

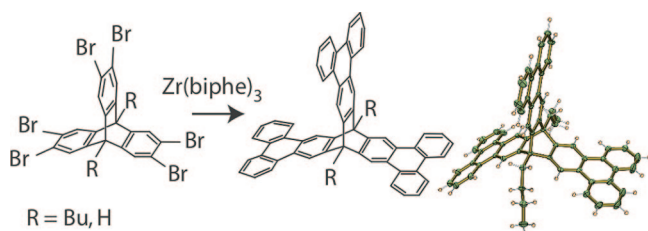
## A Triphenylene-Based Triptycene with Large Free Volume Synthesized by Zirconium-Mediated Biphenylation

Cameron L. Hilton, Christopher R. Jamison,  
Hannah K. Zane, and Benjamin T. King\*

Department of Chemistry, University of Nevada,  
Reno, Nevada 89557-0216

king@chem.unr.edu

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Biphenylation using  $(\text{Li}(\text{THF})_4)_2 \cdot \text{Zr}(\text{biphe})_3$  of hexabromotriptycenes bearing H (**1-H**) or Bu (**1-Bu**) at the bridgeheads gave triptycenes with triphenylene blades. The blades extend both perpendicular and parallel to the 3-fold axis and generate a large intramolecular free volume (IMFV) (**1-H**, AM1, 710 Å<sup>3</sup>; cf. triptycene, AM1 71 Å<sup>3</sup>). Crystals of **1-H** could not be obtained. Triptycene **1-Bu**, in which the Bu groups fill the voids near the bridgehead, was crystalline. X-ray diffraction analysis revealed crystal packing with alternating, interlocked corrugated and distorted hexagonal layers.

Triptycene is a useful building block in supramolecular chemistry. Its rigidity, paddlewheel shape, and ease of functionalization<sup>1–4</sup> make triptycene a useful rotor<sup>5</sup> or stator<sup>6</sup> component in nanodevices, a rigid spacer for the construction of host–guest complexes,<sup>7</sup> a framework for the construction of chelating ligands,<sup>1,8,9</sup> and a subunit of molecular cages.<sup>2</sup> Electron-rich clefts between the arene blades of triptycene allow it to form inclusion complexes<sup>10</sup> with C<sub>60</sub>. The rigid paddlewheel

shape of triptycene is credited with improving the mechanical properties of polymers in which it is incorporated.<sup>11–13</sup>

Triptycene can be extended by increasing the size of its arene blades. With a few exceptions,<sup>14,15</sup> this has been done by increasing the length of the blade in a direction perpendicular<sup>16</sup> to the 3-fold axis of the triptycene (e.g., benzene blades to anthracene blades). Extended triptycenes have primarily served as starting materials for the synthesis of higher triptycenes.<sup>17</sup> Pascal's dodecaphenyltriptycene is an especially noteworthy analogue.<sup>18</sup>

We chose to synthesize 6,13-(2,3-triphenylene)-6,13-dihydro[*a,c,l,n*]tetrabenzopentacene (**1-H**), which is a rare example of a triptycene that has been extended both parallel and perpendicular to its highest symmetry axis. This extension generates large voids above the bridgehead sites and between the blades and gives rise to a large internal molecular free volume<sup>12</sup> (IMFV). Swager defines IMFV as “the difference in volume between that which is generated by the geometry of the structure and that occupied by the structure itself.”<sup>12</sup> The IMFV of **1-H**, from the calculated AM1 geometry, is 710 Å<sup>3</sup>. The free volume of parent triptycene, 74 Å<sup>3</sup>, is 1 order of magnitude less than that of **1-H** but is nonetheless sufficient to permit its use as a stator for molecular gyroscopes<sup>6</sup> and as a “barbed-wire” component of polymers, which inhibits chain–chain slippage and improves mechanical properties.<sup>12,13</sup> We feel the large IMFV of **1-H** and its derivatives may enable similar applications but more effectively and on a somewhat larger scale.

