

Tetrabenzo[8]circulene: Aromatic Saddles from Negatively Curved Graphene

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S Supporting Information

ABSTRACT: An aromatic saddle was designed from the hypothetical three-dimensional graphene with the negative Gaussian curvature (Schwarzite P192). Two aromatic saddles, tetrabenzo[8]circulene (TB8C) and its octamethyl derivative OM-TB8C, were synthesized by the Scholl reaction of cyclic octaphenylene precursors. The structure of TB8C greatly deviates from planarity, and the deep saddle shape was confirmed by single-crystal X-ray crystallography. There are two conformers with the S_4 symmetry, which are twisted compared to the DFT structure (D_{2d}). The theoretical studies propose that the interconversion of TB8C via the planar transition state ($125 \text{ kcal mol}^{-1}$) is not possible. However, the pseudorotation leads to a low-energy tub-to-tub inversion via the nonplanar transition state ($7.3 \text{ kcal mol}^{-1}$). The ground-state structure of TB8C in solution is quite different from the X-ray structure because of the crystal-packing force and low-energy pseudorotation. OM-TB8C is a good electron donor and works as the p-type semiconductor.

Graphene and curved graphenes have been extensively investigated by both chemists and physicists because of their unique structures and properties.^{1–4} C_{60} fullerene is spherical and has the positive Gaussian curvature. Carbon nanotubes (CNTs) have the cylindrical structures with the zero Gaussian curvature. The introduction of curvatures to graphene changes the dimensionality and electronic properties. For example, graphene is a two-dimensional zero-gap semiconductor with the ambipolar character (both p- and n-types). C_{60} is a zero-dimensional n-type semiconductor, and CNTs are one-dimensional p-type semiconductors or metals. It is interesting to see how the negative curvature influences the structure and properties of graphene.⁵

In 1991, just before the report of CNTs,⁶ Mackay and Terrones proposed a hypothetical three-dimensional graphene with the negative Gaussian curvature (Figure 1a).⁷ Its unit cell (O_h symmetry, Figure 1b) consists of 192 carbon atoms (eight coronene molecules). When two unit cells are connected, the hyperboloid structure with the negative curvature appears (Figure 1c). On the saddle surface, four octagons are newly formed. Each unit cell is joined to six other unit cells, which produces the infinite 3D graphene. This structure resembles the Schwarz P-surface, one of periodic minimal surfaces,⁸ and was later called “Schwarzite P192”.⁹ From organic chemist’s point of view, there are two types of aromatic sextet rings, indicated with

