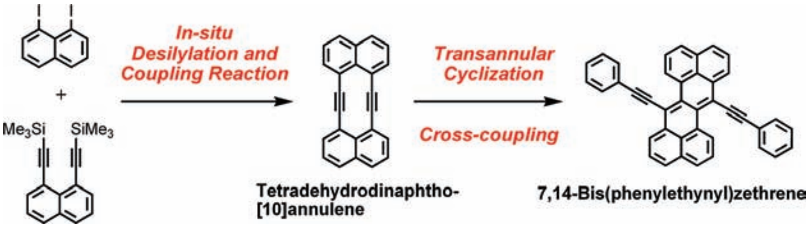
Rui Umeda,[†] Daijiro Hibi, Koji Miki,[‡] and Yoshito Tobe*

Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka 560-8531, Japan

tobe@chem.es.osaka-u.ac.jp

Received July 13, 2009

ABSTRACT



The synthesis and structural characterization of hitherto unknown tetradehydrodinaphtho[10]annulene, a hydrocarbon whose synthesis had been attempted four decades ago, was achieved for the first time. Moreover, the dinaphtho[10]annulene was transformed smoothly into stable zethrene derivatives substituted at its 7,14-positions, showing that it serves as a good reservoir of zethrene derivatives. Optical and electrochemical properties of a disubstituted zethrene derivative are also presented.

About four decades ago, Staab and Sondheimer attempted independently to synthesize tetradehydrodinaphtho[10]annulene (**1**) via cross-coupling of iodo and/or ethynylcopper(I) substituted derivatives of naphthalene by heating in pyridine, but they isolated zethrene (**2a**, dibenzo[*de*,*mn*]naphthacene) in 50 or 22% yield instead of the purported **1**.[1] Although the first synthesis of **2a** was reported by Clar in 1955,[2] the above unexpected finding provides a more convenient access to **2a**,[3] which would potentially serve as an organic semiconductor. Theoretical calculations predict that the HOMO/LUMO gap of **2a** (2.52 eV) is almost equal to that of the well-known semiconductor pentacene (2.40 eV).[4] Computational studies also predict that **2a** would serve as a potential candidate for nonlinear optical (NLO) organic materials.[5] In addition, there are a few patents for the use of derivatives of **2a** in organic electronic devices, though the preparative methods are not reported.[6] However, **2a** was not as well studied as aromatic compounds of related structures like

---

[†] Present address: Faculty of Chemistry, Materials and Bioengineering, Kansai University.

[‡] Present address: Graduate School of Engineering, Kyoto University.

(1) (a) Mitchell, R. H.; Sondheimer, F. *Tetrahedron* **1970**, *26*, 2141–2150. (b) Staab, H. A.; Nissen, A.; Ipaktschi, J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 226. (c) Staab, H. A.; Ipaktschi, J.; Nissen, A. *Chem. Ber.* **1971**, *104*, 1182–1190, The formation of **2a** was interpreted in terms of spontaneous cyclization of **1** to form a diradical intermediate which abstracts hydrogen atoms from the reaction medium.

(2) Clar, E.; Lang, K. F.; Schulz-Kiesow, H. *Chem. Ber.* **1955**, *88*, 1520–1527.

(3) Although the formation of **2a** was invoked in the purported synthesis of dinaphtho[10]annulene too, this method is less practical than the one via reported in ref 1. See ref 1c and the following papers: (a) Kemp, W.; Storie, I. T.; Tulloch, C. D. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2812–2817. (b) Gleiter, R.; Schaaff, H. P.; Rodewald, H.; Jahn, R.; Irngartinger, H. *Helv. Chim. Acta* **1987**, *70*, 480–487.

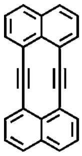
(4) Ruiz-Morales, Y. *J. Phys. Chem. A* **2002**, *106*, 11283–11308.

(5) (a) Knežević, A.; Maksić, Z. B. *New J. Chem.* **2006**, *30*, 215–222. (b) Nakano, M.; Kishi, R.; Takebe, A.; Nate, M.; Takahashi, H.; Kubo, T.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E. *Comp. Lett.* **2007**, *3*, 333–338.