The synthesis of **1-H** is carried out in two steps. First, bromination of triptycene yields 2,3,6,7,12,13-hexabromotriptycene (**2-H**),<sup>4</sup> which is followed by the substitution of three biphenyl units for the three pairs of *o*-dibromides using the recently reported<sup>19</sup> reagent,  $(\text{Li}(\text{THF})_4)_2 \cdot \text{Zr}(\text{biphe})_3$  (**3**), where biphe is biphenyl(2,2'-diyl). A traditional Diels–Alder approach would require tetrabenzo[*a,c,l,n*]pentacene,<sup>20</sup> which is difficult to prepare, and 2,3-didehydrotriphenylene.<sup>21</sup>

The synthesis **1-H** was facilitated by the development of an improved synthesis of hexabromide **2-H** from triptycene. Our improved synthesis provides a one-step, multigram preparation of **2-H** in 64% yield. Hexabromide **2-H** may be a versatile building block for other large triptycenes.

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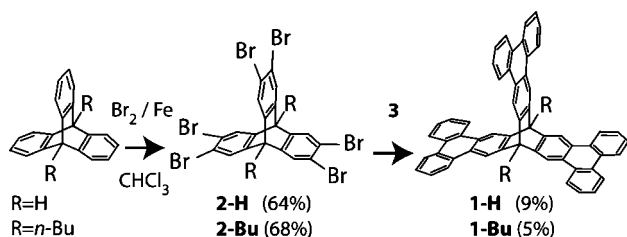
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SCHEME 1. Synthesis of Extended Triptycenes **1-H** and **1-Bu**

The synthesis of **1-H** relies on reagent **3** to affect the 3-fold biphenylation of **2-H**. The reaction gives a double *ipso* substitution on an *o*-dihaloarene to form a triphenylene fragment<sup>22</sup> (Scheme 1).

A modification to the reported<sup>22</sup> workup for reactions using **3** simplifies purification. In the original procedure, protic quench yielded neutral oligophenylys, which were difficult to separate from the products. In our improved procedure, a CO<sub>2</sub> quench afforded oligophenylcarboxylates, which could be easily separated by flash chromatography on alumina. The remaining mixture contained **1-H**, incompletely biphenylated products, and reduced products and was separated using normal-phase HPLC to give pure **1-H** in 9% yield.

We were particularly interested in obtaining a crystal structure of **1-H** in order to determine its shape and solid-state packing. Despite exhaustive efforts, crystals of **1-H** suitable for single-crystal X-ray diffraction could not be grown. Attempts to cocrystallize **1-H** with picric acid, trinitrofluorenone, C<sub>60</sub>, and adamantane also failed. In every case, only films were obtained. No sample exhibited evidence of crystallinity by microscopy with crossed polarizers. In addition, **1-H** tenaciously retained solvent. Vacuum (30 mTorr) at elevated temperatures (75 °C) failed to fully remove acetone or dichloromethane.

The reluctance of **1-H** to crystallize was intriguing—triphenylene and triptycene crystallize easily from a variety of solvents. We hypothesized that the free volume of **1-H**, especially around its bridgeheads, frustrates packing and inhibits crystallization.

To test this hypothesis, we synthesized 6,13-(2,3-triphenylene)-6,13-di-*n*-butyl[*a,c,l,n*]tetrabenzopentacene (**1-Bu**) using the same synthetic scheme that provided **1-H**, except starting with 9,10-dibutyltriptycene.

Dibutyltriptycene was synthesized in three steps. First, 9,10-anthraquinone was allowed to react with *n*-butyllithium to yield a mixture of diastereomeric diols, which was reduced with SnCl<sub>2</sub> in AcOH<sup>23</sup> to give 9,10-dibutylanthracene (7 g, 40% over two steps). Diels–Alder cycloaddition of benzyne gave 9,10-dibutyltriptycene (70%). Bromination gave **2-Bu** (68%). Biphenylation of **2-Bu** with **3** gave **1-Bu**, but in lower yield (20 mg, 5%).

On our first attempt, we were able to grow crystals of **1-Bu** suitable for single-crystal X-ray diffraction analysis (Figure 1).<sup>24</sup> The bridgehead butyl groups promote crystallinity.

The asymmetric unit comprised two independent molecules of **1-Bu** and two molecules of benzene. The IMFV of each, calculated using a C–H bond length of 1.09 Å, was 680 Å<sup>3</sup> and 720 Å<sup>3</sup>, bracketing the calculated (AM1) value of 710 Å<sup>3</sup>.

