



Synthesis of a three-dimensional spiro-annulated polycyclic aromatic hydrocarbon

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ABSTRACT

We describe the results of our investigation on the preparation, structural characterization, and optical properties of a spiro-annulated polycyclic aromatic hydrocarbon prepared by the cyclodehydrogenation of a hexa{2-(9,9'-spirobifluorenyl)}benzene precursor molecule. Single-crystal X-ray diffraction analysis reveals that the anthracene backbone adopts one of the largest end-to-end twists thus far reported.

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Over the past few decades, 9,9'-spirobifluorene (SBF) has been recognized as a relatively rigid three-dimensional segment for the construction of well-defined oligomers and polymers with high glass transition temperatures, good thermal stability, and no long-wavelength emission.¹ These features allow them to be considered for a variety of applications including light-emitting diodes,² photovoltaic cells,³ plastic lasers,⁴ and field-effect transistors.⁵ Approaches have been reported to incorporate SBF units into molecular assemblies to study intramolecular photo-induced electron and energy-transfer processes, combining architectural and optical properties at a single chromophore level.⁶

The planarization of three-dimensional oligophenylenes by oxidative cyclodehydrogenation has facilitated the rapid advancement of polycyclic aromatic hydrocarbon (PAH) chemistry.⁷ However, as a consequence of the geometry of precursor molecules, the outcome of the cyclodehydrogenation can inadvertently result in a completely different three-dimensional architecture than was originally predicted, such as propeller-shaped molecules,⁸ 'double-concave' graphenes,⁹ and 3D-graphitic materials.¹⁰ Recently, Pei and co-workers have reported the synthesis of molecules **1a–b** with three-dimensional architectures in which trigonal SBF units are combined to exhibit excellent photophysical characteristics (Fig. 1).¹¹ This finding prompted us to explore new three-

dimensional spiro-annulated PAHs under traditional cyclodehydrogenation conditions.

Spiro-annulated PAH **6** was synthesized in three simple steps from commercially available starting materials (Scheme 1). The synthesis of the symmetric di{2-(9,9'-spirobifluorenyl)}-acetylene **4** was based on a stille-type coupling of 2-bromo-9,9'-spirobifluorene **3**¹² with bis(tributylstannyl) acetylene in moderate yield

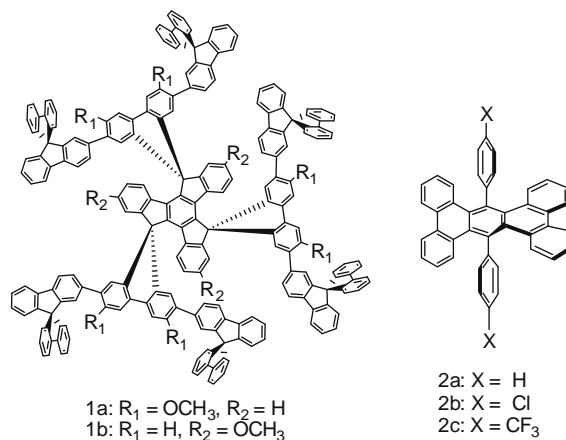
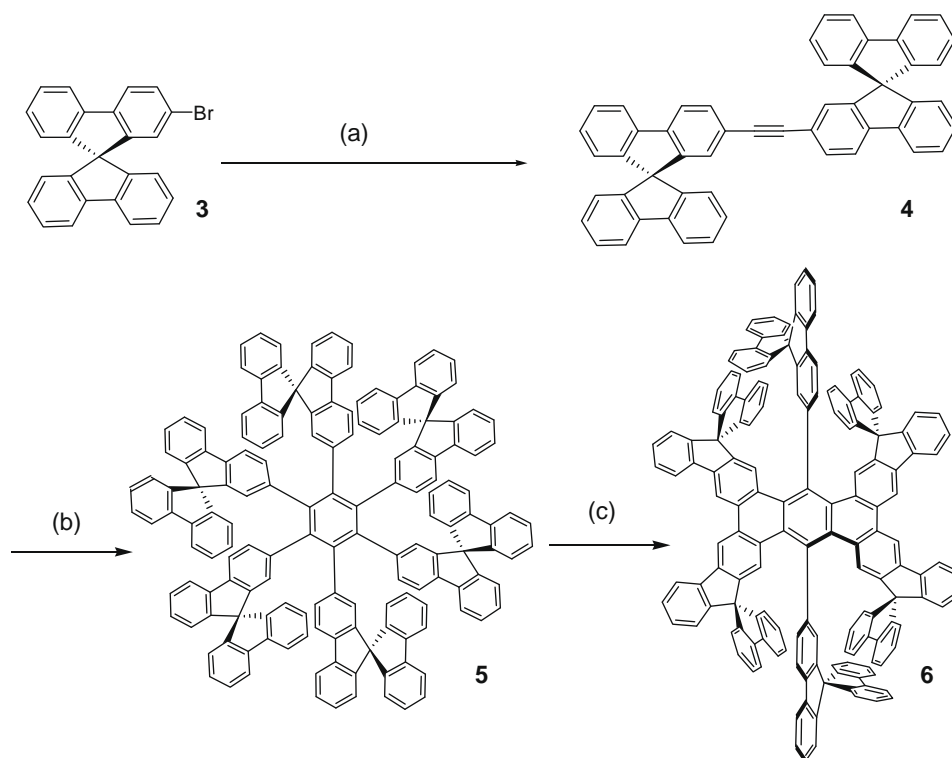


