Helically Twisted Tetracene: Synthesis, Crystal Structure, and Photophysical Properties of Hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene

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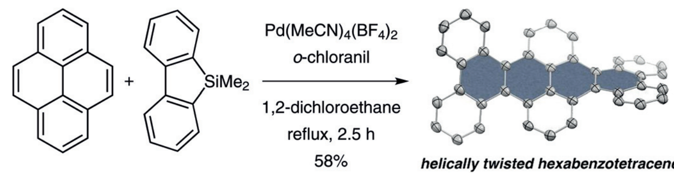

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Abstract The synthesis, X-ray crystal structure, and photophysical properties of unsubstituted hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene are described. Unlike the previously reported *tert*-butyl-substituted analogues, unsubstituted hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene showed a helically twisted conformation in the solid state. Density functional theory calculations on the possible conformers were also studied.

Key words hexabenzotetracene, twisted acenes, polycyclic aromatic hydrocarbons, nonplanar π-system

Acenes, a class of polycyclic aromatic hydrocarbons (PAHs) consisting of linearly fused benzene rings, can be twisted by bulky substituents, benzannulation, or a combination of the two.[1] Owing to their nonplanar and chiral structures, helically twisted acenes (Figure 1, a) have been paid attention by organic chemists. Because of the growing interest and importance of nonplanar PAHs in materials science,[2] efficient synthetic methods such as direct C–H arylation reaction of PAHs have been highly demanded.[3]

Recently, we developed a K-region-selective annulative π-extension (APEX) reaction of PAHs as an effective way to grow the π-system of PAHs in a step-economical fashion.[4] We herein report the single-step synthesis of unsubstituted hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene (**1**) from pyrene and dibenzosilole using our palladium-catalyzed APEX reaction. Helically twisted structure of **1** was revealed by X-ray crystallography. These results were somewhat surprising because previously reported X-ray structures of *tert*-butyl-substituted hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracenes[5] were not 'helical' but rather 'waggling'[6] conformations (Figure 1, b). Adding to the synthesis and X-ray crystallography of **1**, conformational analysis of **1** was also investigated by density functional theory (DFT) calculations.

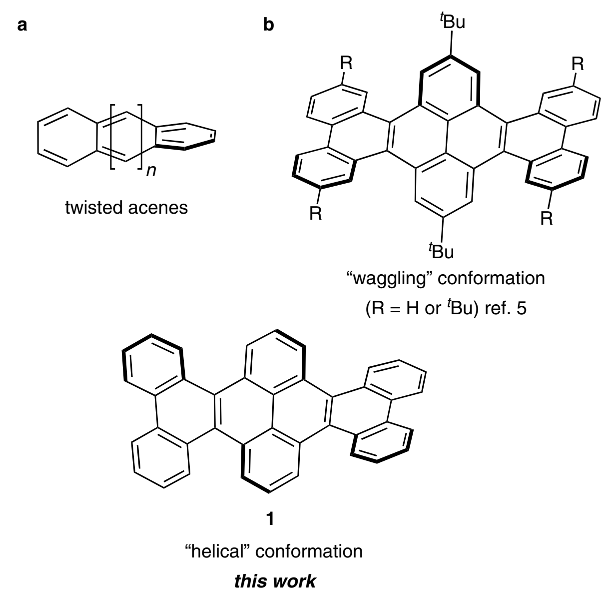
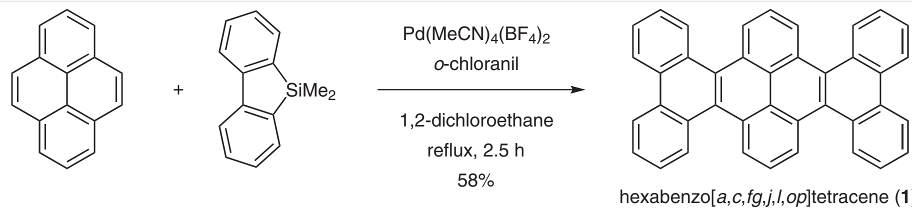


Figure 1 (a) Twisted acenes. (b) Two conformations ('waggling' and 'helical') of hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracenes.