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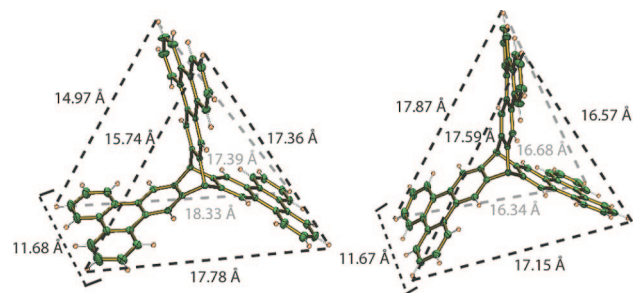


FIGURE 1. Thermal ellipsoid plots for **1-Bu** from the corrugated plane (left) and the distorted hexagonal plane (right).

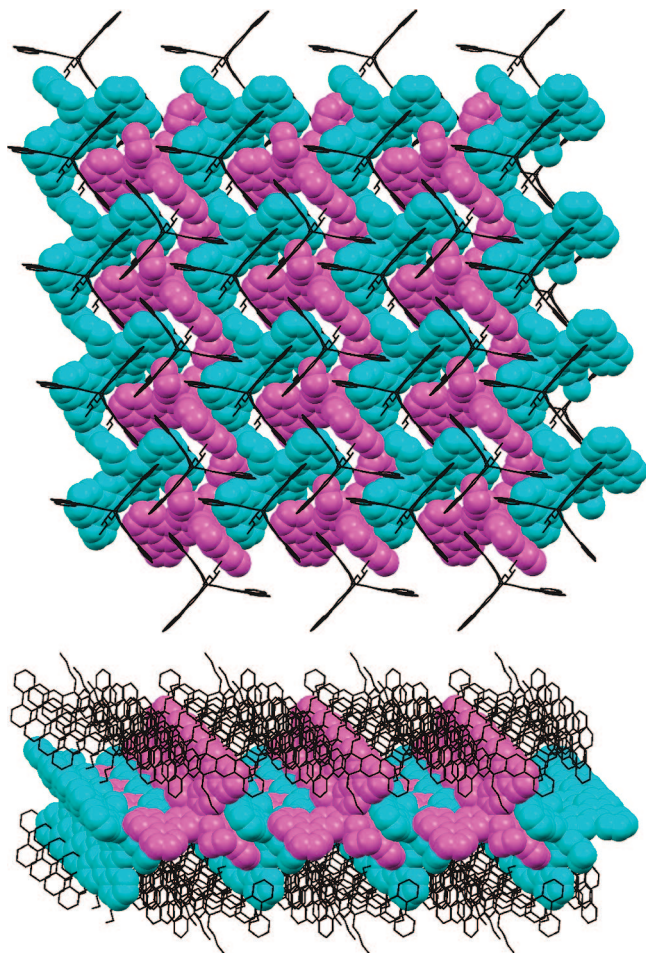
Examination of packing of **1-Bu** reveals interlocking planes organized by  $\pi$ -stacking, but no large voids. A distorted hexagonal plane contains molecules of **1-Bu** aligned with their bridgehead–bridgehead axis nearly normal to the plane and is stabilized by triphenylene–triphenylene  $\pi$ -stacking. A corrugated plane contains molecules of **1-Bu** with their bridgehead–bridgehead axis aligned ( $\sim 30^\circ$ ) with the plane, and a blade from each **1-Bu** protruding up or down into the voids in the adjacent hexagonal plane. The hexagonal voids flatten to maximize  $\pi$ -stacking with the two interdigitated triphenylene blades, expanding the triphenylene–triphenylene dihedral from the expected  $120^\circ$  to  $138^\circ$ . One benzene molecule fills, along with the butyl group, a void above the bridgeheads of the hexagonal layer. The other benzene molecule fills a void in the corrugated layer (Figure 2).

We have synthesized two new extended triptycenes, **1-H** and **1-Bu**, that bear triphenylene blades. These triphenylene blades extend the triptycene base both perpendicular and parallel to its 3-fold axis. The synthesis of extended triptycenes **1-H** and **1-Bu** was made possible by the recently developed biphenylating agent **3**; this reagent formed six new C–C bonds in one step. Compound **1-H** proved reluctant to crystallize, possibly due to voids about its bridgeheads that inhibit packing. Compound **1-Bu**, in which a butyl group partially occupies the bridgehead voids, is easily crystallized. This supports our hypothesis that the large voids in **1-H** inhibit packing.