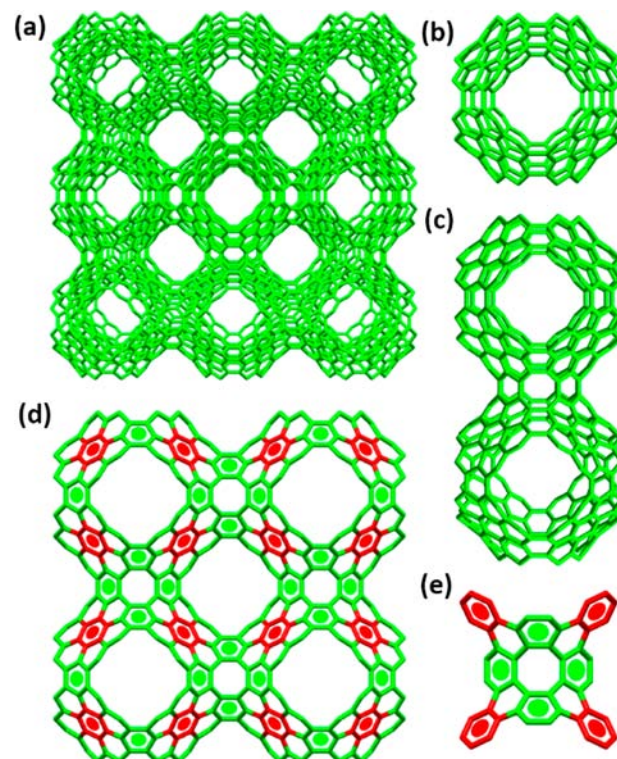


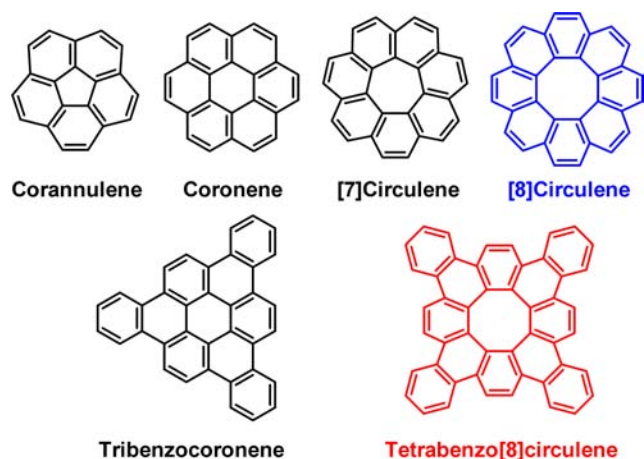
Figure 1. (a) Schwarzite P192 with the negative Gaussian curvature. (b) A unit cell of Schwarzite P192 consists of 192 carbon atoms. (c) Two unit cells have four octagons at the junction. (d) Two types of aromatic sextet rings (red and green circles) in Schwarzite P192. (e) A repeating molecular unit for Schwarzite P192.

red and green circles in Figure 1d.¹⁰ A red sextet ring is surrounded by six hexagons, and a green sextet ring is located between two octagons and highly distorted. A repeating molecular unit in Figure 1e has an interesting octagon-containing structure and should be highly strained.¹¹ Is it possible to synthesize this aromatic saddle as a stable compound ($C_{48}H_{24}$)?

The literature search shows that this aromatic saddle is a tetrabenzo derivative of [8]circulene (Chart 1). [5]- and [6]circulenes are known as corannulene and coronene, respectively.^{12,13} [7]Circulene was synthesized in 1983 by Yamamoto et al., and the X-ray analysis exhibited the shallow saddle structure.¹⁴ Recently, King et al. reported the synthesis

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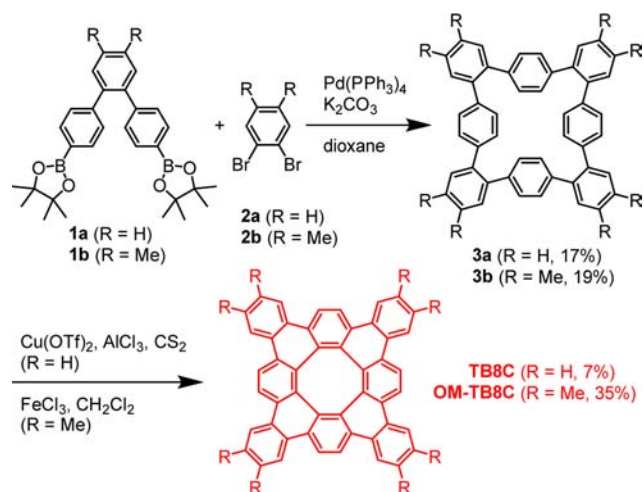
Chart 1. [*n*]Circulenes and Their Benzo Derivatives

and structure of a tetrabenzo[4]circulene derivative.¹⁵ Obviously, [8]circulene has been the next synthetic target, but only some attempts were reported.^{16,17} Very recently, Wu et al. finally prepared *peri*-substituted [8]circulenes with eight bulky groups.¹⁸

We performed the DFT calculations on [8]circulene at the B3LYP/6-31G(d) level. The optimized structure is a rather deep saddle with the D_{2d} symmetry (Figure S1).¹⁹ The strain energy compared to the planar coronene (D_{6h}) is 109.7 kcal mol⁻¹ (Figure S2), which is much larger than those of corannulene (C_{5v} , 61.2 kcal mol⁻¹) and [7]circulene (C_7 , 58.3 kcal mol⁻¹).²⁰ Our target molecule, tetrabenzo[8]circulene (TB8C), also has a high strain energy (D_{2d} , 99.3 kcal mol⁻¹) compared to the planar tribenzocoronene (D_{3h}).^{21,22}

The synthesis of TB8C was done by the Scholl reaction of cyclic octaphenylene precursor **3a** (Scheme 1). Cycloocta-