Unsubstituted hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene (**1**) was synthesized by a palladium-catalyzed double C–H/C–Si coupling, a so-called APEX reaction. A mixture of pyrene (1 equiv) and 5,5-dimethyldibenzo[*b*,*d*]silole (3 equiv) in 1,2-dichloroethane was heated under reflux conditions for 2.5 hours in the presence of $Pd(MeCN)_4(BF_4)_2$ (5 mol%) and *o*-chloranil (4 equiv) to afford **1** in 58% yield (Scheme 1).[7] The product was identified by NMR spectroscopy (^{1}H and ^{13}C) and high-resolution mass spectrometry. In spite of the unsubstituted PAH structure, **1** showed sufficient solubility for purification and analysis (8.9 mg/mL in 1,1,2,2-tetrachloroethane), which may be due to the nonplanar struc-



Scheme 1 Synthesis of hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene (**1**)

ture. High thermostability of **1** was also observed when the crystal of **1** was heated over 300 °C.

The structure of **1** was confirmed by X-ray crystallography.[8] Suitable single crystal of **1** was obtained from tetrahydrofuran/pentane solution. Unlike previously reported waggling conformations of *tert*-butyl-substituted hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene derivatives,[5] **1** adopts a helically twisted conformation as shown in Figure 2 (a). The end-to-end twisted angle of the tetracene moiety of **1** is 80.5°, which is higher than those of previously reported unsubstituted benzannulated acenes.[9] The highly twisted structure of **1** was realized by the combination of four [4]helicene substructures. The packing mode of **1** in the crystal is shown in Figure 2 (b). Similar to dibenzo[*g*,*p*]chrysene,[10] one-dimensional π-π stacking of the nonplanar π-systems was found.

The conformation of **1** was studied by DFT calculations with the B3LYP/6-31G(d) level of theory. Seven isomers including two pairs of enantiomers of **1** could be generated by the combination of the chirality of each [4]helicene moiety (***P*** or ***M***) as shown in Figure 3. The twisted form **1a** observed by X-ray crystallography was the most stable conformation among the five ground states **1a**–**e**. The Gibbs free energy of the waggling conformation **1b** is 0.6 kcal mol^{-1}, which is higher than that of **1a**. The conformation of **1d**, which was observed in a chlorinated hexabenzo[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene derivative,[11] has 3.7 kcal mol^{-1} higher energy in the case of **1**. The other conformer **1e** was much unstable (17.4 kcal mol^{-1}) relative to **1a**. Then, the isomerization pathway from **1a** to **1b** was determined to gain insight into whether conformation **1a** was a thermodynamic product or a kinetic product. From **1a** to **1b**, one intermediate **1c** and two transition states (**TSa–c** and **TSb–c**, Figure 4) were found and the rate-determining step was determined to be **TSb–c**. Two additional transition states, **TSc–d** and **TSc–e**, were also found (see the Supporting Information for detail). Considering the energy value of **TSb–c** (10.6 kcal mol^{-1}) relative to that of **1a**, the isomerization between **1a** to **1b** can easily proceed under ambient temperature. It was also found that the isomerization barrier was almost the same (11.1 kcal mol^{-1}) in the case of the di-*tert*-butyl derivative of **1** (**1′**). Thus, the helical and waggling conformations of **1** interconverted into the solution state, and the conformation in the crystalline state was controlled by the packing interaction: π-π interaction (**1**) or C–H-π interaction (**1′**).[5]

The photophysical properties of **1** in the solution state were measured. Figure 5 shows absorption and fluorescence spectra of the diluted cyclohexane solution of **1**. The absorption peaks were observed at 267, 310, 324, 375, and 394 nm, and the fluorescence spectrum had two peaks at 418 and 430 nm when a solution was excited at 325 nm. A bluish-green fluorescence of **1** with a moderate quantum yield (Φ_F = 0.31) was observed.