The large IMFV of **1-R** (710 Å<sup>3</sup>) suggest applications in molecular devices and polymers. Both triptycene **1-H** and **1-Bu** provide a new rigid scaffold geometry which may enable their use in molecular devices and as rigid frameworks for the construction of chelating ligands. The large electron rich clefts between their triphenylene blades make them candidates for use in new inclusion complexes. Compound **1-H** may be capable of modulating the mechanical properties of polymers, perhaps to a larger extent than triptycene,<sup>12,13</sup> due to its significantly increased IMFV.

## Experimental Section

**Synthesis of 2-H.** Triptycene (1.06 g, 4.18 mmol) was dissolved in chloroform (80 mL) in a round-bottom flask. Iron filings (30 mg) were added, and the solution was stirred at 25 °C. Bromine (1.35 mL, 26.3 mmol) was added, and the solution was refluxed for 1 h, during which time the initially reddish-brown solution turned reddish-orange. The flask was removed from heat, and chloroform and excess bromine were removed under vacuum. The resulting brown powder was dissolved in chloroform (100 mL) and flushed through a pad of silica using additional chloroform as eluent (100 mL). The filtrate was evaporated to dryness. The crude white powder (2.83 g, 98%) was crystallized from acetone yielding C<sub>20</sub>H<sub>8</sub>Br<sub>6</sub>(acetone)<sub>2</sub> (0.88 g, 29%), mp > 350 °C. The mother liquor



**FIGURE 2.** Packing of **1-Bu**. Black, distorted hexagonal plane; purple, corrugated lattice upward; blue, corrugated plane downward. Purple and blue molecules are crystallographically equivalent. Benzene solvent and hydrogen atoms are omitted.

was evaporated and the residue was crystallized from acetone to afford a second crop of crystals (0.97 g,  $C_{20}H_8Br_6 \cdot (\text{acetone})_2$ , 32%). The combined yield was 1.85 g, 61%:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (s, 3H), 5.24 (s, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDBr}_3$ )  $\delta$  141.7, 127.1, 119.9, 48.6; UV-vis  $\lambda_{\text{max}}/\text{nm}(\log \epsilon)$ : 229 (4.95), 285 (3.49), 295 (3.83). Anal. Calcd for  $C_{20}H_8Br_6$ : 33.01, 1.11, 65.88. Found: 33.17, 1.19, 65.68.

**Synthesis of 1-H.**  $\text{Li}(\text{THF})_4 \cdot 2 \cdot \text{Zr}(\text{biphe})_3$  (3.41 g, 3.00 mmol) was added as a powder to a solution of 2,3,6,7,12,13-hexabromotriptycene (0.364 g 0.50 mmol) in toluene (50 mL). The reaction mixture was stirred under argon, at room temperature, for 2 days and then quenched by addition of anhydrous carbon dioxide gas. The mixture was passed through a column of basic alumina using toluene. The eluent was evaporated, and the resulting residue was purified using preparative HPLC (silica, 40:60  $\text{CHCl}_3/\text{hexane}$ ) yielding **1-H** (29 mg, 9%): mp  $>350$  °C;  $^1\text{H NMR}$  (500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ )  $\delta$  8.87 (s, 6H), 8.74 (d,  $J = 5$  Hz, 6H), 8.63 (d,  $J = 5$  Hz, 6H), 7.72 (m, 6 H), 7.65 (m, 6 H), 6.19 (s, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.7, 133.3, 133.2, 131.4, 130.3, 130.2, 126.6, 121.7, 58.0; UV-vis  $\lambda_{\text{max}}/\text{nm}(\log \epsilon)$  263 (5.12) sh 273; HRMS calcd for  $\text{C}_{56}\text{H}_{32}$  704.2504, found 704.2451.

**Synthesis of 9,10-Dibutylanthracene.** Anthraquinone (10.4 g, 50 mmol) was added to a stirred solution of *n*-butyllithium (273 mmol) in hexane (100 mL) and anisole (100 mL) at room temperature. The reaction was stirred for 1 day and quenched by addition of ammonium chloride. The organic layer was separated, washed with water ( $2 \times 200$  mL), and evaporated. The resulting

residue was dissolved in THF (75 mL) and added dropwise to a solution of tin dichloride (56.25 g, 250 mmol) in acetic acid (300 mL). The resulting suspension was stirred for 1 day, and the organic material was extracted with hexane (1 L). The organic extract was washed with 5% ammonium hydroxide (500 mL) and evaporated to dryness. The residue was crystallized from 2-propanol to give pure 9,10-dibutylanthracene (4.2 g, 40%): mp 105 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (m, 4H), 7.51 (m, 4H), 3.61 (t,  $J = 8$  Hz, 4H), 1.82 (m, 4H), 1.62 (m, 4H), 1.05 (t,  $J = 7$  Hz, 6H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.0, 129.6, 125.5, 125.0, 33.8, 28.1, 23.7, 14.3. Anal. Calcd for  $\text{C}_{22}\text{H}_{26}$ : C, 90.98, H, 9.02. Found: C, 91.06, H, 8.91.