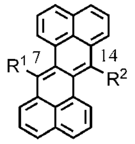
(6) For examples, see: (a) Sotoyama, W.; Sato, H.; Matuura, A. PCT Int. Appl. WO 03/002687, A1, **2003**. (b) Moon, J. M. KR 2007101430, A, **2007**.

10.1021/ol9015942 CCC: $40.75

pentacene[7] because of the still low accessibility and high sensitivity in the presence of oxygen particularly in dilute solution. In this respect, attachment of substituents at the most sensitive 7,14-position of **2a** possessing the largest HOMO coefficients would substantially enhance its kinetic stability as in the case of large acenes.[7a] In this connection, and in view of the interest inherent in the hitherto unknown dehydroannulene **1** itself, we report here the first synthesis and structural characterization of **1** and its transformation into stable 7,14-disubstituted zethrene derivatives **2b** and **2c** based on an electrophile-induced transannular cyclization of **1**.

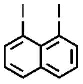


1

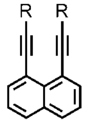


2a; $R^1 = R^2 = H$
2b; $R^1 = R^2 = I$
2c; $R^1 = R^2 = {\equiv}{-}Ph$
2d; $R^1 = H$, $R^2 = I$

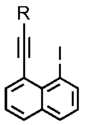
Table 1. In-situ Desilylation and Pd(0)/Cu(I)-catalyzed Coupling Reactions of **5b** or **3** and **4b**[a]



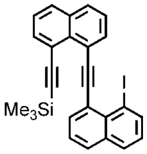
3



4a; R = H
4b; R = $SiMe_3$



5a; R = H
5b; R = $SiMe_3$



6

entry	starting material(s)	additive	products (yield[f])
1	**5b**	H_2O[b]	no reaction[g]
2	**5b**	NaOH/H_2O[c]	no reaction[g]
3	**5b**	TBAF[d]	**2d** (6%)
4	**3** and **4b**	H_2O[b]	**1** (6%), **2d** (trace), **6** (33%)
5	**3** and **4b**	NaOH/H_2O[c]	**1** (22%), **2d** (4%)
6	**3** and **4b**	TBAF[e]	**2a** (<3%)

[a] General reaction conditions: A solution of starting material(s) (0.23 mmol (each), 1 equiv), $Pd(PPh_3)_4$ (0.2 equiv), CuI (0.2 equiv), DBU (2 equiv), and additive in benzene (ca. 8 mL) was stirred at rt for 4−8 h. [b] A few drops. [c] NaOH (1 equiv)/H_2O (0.1 mL). [d] One equivalent of a solution of TBAF in THF. [e] Two equivalents of a solution of TBAF in THF. [f] Isolated yield. [g] Most of starting material **5b** was recovered.

For the synthesis of **1**, we planned to use the Sonogashira-Hagihara reaction that can be performed at ambient temperature to form the C(sp)-C(sp^2) bonds of **1**. First, we examined the reactions of terminal acetylene derivatives with iodides, that is, coupling of 1,8-diiodonaphthalene (**3**) with 1,8-diethynylnaphthalene (**4a**)[1c,8] and self-coupling of 1-ethynyl-8-iodonaphthalene (**5a**),[1b,c] under standard Sonogashira−Hagihara conditions at room temperature. Although a trace amount of **1** was detected in the ^{1}H NMR spectra of the products, the major products were unidentified oligomeric products derived from random coupling and the results lacked reproducibility too. Next, we adopted cross-coupling accompanying in situ desilylation.[9] The optimization results are summarized in Table 1. After several trials, the best result was obtained when the coupling reaction of **3** and **4b** was undertaken in the presence of 1 equiv of aqueous NaOH, furnishing **1** in 22% yield together with monoiodozethrene **2d**[1a] (4%) (entry 5). In the absence of NaOH, the reaction terminated at the stage of single coupling product **6**[1a] (entry 4). To the contrary, desilylation-coupling reaction of iodoethynyl derivative **5b** under similar conditions did not give the desired product **1**, resulting in recovery of the starting material (entries 1 and 2).[10] However, the use of powerful desilylation reagent (TBAF) was not useful (entries 3 and 6). It is worth noting that **1** is easily handled without any visible decomposition at room temperature, in contrast to the structurally resembled compounds such as tetradehydro[10]annulene[11] and dinaphtho-[8] and diacenaphthooctadehydro[14]annulenes.[12] The aromatic protons of **1** resonate at 7.80 (dd), 7.71 (dd), and 7.45 (dd) ppm, indicating that **1** does not exhibit 10π aromaticity.[13] In accord with this observation, the NICS value (+1.45) at the center of the 10π system of **1** suggests its nonaromatic character.[14] Compound **1** exhibits strong fluorescence at 422 and 448 nm with a quantum yield of 0.91 as shown in Figure 1 and Table S1 (Supporting Information).