Scheme 1. Synthesis of TB8C and OM-TB8C



o,p,o,p,o,p,o,p-phenylene (**3a**) was prepared by the Suzuki coupling of **1a** and **2a** in 17% yield. Figure S3 shows the X-ray structure of **3a**. The strain energy at this stage is only 6.4 kcal mol⁻¹. The oxidative cyclodehydrogenation of **3a** with Cu(OTf)₂ and AlCl₃ in CS₂²³ afforded TB8C as a yellow solid in 7% yield. The ¹H NMR spectrum showed three signals at 8.10 (dd, 8H), 7.68 (s, 8H), and 7.56 ppm (dd, 8H). We have tried many different oxidants and acids for the Scholl

reaction but could not improve the yield. Because we always observed the dimer (C₉₆H₄₆) of TB8C as a byproduct, the intermolecular oxidation of TB8C might be responsible for the low yield.²⁴ To prevent such dimerization, we introduced eight methyl groups to compound **3a**. This new precursor **3b** worked well, and the Scholl reaction with FeCl₃ in CH₂Cl₂ gave octamethyl-tetrabenzo[8]circulene (OM-TB8C) in 35% yield. TB8C and OM-TB8C were purified by train sublimation²⁵ and used for further characterization. They are stable yellow solids and soluble in chloroform and toluene.

Single crystals of TB8C were grown from the solution in toluene. A yellow plate was used for X-ray crystallography. The structure of TB8C greatly deviates from planarity, and the deep saddle shape was confirmed (Figure 2). There are two

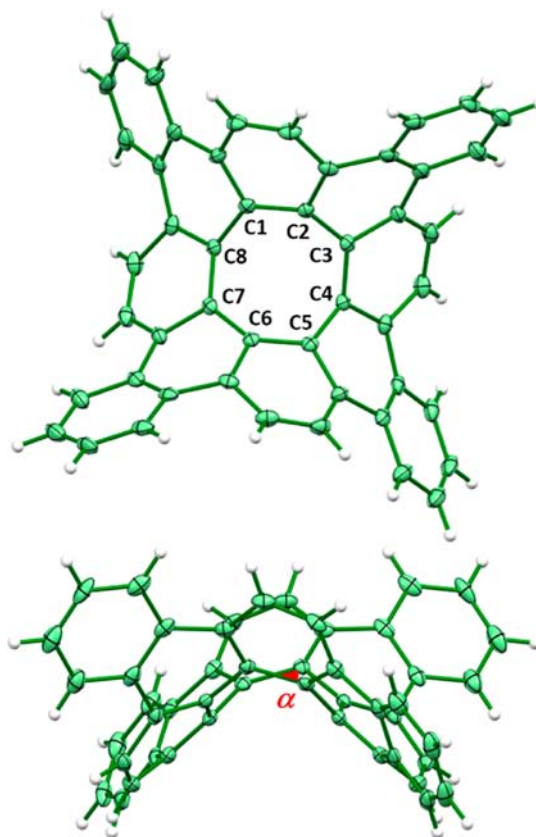


Figure 2. Single-crystal X-ray structure of TB8C (conformer A) from the top and the side. The thermal ellipsoids are shown at 50% probability. Bond lengths (Å) and angles (deg) in the octagon for conformer A (conformer B): C1–C2, 1.434 (1.437); C2–C3, 1.482 (1.476); C1–C2–C3, 121.5 (121.6); C2–C3–C4, 127.2 (127.1); α , 32.1 (37.4).

conformers, A (S_4) and B (S_4), in a 1:1 ratio (Figure S4). Interestingly, both conformers are twisted with the angles α = 32.1 and 37.4°, respectively, compared to the DFT structure (*Tub-1* in Figure 3). The angle α is defined as the torsion angle between the C1–C2 and C5–C6 bonds in the central cyclooctatetraene (COT) part. Although the S_4 symmetry should give six signals in the ¹H NMR spectrum, only three signals (D_{2d}) were observed in solution. This suggests that TB8C would be a rather flexible molecule. The bond lengths and angles in the octagon (Figure 2 caption) are close to those for the DFT structure (C1–C2, 1.430 Å; C2–C3, 1.480 Å; C1–C2–C3, 124.8°; C2–C3–C4, 124.8°). A short C–C