Figure 1. Structures of 3D molecules **1a–b** and diaryltetrabenz[*a,c,h,j*]anthracenes **2a–c**.

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Scheme 1. Reagents and conditions: (a) bis-(tributylstannyl)-acetylene, Pd(PPh₃)₄, toluene, 120 °C, 12 h, 62%; (b) Co₂(CO)₈, 1,4-dioxane, 100 °C, 16 h, 92%; (c) FeCl₃, CH₂Cl₂, rt, 30 min, 80%.

(62%). Subsequent Co₂(CO)₈-catalyzed cyclotrimerization of **4** yielded the hexa{2-(9,9'-spirobifluorenyl)}benzene precursor molecule **5** as a white solid in 92% yield. An intramolecular oxidative cyclodehydrogenation reaction, followed by reductive work-up with methanol, was then carried out to afford the spiro-annulated PAH **6**, generating new C–C bonds between two pairs of adjacent SBF groups. The crude product was purified by column chromatography on silica gel to give **6** as a light-yellow solid in 80% yield for the final step. In addition, the structure and purity of **5** and **6** were confirmed by ¹H NMR, ¹³C NMR, HRMS, and X-ray single-crystal analyses.

The spiro-configured compound **5** is readily soluble in common organic solvents, for example, dichloromethane, tetrahydrofuran, and toluene, but **6** has limited solubility in these solvents. Compounds **5** and **6** are sensitive to chloroform, readily forming unidentified dark impurities at room temperature. The UV–vis absorption and fluorescence spectra of **5** and **6** were measured in tetrahydrofuran solution (Fig. 2). Precursor molecule **5** exhibits a strong absorption band in the ultraviolet region at 309 nm, and a blue emission band with a maximum at 370 nm (Stokes shift is 61 nm). Spiro-annulated PAH **6** displays well-resolved spectra with the absorption and emission maxima at 379 nm and 478 nm, respectively, a remarkable wavelength shift that shows **6** to be green light-emitting. The sizeable Stokes shift of 99 nm suggests that the core of this PAH is extremely twisted. Furthermore, in tetrahydrofuran solution, the fluorescence quantum yields of **5** and **6** were measured to be 0.47 and 0.22, respectively, by the optically dilute method with quinine bisulfate ($\Phi_f = 0.55$ in 1.0 M H₂SO₄) as the reference.¹³

To better understand their three-dimensional structure, single-crystal X-ray diffraction analyses were conducted for **5** and **6**.¹⁴ Colorless crystals of **5** suitable for X-ray analysis were obtained by slow evaporation of tetrahydrofuran and acetonitrile

at room temperature. The crystal lattice of **5** belongs to the monoclinic P2₁/c space group and shows **5** sitting on an inversion center (Fig. 3).¹⁵ The steric congestion of adjacent SBF groups forces the outer fluorene units to flip up and down in an alternating manner with respect to the inner phenyl plane, giving the molecule a pseudo-threefold rotation axis. The SBF groups attached to C2/C2A are arranged nearly orthogonally to the phenyl plane with a dihedral angle of 85.6°. The dihedral angles between the other SBF planes and the central phenyl plane deviate significantly from 90° (61.7° and 62.7°, respectively). The nonbonded distances between the ipso-position of the SBF groups (C29A–C4A, C4A–C54, and C54–C29) are shorter (2.92, 2.92 and 2.94 Å) than the sum of the van der Waals radii of two C sp² atoms (3.45 Å), suggesting a possible through-space interaction between them. Also of note is the existence of atropisomerism as a consequence of restricted rotation of the SBF groups, which can be proved by multiple sets of resonances in the ¹H NMR data at different temperatures (from 193 to 298 K). Separation of isomers was not attempted here, and is likely a difficult but interesting endeavor.