An X-ray crystallographic structure analysis of **1** (Figure 2) showed that the bond lengths and bond angles of its [10]annulene framework are in good agreement with the calculated values.[14] As expected from the ^{1}H NMR study, the [10]annulene framework of **1** clearly exhibits bond length alternation (Table S2, Supporting Information). The acetylene units are almost linear with bending angles of less than 5° and the π-conjugated backbone is distinctly planar. The crystal packing structure revealed that $\pi-\pi$ stacking interactions of the two naphthalene units lead to the formation of a dimeric unit, which contacts with two neighboring dimeric units by $\pi-\pi$ stacking and CH/π interactions, respectively, furnishing an alignment classified as sandwich-herringbone.[15]

---

(7) For recent reviews, see: (a) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452–483. (b) Ruiz, R.; Choudhary, D.; Nickel, B.; Toccoli, T.; Chang, K.-C.; Mayer, A. C.; Clancy, P.; Blakely, J. M.; Headrick, R. L.; Iannotta, S.; Malliaras, G. G. *Chem. Mater.* **2004**, *16*, 4497–4508. (c) Katz, H. E. *Chem. Mater.* **2004**, *16*, 4748–4756.

(8) Mitchell, R. H.; Sondheimer, F. *Tetrahedron* **1968**, *24*, 1397–1405.

(9) In-situ desilylation and Pd(0)/Cu(I)-catalyzed coupling methods were reported previously: (a) Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199–3202. (b) Wan, W. B.; Kimball, D. B.; Haley, M. M. *Tetrahedron Lett.* **1998**, *39*, 6795–6798.

(10) We do not understand the reason for the innertness of **5b** under the basic conditions.

(11) Myers, A. G.; Finney, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 10986–10987.

(12) Palmer, G. J.; Parkin, S. R.; Anthony, J. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 2509–2512.

(13) For example, the aromatic protons of 1,8-diethynylnaphthalene (**4a**) resonate at 7.85−7.80 (m, 4H) and 7.42 (dd, 2H) ppm (300 MHz, $CDCl_3$).

(14) The structure optimization was carried out by DFT method with the B3LYP/6-31G(d) basis-set and the NICS value was calculated by GIAO-HF/6-31G(d) using Gaussian 03.

(15) (a) Desiraju, G. R.; Gavezzotti, A. *J. Chem. Soc., Chem. Commun.* **1989**, 621–623. (b) Gavezzotti, A.; Desiraju, G. R. *Acta Crystallogr., Sect. B* **1988**, *44*, 427–434.

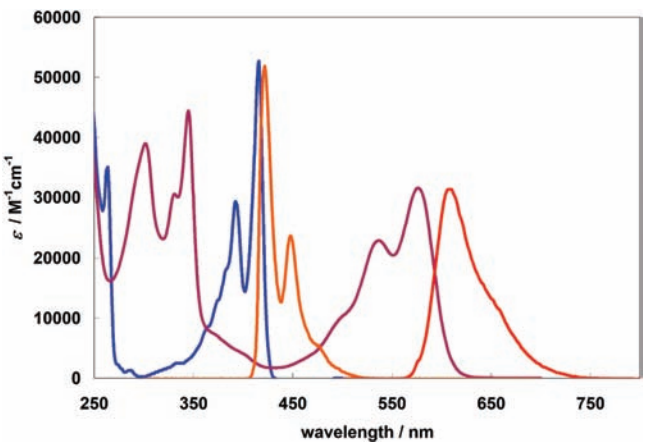


Figure 1. UV−vis (blue line) and FL (orange line) spectra of **1** and UV−vis (purple line) and FL (red line) spectra of **2c** in CH_2Cl_2 at 25 °C. The FL intensities are normallized to the corresponding lowest energy absorption bands.