In summary, we have investigated the synthesis, X-ray crystal structure, and photophysical properties of unsubsti-

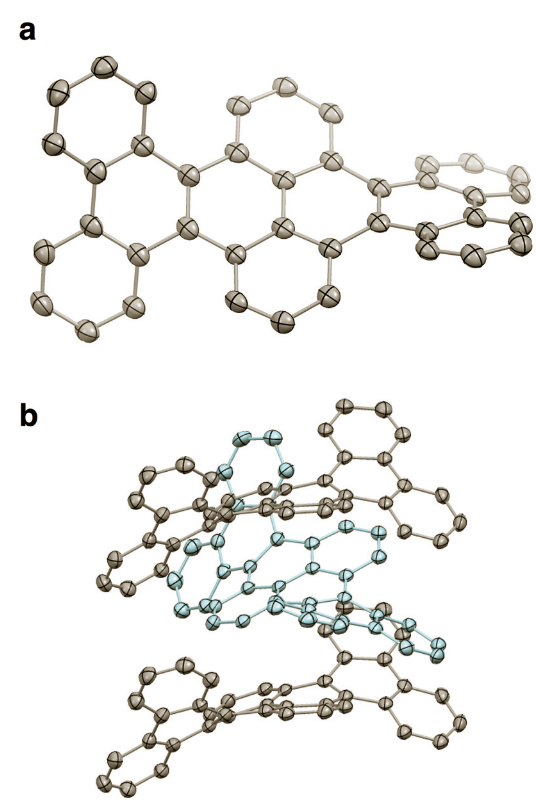


Figure 2 (a) ORTEP drawings of **1** with 50% probability; all hydrogen atoms are omitted for clarity. (b) Packing structure of **1**.

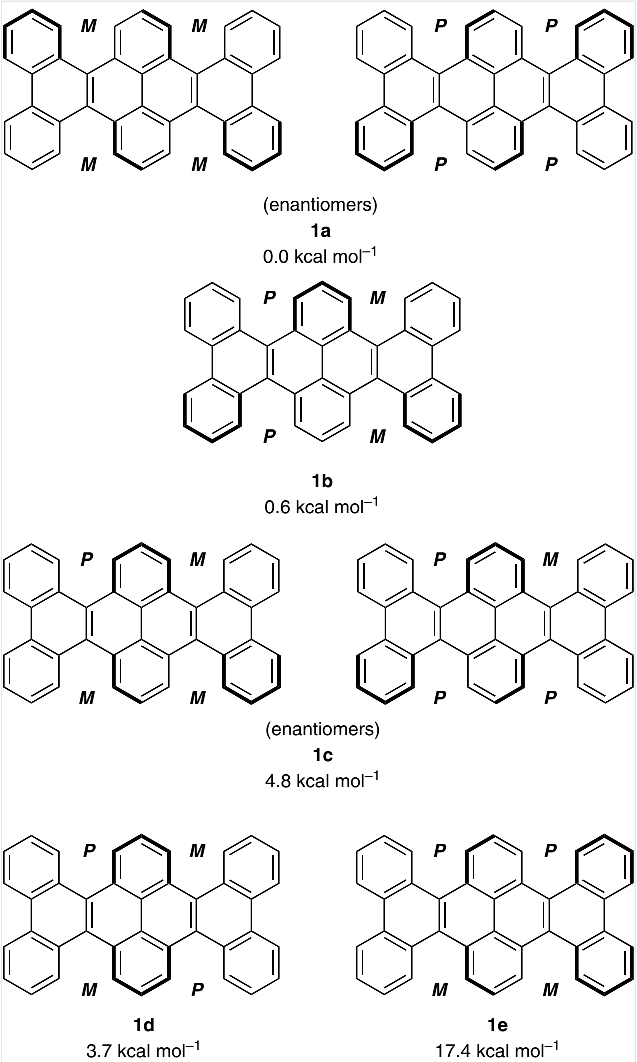


Figure 3 Seven conformers of **1** with Gibbs free energies (kcal mol^{-1}) relative to that of **1a**. Chirality of each [4]helicene moiety is represented by ***P*** or ***M***.