Yellow crystals of **6** suitable for X-ray analysis were obtained by slow evaporation of toluene at room temperature. The molecules of **6** (along with two partially disordered toluene molecules) crystallize in the orthorhombic space group *Pbcn* (Fig. 4).¹⁶ The molecular core is found to be markedly twisted as a consequence of the presence of pronounced steric hindrance including peri-interactions. It adopts a twist-boat conformation that twists the molecule about the long axis of the tetrabenzo[*a,c,h,j*]anthracene skeleton in order to relieve severe hydrogen-carbon steric interactions between the bulky SBF substituents. The dihedral angle between the SBF planes (C1–C6) and the anthracene core deviates clearly from orthogonality, at 65.1°. The anthracene nucleus is twisted by 58.3° end-to-end

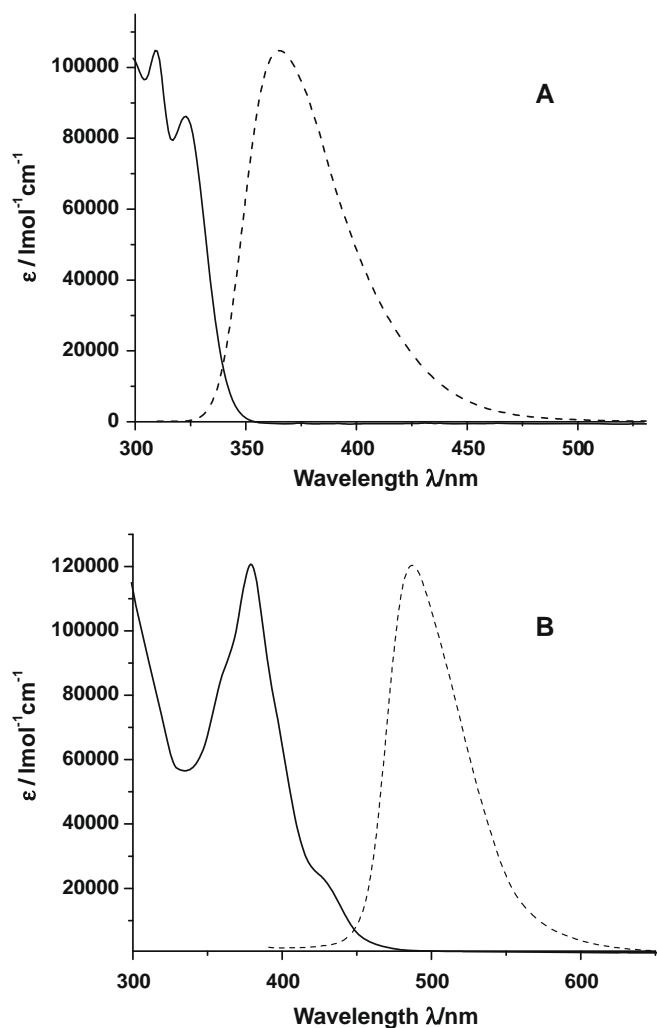


Figure 2. UV-vis absorption (solid line) and emission (dashed line) spectra of **5** (A) and **6** (B) measured in tetrahydrofuran solution at room temperature, and excited at absorption maxima for emission spectra.

(C29–C55/C29A–C55A torsion angle). Each ring of the anthracene unit exists in a shallow twist-boat conformation with the central ring experiencing the greatest torsional twist (24.7°), compared with the terminal rings (16.8°). The C–C bond lengths of the anthracene central ring are almost uniform (1.42 \AA), but the two adjacent rings show substantial bond alternation with long bonds averaging to 1.47 \AA and the short bonds averaging to 1.42 \AA .