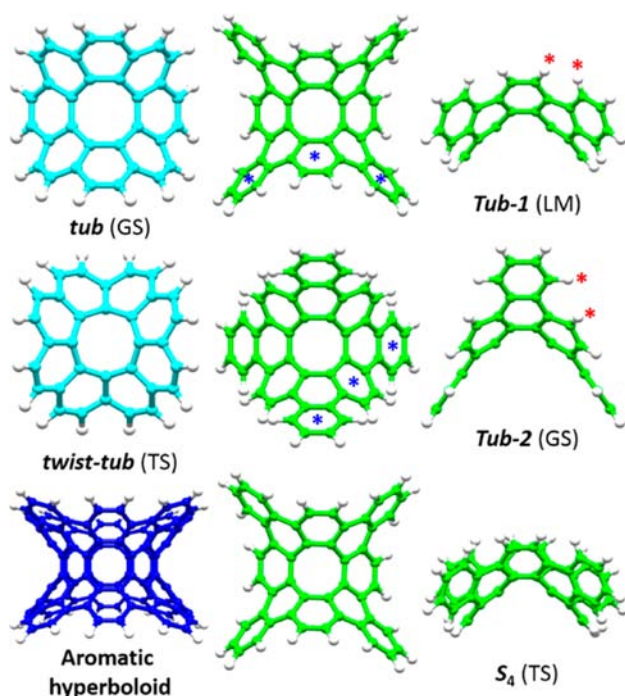


Figure 3. Calculated conformations for [8]circulene and TB8C at the B3LYP/6-31(d) level. The *tub* conformation (D_{2d}) of [8]circulene as the ground state (GS). The *twist-tub* conformation (D_{2d}) of [8]circulene as the transition state (TS). *Tub-1* conformation (D_{2d}) of TB8C as the local minimum (LM). *Tub-2* conformation (D_{2d}) of TB8C as the ground state. The S_4 structure of TB8C as the transition state. The structure of an aromatic hyperboloid ($C_{120}H_{40}$).

contact (3.22 Å) less than the sum of van der Waals radii (3.40 Å) was observed between the conformers A and B. This face-to-face π - π interaction makes the 3D π network in the crystal. (Figure S5).

The interconversions of corannulene and [7]circulene can be easily achieved via the planar transition states (Figure S6). The calculated activation energies are only 9.0 and 11.2 kcal mol⁻¹ for a bowl-to-bowl inversion of corannulene²⁶ and a saddle-to-saddle inversion of [7]circulene,²⁷ respectively. Because the planar transition state for [8]circulene has a much higher energy (125 kcal mol⁻¹), the interconversion by this mechanism is impossible at room temperature. However, our DFT calculations (Figure 3) indicate that the interconversion of the *tub* conformation (D_{2d}) is easily done via the *twist-tub* conformation (D_{2d}). The activation energy for this tub-to-tub inversion is only 2.9 kcal mol⁻¹ (Figure S7). This mechanism is known as the pseudorotation, which is often found in cycloalkanes such as cyclopentane.²⁸ A continuous wave of the eight hexagons turns around the octagon as if the entire molecule rotates on the principal axis (Figure S8). The low-frequency vibration found in the *tub* conformation (12 cm⁻¹) corresponds to the pseudorotational mode.²⁹ Paquette et al. also proposed the pseudorotation pathway for COT with a transition state similar to *twist-tub*.³⁰

In the case of our new compound TB8C, there are two tub forms (Figure 3), *Tub-1* (D_{2d}) and *Tub-2* (D_{2d}). It turned out that the *Tub-1* form mentioned in the discussion on the X-ray structure was not the ground state but the local minimum. *Tub-2* is the ground state and more stable than *Tub-1* by 5.1 kcal mol⁻¹. The transition state has the S_4 symmetry ($\alpha = 5.1^\circ$) and is close to *Tub-1* ($\alpha = 0.0^\circ$). The activation energy is estimated

to be only 7.3 kcal mol⁻¹ (Figure S9). The low-frequency vibrations for the pseudorotation are also found in *Tub-1* and *Tub-2* (4 and 8 cm⁻¹, respectively). Both experimental and theoretical results suggest a rapid tub-to-tub inversion of TB8C at room temperature. *Tub-2* is the structure in solution (even at -90 °C by variable-temperature ¹H NMR) but not in the solid state because of the crystal-packing force and low-energy pseudorotation. The solid-state structures (conformers A and B) can be viewed as the frozen pseudorotation. The substitution of [8]circulene with four (not eight) benzo groups leads to great structural and electronic changes during the pseudorotation (Figure S8).

The HOMO-LUMO gaps estimated by the DFT calculations are 3.57 eV for *Tub-1* and 2.62 eV for *Tub-2*, which may indicate that the ground state *Tub-2* is electronically less stable (Figure S10). This is also supported by nucleus-independent chemical shifts (NICS) as an aromaticity criterion³¹ (Figure S11). All eight sextet rings are aromatic (-7.7 and -8.4) in *Tub-1*, but four sextet rings are weakly aromatic (-3.8 and -9.2) in *Tub-2*. We conclude that the steric effect is the reason for the relative high energy of *Tub-1*. The dihedral angle of the *p*-terphenyl part in *Tub-1* (indicated with blue asterisks) is very small (14.0°) compared to that in *Tub-2* (31.5°). The repulsion between two hydrogen atoms (marked with red asterisks) is much larger in *Tub-1*. However, this is not the case for Schwarzite P192 because it has no hydrogen atoms.