**Synthesis of 9,10-Dibutyltriptycene.** Anthranillic acid (4.00 g, 28.8 mmol) was dissolved in THF (180 mL) and added dropwise over 4 h to a solution of isoamyl nitrite (4.2 mL, 31 mmol) and 9,10-dibutylanthracene (4.00 g 13.8 mmol) in refluxing chloroform (250 mL). After the addition was complete, the reaction was refluxed for a further 15 min, and the solvent was evaporated to dryness. The remaining solids were dissolved in xylenes (200 mL), and maleic anhydride (1.896 g, 19.32 mmol) was added. This mixture was refluxed for 15 min and allowed to cool. Aqueous workup and filtration through a plug of silica gel afforded dibutyltriptycene (3.485 g, 69%): mp 247 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (bs, 6H), 7.06 (bs, 6H), 3.03 – 2.94 (m, 4H), 2.27 – 2.15 (m, 4H), 1.94 – 1.73 (m, 4H), 1.22 (t,  $J = 7$  Hz, 6H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDBr}_3$ )  $\delta$  147.33, 123.45, 121.14, 52.15, 27.47, 26.71, 24.14, 14.01. Anal. Calcd for  $\text{C}_{28}\text{H}_{30}$ : C, 91.75, H, 8.25. Found: C, 91.34, H, 8.51.

**Synthesis of 2-Bu.** The procedure for **2-H** was followed, but on a smaller scale: 9,10-dibutyltriptycene (0.425 g, 1.16 mmol, chloroform (30 mL), iron filings (20 mg), and bromine (0.38 mL, 7.3 mmol). The crude white powder (0.90 g, 93%) was washed with acetone yielding pure **2-Bu** (0.628 g, 65%): mp 297–300 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (bs, 6H), 2.80–2.66 (m, 4H), 2.04–1.95 (m, 4H), 1.85–1.75 (m, 4H), 1.20 (t,  $J = 7$  Hz, 6H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  147.49, 128.02, 121.66, 52.33, 27.57, 27.16, 24.81, 14.25.

**Synthesis of 1-Bu.**  $\text{Li}(\text{THF})_4 \cdot 2 \cdot \text{Zr}(\text{biphe})_3$  (3.41 g, 3.00 mmol) was added as a powder to a solution of **2-Bu** (0.419 g, 0.502 mmol) in toluene (50 mL). The reaction mixture was stirred at room temperature for 2 days and then quenched by addition of anhydrous carbon dioxide gas. The mixture was passed through a column of basic alumina using toluene. The eluent was collected and evaporated, and the residue was purified using preparative HPLC (silica/ 15:85  $\text{CH}_2\text{Cl}_2/\text{hexane}$ ) yielding **1-Bu** (22 mg, 5%): mp  $>350$  °C;  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ , 72 °C)  $\delta$  8.89 (s, 6H), 8.77 (d,  $J = 8$  Hz, 6H), 8.46 (d,  $J = 8$  Hz, 6H), 7.53 (t,  $J = 7$  Hz, 6H), 7.43 (t,  $J = 7$  Hz, 6H) 3.53 – 3.45 (m, 4H), 2.67–2.52 (m, 4H), 2.20–2.10 (m, 4H), 1.31 (t,  $J = 7$  Hz, 6H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDBr}_3$ )  $\delta$  144.1, 127.9, 127.8, 125.2, 124.9, 124.8, 121.4, 121.0, 115.0, 51.5, 26.6, 26.3, 23.8, 13.3; HRMS calcd for  $\text{C}_{64}\text{H}_{48}$  816.3756, found 816.3734.

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**Supporting Information Available:** Synthetic procedures, NMR spectra, full thermal ellipsoid plots, crystallographic parameters, and crystallographic information files for 9,10-dibutyltriptycene, **2-H**·acetone, **2-H**, **2-Bu**, and **1-Bu**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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