The conformation of **5** provides an indicator of how cyclodehydrogenation is likely to occur. The spatial overcrowding prohibits the full planarization of all groups attached to the central ring. Two pairs of the periphery SBF groups undergo dehydrogenation cyclization to spirobifluorene-annulated anthracene skeleton and two SBF groups remain nonreacted. The two remaining SBF groups must be para to each other, otherwise the anthracene skeleton would have lost symmetry. The molecule **5** should turn the two ortho-SBF groups into each other and close the distance between two hydrogen atoms (at C54/C4A and C54A/C4, Fig. 3) until H_2 split-off and C–C bond formation occur simultaneously. The mechanism's pathway may follow the arenium cation mechanism: the peripheral SBF group is protonated, and the resulting electrophilic π complex reacts with ortho-SBF group to generate a new C–C bond.¹⁷

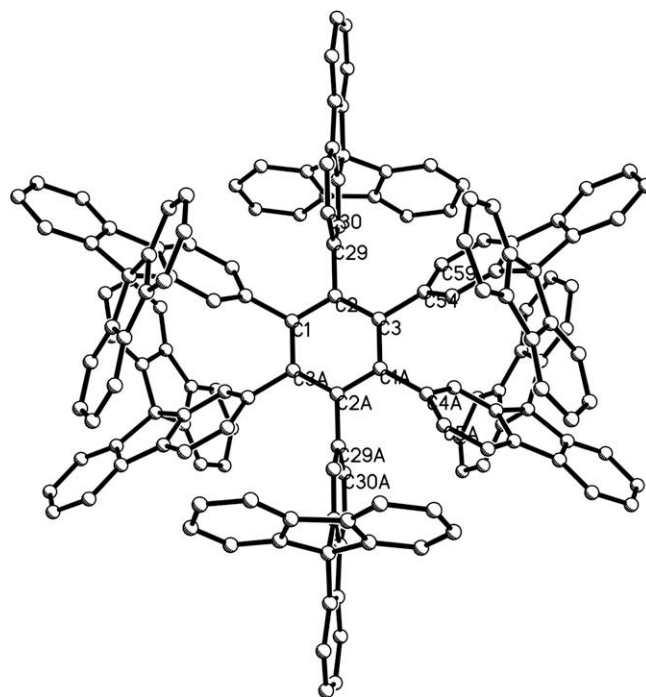


Figure 3. Molecular diagram of the structure of **5** with 30% probability ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity.

X-ray analysis has revealed that the graphene molecule **6** consists of spirobifluorene-annulated anthracene skeleton with a notable twisted conformation. A similar skeletal structure has been observed in 9,18-diphenyltetrabenz[*a,c,h,j*]anthracene **2a**¹⁸ which is a well-known twist-boat unit for the construction of liquid crystals, molecular batteries, and metal complexes (Fig. 1).¹⁹ Derivatization at the para-position of the phenyl substituents of **2a** afforded a range of end-to-end twists as observed in the solid state; **2a** (66°), **2b** (61°), and **2c** (70°). The degree of twisting was proposed to be independent of the electronic properties of the substituents and more likely to be a crystal packing effect. A dramatic effect of crystal packing forces in some particular crystal forms results in smaller end-to-end twist than theoretical calculation.²⁰ The molecular structure of **6** was computationally optimized using LDA-DFT methods²¹ as implemented in the DMol3 package.²² The total energy of molecule calculated with the conformation in single crystal was -5941.07 au , and was -5942.29 au in the optimized conformation. The calculated low-energy conformation exhibits an end-to-end twist of 59.3° for compound **6**, which is in good agreement with the observed twist (58.3°) in the solid state. It is suggested by the difference between the computed and crystal structures of **6** that the crystal packing forces possibly lead to a slight decrease in the end-to-end twist angle.

In conclusion, we have detailed the synthesis of a branched oligophenylene molecule **5** with bulky 9,9'-spirobifluorene groups, and its partial planarization to afford a spiro-annulated PAH **6** with an anthracene backbone. The attachment of SBF units to the π -conjugated PAH framework not only results in a higher solubility, but also offers some unique optical properties. X-ray single-crystal analysis of **6** reveals that the introduction of rigid SBF units leads to a significantly end-to-end twisted anthracene skeleton, which is in good agreement with the calculation. Further functionalization and investigation of properties of this compound class are in progress.