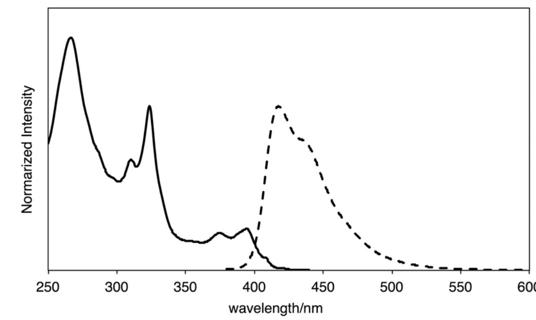


Figure 5 UV–vis absorption (solid line) and fluorescence (broken line) of cyclohexane solution of **1**

tuted hexabenzo[*a,c,fg,j,l,op*]tetracene (**1**). The palladium-catalyzed oxidized double C–H/C–Si coupling, an APEX reaction, smoothly supplied **1** in one step from commercially available materials. Unlike the previously reported derivatives of **1**, the structure of **1** observed by X-ray crystallography was a helical conformation. The twist angle of the tetracene moiety of **1** (80.5°) was the highest among the tetracene moieties in unsubstituted benzannulated acenes. Further structural analysis by using DFT calculations indicated that helical (**1a**) and waggling conformations (**1b**) could be interconverted in the solution state.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561455.

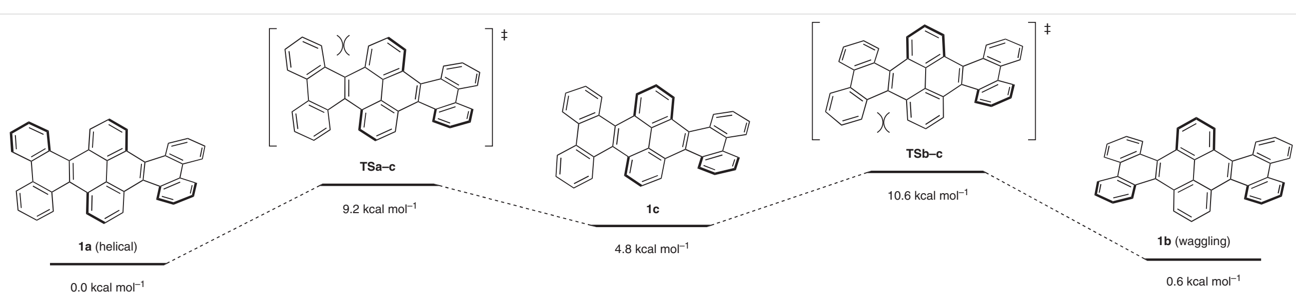

Figure 4 Isomerization pathway from **1a** to **1b** calculated with the B3LYP/6-31G(d) level of theory with Gibbs free energy values (1 atm, 298.15 K, gas phase).

References and Notes

(1) (a) Pascal, R. A. *Chem. Rev.* **2006**, *106*, 4809. (b) Rickhaus, M.; Mayor, M.; Juricek, M. *Chem. Soc. Rev.* **2016**, *45*, 1542.

(2) Reviews on nonplanar π-systems: (a) Rieger, R.; Müllen, K. *J. Phys. Org. Chem.* **2010**, *23*, 315. (b) Dodziuk, H. *Strained Hydrocarbons: Beyond the van't Hoff and Le Bel Hypothesis*; Wiley-VCH: Weinheim, **2009**. (c) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, **1997**. (d) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868. (e) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843.

(3) Reviews on C–H arylation of PAHs: (a) Wencel-Delord, J.; Glorius, F. *Nat. Chem.* **2013**, *5*, 369. (b) Segawa, Y.; Maekawa, T.; Itami, K. *Angew. Chem. Int. Ed.* **2015**, *54*, 66.

(4) Ozaki, K.; Kawasumi, K.; Shibata, M.; Ito, H.; Itami, K. *Nat. Commun.* **2015**, *6*, 6251.

(5) Kumar, B.; Strasser, C. E.; King, B. T. *J. Org. Chem.* **2012**, *77*, 311.

(6) (a) Zhong, Y.; Kumar, B.; Oh, S.; Trinh, M. T.; Wu, Y.; Elbert, K.; Li, P.; Zhu, X.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2014**, *136*, 8122. (b) Qian, H.; Negri, F.; Wang, C.; Wang, Z. *J. Am. Chem. Soc.* **2008**, *130*, 17970.