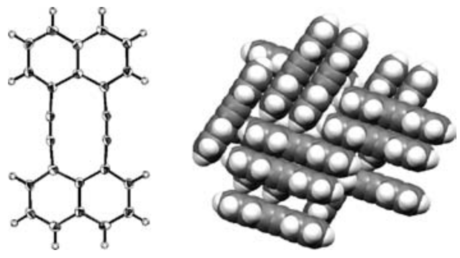


Figure 2. ORTEP drawing (left) and crystal packing (right) of **1**.

Treatment of a solution of **1** in $CHCl_3$ with I_2 at room temperature afforded **2b** in 65% isolated yield as a sole product. With the key intermediate **2b** for functionalization at the 7,14-positions of the zethrene framework in hand, we undertook cross-coupling reaction with an acetylene derivative. Thus, reaction of **2b** with phenylacetylene gave 7,14-bis(phenylethynyl)zethrene (**2c**) in 65% yield. The zethrene derivatives **2b** and **2c** display significantly enhanced stability than extremely sensitive **2a**.[16] UV−vis absorption maxima (CH_2Cl_2) of **2c** are observed at 576 (31600) and 537 (22900) nm and its fluorescence emission at 610 nm with a quantum yield of 0.07 (Figure 1 and Table S1, Supporting Information). To evaluate the electrochemical properties of **2c**, cyclic voltammetry measurement was undertaken (Figure 3). As shown in Figure 3, **2c** showed reversible first oxidation and reduction waves at $^{ox}E_1 = 0.29$ and $^{red}E_1 = -1.64$ V vs ferrocene/ferrocenium (Fc/Fc$^+$), respectively. In addition, irreversible second oxidation and reduction waves were observed at $^{ox}E_2 = 0.79$ V and $^{red}E_2 = -2.03$ V vs Fc/Fc$^+$, respectively. The first oxidation and reduction potentials of **2c** are comparable to those of pentacene[17] and its bis(triisopropylsilyl)ethynyl derivative,[18] suggesting that **2c** may serve as a good organic semiconductor.

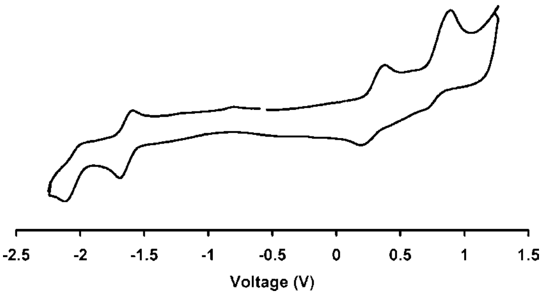


Figure 3. Cyclic voltammogram of **2c** (1.0 mM, V versus (Ag/Ag$^+$) in 0.1 M with nBu$_4$NClO$_4$ in CH_2Cl_2, scan rate: 100 mV/s, working electrode Pt, Fc/Fc$^+$ = 0 V).

In conclusion, the first synthesis of tetradehydrodinaphtho[10]annulene (**1**) was achieved by in situ desilylation and a cross-coupling reaction. Annulene **1** was transformed smoothly into stable zethrene derivatives **2b** and **2c** having substituents at the 7,14-positions based on transannular cyclization of the proximate triple bonds. Thus, **1** turned out to serve as a good reservoir for 7,14-disubstituted zethrene derivatives. Preparation of other zethrene derivatives and investigation of their physical properties are currently underway.

Acknowledgment. We thank Dr. I. Hisaki (Graduate School of Engineering, Osaka University) for helpful discussion about X-ray crystallography. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental details, spectroscopic data; X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OL9015942

---

(16) Neither dilute solutions of **2b** and **2c** were sensitive to light and oxygen. When heated, solid samples of **2b** and **2c** started to decompose from 120 and 220 °C, respectively, and did not show melting points.

(17) $^{ox}E = 0.3$ V, $^{red}E = -1.87$ V, vs Fc/Fc$^+$ in $C_6H_4Cl_2$: Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S *J. Am. Chem. Soc.* **2004**, *126*, 8138–8140.

(18) $^{ox}E_1 = 0.38$ V, $^{red}E_1 = -1.72$ V, $^{red}E_2 = -2.23$ V, vs Fc/Fc$^+$ in THF: Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7*, 3163–3166.