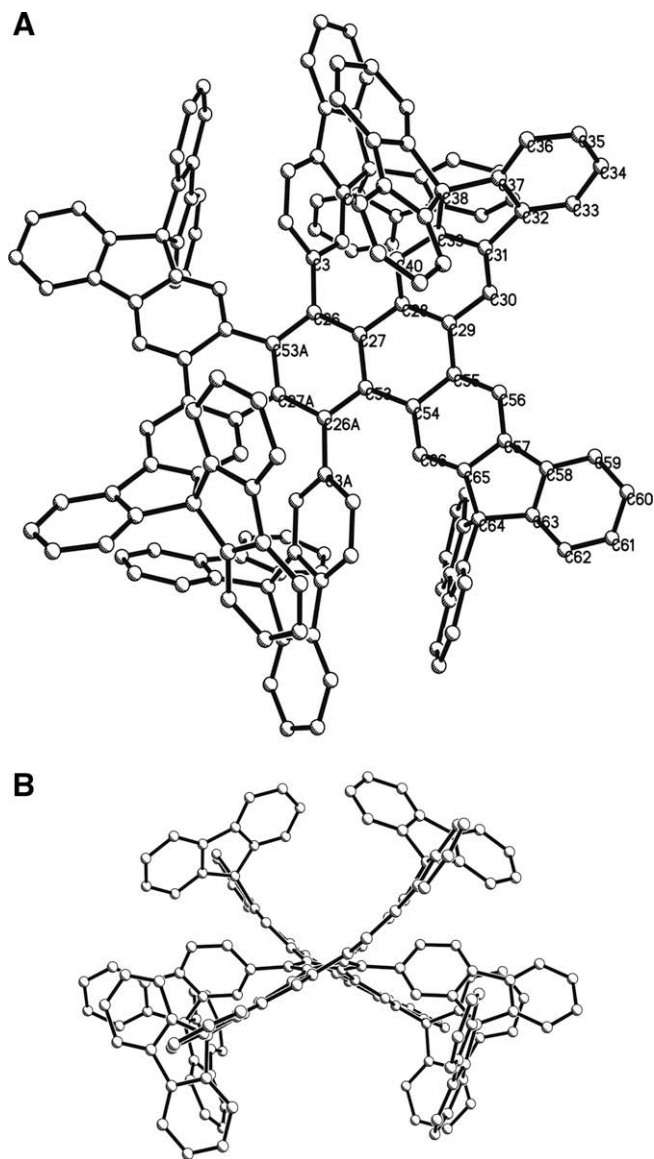


Figure 4. Molecular structure of **6** as determined by single-crystal X-ray structure analysis. (A) Top view; (B) end view. The hydrogen atoms and solvent molecules are omitted for clarity.

Acknowledgments

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Supplementary data

Supplementary data (general experimental methods, X-ray data of **5** and **6**, and ^1H NMR, ^{13}C NMR, and MALDI-TOF-MS of new compounds, the calculated low-energy conformation of **6**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.04.109.

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- Crystallographic data (excluding structure factors) for the structures in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 720481 (for **5**) and 720482 (for **6**). A copy of the data can be obtained free of charge, from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 0 1223-336033; e-mail: deposit@ccdc.cam.ac.uk].
- Crystal data of 5-2C₇H₉O-4C₂H₃N*. The measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$) at 113 K. C₁₇₂H₁₁₈N₄O₂, $M = 2272.70$, colorless prisms, crystal dimension $0.42 \times 0.32 \times 0.24 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 18.405(9) \text{ \AA}$, $b = 18.451(9) \text{ \AA}$, $c = 24.165(9) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 128.69(2)^\circ$, $\gamma = 90.00^\circ$, $V = 6405(5) \text{ \AA}^3$, $Z = 2$, $D_c = 1.178 \text{ g/cm}^3$, $\mu = 0.069 \text{ mm}^{-1}$, θ range $1.60\text{--}25.00^\circ$. Of the 62,896 reflections that were collected, 11,256 were unique ($R_{\text{int}} = 0.0623$), $\text{GOF} = 1.109$, 824 parameters, $R_1 = 0.0618$, $wR_2 = 0.1536$ for reflections with $I > 2\sigma(I)$.
- Crystal data of 6-3C₇H₉*. The measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 113 K. C₁₇₇H₁₁₀, $M = 2236.64$, yellow prisms, crystal dimension $0.10 \times 0.08 \times 0.04 \text{ mm}$, orthorhombic, space group $Pbcn$, $a = 19.256(4) \text{ \AA}$, $b = 28.344(6) \text{ \AA}$, $c = 21.979(4) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 90^\circ$, $\gamma = 90.00^\circ$, $V = 11,996(4) \text{ \AA}^3$, $Z = 8$, $D_c = 1.238 \text{ g/cm}^3$, $\mu = 0.070 \text{ mm}^{-1}$, θ range $1.58\text{--}25.02^\circ$. Of the 71,174 reflections that were collected, 10,594 were unique ($R_{\text{int}} = 0.1117$), $\text{GOF} = 1.190$, 781 parameters, $R_1 = 0.1051$, $wR_2 = 0.2293$ for reflections with $I > 2\sigma(I)$.
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