(7) **Synthesis of Hexabenzo[*a,c,fg,j,l,op*]tetracene (1)**
To a 10 mL Schlenk tube containing a magnetic stirring bar were added pyrene (81.0 mg, 400 µmol), 5,5-dimethyldibenzo[*b,d*]silole (253 mg, 1.20 mmol), *o*-chloranil (394 mg, 1.60 mmol), and $Pd(MeCN)_4(BF_4)_2$ (8.9 mg, 20 µmol). After dry DCE (4 mL) was added via a syringe through the septum, the septum was then replaced with argon-balloon-equipped condenser. The resultant mixture was stirred at reflux for 2.5 h. After the reaction mixture was cooled down to room temperature, this mixture was passed through a short pad of silica gel, washed with CH_2Cl_2, and solvents were removed under reduced pressure. The residue was subjected to silica gel chromatography (hexane–CH_2Cl_2, 10:1) to afford **1** (116 mg, 58%) as a white solid.
^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.70 (t, J = 7.1 Hz, 4 H), 7.77 (t, J = 7.1 Hz, 4 H), 8.12 (t, J = 7.5 Hz, 2 H), 8.81 (d, J = 8.2 Hz, 4 H), 8.88 (d, J = 8.2 Hz, 4 H), 8.99 (d, J = 7.5 Hz, 4 H). ^{13}C NMR (150 MHz, $C_2D_2Cl_4$): δ = 123.6 (CH), 124.2 (C_q), 125.6 (CH), 125.8 (CH), 126.8 (CH), 127.0 (CH), 127.7 (C_q), 128.1 (C_q), 128.5 (CH), 129.3 (C_q), 130.8 (C_q). HRMS–FAB: *m/z* calcd for $C_{40}H_{22}$ $[M]^+$: 502.1716; found: 502.1719; mp >300 °C. All other experimental procedures and characterization data of **1** can be found in the Supporting Information.

(8) **Crystal Data of 1**
Rigaku MicroMax007HF with PILATUS diffractometer, graphite-monochromated Mo Kα radiation (λ = 0.71075 Å), formula: $C_{44}H_{22}$, *FW* = 502.58, *T* = 123(2) K, monoclinic, $P2_1/a$, a = 7.839(4) Å, b = 26.538(11) Å, c = 11.640(5) Å, β = 98.627(12)°, V = 2394.1(19) Å^3, Z = 4, D_{calc} = 1.394 g/cm^3, μ = 0.079 mm^{-1}, F(000) = 1048, crystal size: 0.20 × 0.20 × 0.01 mm^3, θ range: 3.04–25.00°, reflections collected: 29984, independent reflections: 4172, R_{int} = 0.0760, param.: 361, GOF on F^2: 1.121, R_1 = 0.0832, wR_2 = 0.2285 ($I > 2\sigma(I)$), R_1 = 0.1036, wR_2 = 0.2634 (all data) The structures were solved by direct methods with SIR-97 and refined by full-matrix least-squares techniques against F^2 (SHELXL-97). The intensities were corrected for Lorentz and polarization effects. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC 1450739 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

(9) (a) Muir, K. W.; Robertson, J. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 879. (b) Fujisawa, S.; Oonishi, I.; Aoki, J.; Ohashi, Y.; Sasada, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3424. (c) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1988**, *44*, 77. (d) Rossman, M. G. *J. Chem. Soc.* **1959**, 2607. (e) Izuoka, A.; Wakui, K.; Fukuda, T.; Sato, N.; Sugawara, T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 900. (f) Robertson, J. M.; Trotter, J. *J. Chem. Soc.* **1959**, 2614.

(10) (a) Herbstein, F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35*, 1661. (b) Thulstrup, E. W.; Spanget-Larsen, J.; Waluk, J. *Theor. Chim. Acta* **1994**, *89*, 301.

(11) Zöphel, L.; Berger, R.; Gao, P.; Enkelmann, V.; Baumgarten, M.; Wagner, M.; Müllen, K. *Chem. Eur. J.* **2013**, *19*, 17821.