The UV-vis absorption spectrum of TB8C exhibited three maxima at 455, 378, and 299 nm (Figure S12a). These correspond well to the oscillator strengths (f) obtained by the time dependent DFT calculations (TD-DFT) on *Tub-2* (HOMO to LUMO: 663 nm, $f = 0.000$; HOMO-1 to LUMO: 467 nm, 0.077; HOMO to LUMO+1: 384 nm, 0.248). TD-DFT for *Tub-1* is quite different from the experimental result (423 nm, 0.000; 388 nm, 0.095; 348 nm, 0.292). The UV-vis absorption spectrum of OM-TB8C (464, 378, and 305 nm) is similar to that of TB8C (Figure S12b) and in accordance with the TD-DFT calculation (662 nm, 0.000; 475 nm, 0.094; 384 nm, 0.240). The photoluminescence of TB8C and OM-TB8C is almost negligible (quantum yields in chloroform: 0.005 and 0.007, respectively).

The electrochemical measurements on TB8C and OM-TB8C were performed in 1,1,2,2-tetrachloroethane (Figure S13). The cyclic voltammogram (CV) of TB8C showed a reversible oxidation couple at 0.45 V (versus the ferrocene/ferrocenium couple). As expected from the electron-donating nature of methyl groups, the oxidation couple of OM-TB8C (0.33 V) shifted negatively relative to TB8C. These small ionization energies are in good agreement with relatively high HOMO energy levels of TB8C (-4.84 eV) and OM-TB8C (-4.65 eV) by the DFT calculations (e.g., tetracene, -4.86 eV; pentacene, -4.60 eV).

An aromatic hyperboloid (Figure 3) from the junction of two unit cells (Figure 1c) is a higher subunit of Schwarzite P192. The homodesmotic reaction³² indicates that this four-octagon-containing molecule needs almost no extra strain (1.6 kcal mol⁻¹) compared to *Tub-1* (Figure S14). In principle, the synthesis of such a molecular hyperboloid is possible if suitable precursors are available.

We have synthesized the highly strained aromatic saddles, TB8C and OM-TB8C, by the Scholl reaction of cyclic octaphenylene precursors. The intramolecular Scholl reaction is often used for the synthesis of planar graphene molecules such as hexabenzocoronene.³³ All six dehydrogenation steps of

hexaphenylbenzene are exothermic (ΔG : -4.0 , -13.1 , -13.9 , -15.8 , -18.4 , and -28.7 kcal mol $^{-1}$ by the DFT calculations).³⁴ In the case of **TB8C** (Figure S15), the third dehydrogenation step is highly endothermic ($\Delta G = -16.3$, -11.6 , 45.4 , and 2.1 kcal mol $^{-1}$). This suggests that the intramolecular Scholl reaction of cyclic oligophenylenes would be useful for other curved graphene molecules such as aromatic belts.³⁵ Very recently, a large curved nanographene (C₈₀H₃₀) with one pentagon and five heptagons was synthesized by the Scholl reaction.³⁶

The X-ray structure of [7]circulene (C₂)¹⁴ may not be the ground state (C₂) but the twisted intermediate (C₂) of the pseudorotation.²⁷ For [8]circulene, it is easy to distinguish the ground state (D_{2d}) from the twisted intermediate (S₄). This is also the case for **TB8C**. A snapshot of two S₄ intermediates (conformers A and B) is a strong evidence for the low-energy pseudorotation of **TB8C**. The internal dynamics of **TB8C** would be an interesting subject of physical chemistry because there are only a few reports on the pseudorotation of aromatic compounds.³⁷ The concerted conformational movement of **TB8C** is quite different from the random internal motion of the precursor molecule **3a**. As the result, the HOMO–LUMO gap of **TB8C** changes by nearly 1 eV during the pseudorotation.

Our preliminary result on the thin-film transistors shows that **OM-TB8C** works as the p-type semiconductor. Although the hole mobility is still low (10 $^{-4}$ cm² V $^{-1}$ s $^{-1}$), the synthesis of other **TB8C** derivatives is in progress and will be reported elsewhere.

■ ASSOCIATED CONTENT

Supporting Information

Experimental, spectroscopic, and computational details and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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