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Palladium-Mediated Formation of Bowl-Shaped PAHs: Synthesis of *as*-Indaceno[3,2,1,8,7,6,-*pqrstuv*]picenes

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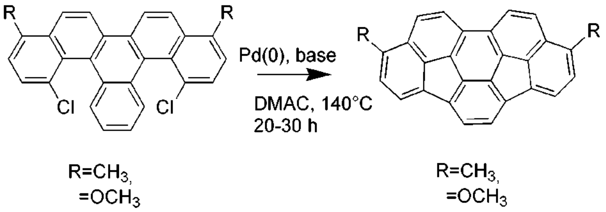
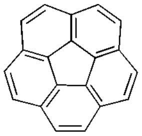
ABSTRACT



Bowl-shaped fullerene fragments, *as*-indaceno[3,2,1,8,7,6-*pqrstuv*]picenes, can be synthesized by a double palladium-mediated cyclization in good to excellent yield. The structure of 1,8-dimethyl *as*-indaceno[3,2,1,8,7,6-*pqrstuv*]picene was confirmed by X-ray analysis. The high yields, mild reaction conditions, and wide range of functional group tolerance are advantages of this method over existing FVP and reductive coupling routes to bowl-shaped PAHs.

Since the discovery of C_{60}, bowl-shaped polycyclic aromatic hydrocarbons (PAHs), a class of compounds representing fullerene subunits, have been the subject of intense study.[1] However, access to these curved molecules, with their high strain energy, is rather limited. A widely used method for the construction of strained fullerene fragments is flash vacuum pyrolysis (FVP), developed first by the Scott group.[2] Although a number of curved molecules, such as corannulene **1**[2] and semibuckminsterfullerenes **2**[3] and **3**,[4] have been synthesized by FVP, the method is problematic because of modest yields, minimum functional group tolerance due to the harsh reaction conditions, and difficulty in scale-up. To overcome these drawbacks, Siegel and co-workers discovered that the highly exothermic reductive coupling of benzylic bromides with Ti(0) and $LiAlH_4$ is a nonpyrolytic route to such compounds.[5] This liquid-phase reductive coupling has resulted in several curved molecules, such as **3**.[6] A simple NaOH-promoted coupling of a tetrakis(dibromomethyl)fluoranthene to a tetrabromocorannulene has recently been reported.[7]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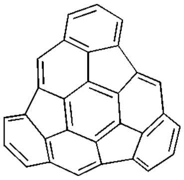
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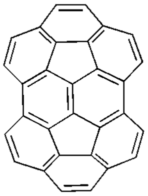
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With its mild reaction conditions, wide range of functional group tolerance, and ease of scale-up, palladium(0)-mediated intramolecular coupling of two aryls has emerged as an excellent tool for the synthesis of cyclized molecules

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(1) For recent reviews on bowl-shaped fullerene-related polycyclic aromatic hydrocarbons, see: (a) Seiders, T. J.; Siegel, J. S. *Chem. Br.* **1995**, *31*, 313−316. (b) Faust, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1429−1432. (c) Rabideau, P. W.; Sygula, A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; Jai Press Inc.: Greenwich, CT, 1995; Vol. 3, pp 1−36. (d) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (e) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (f) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (g) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209−219.

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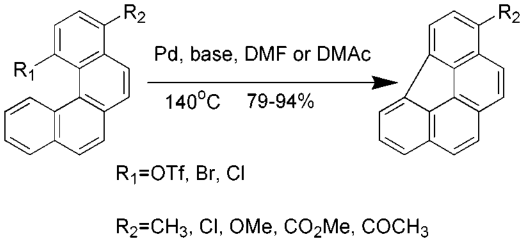
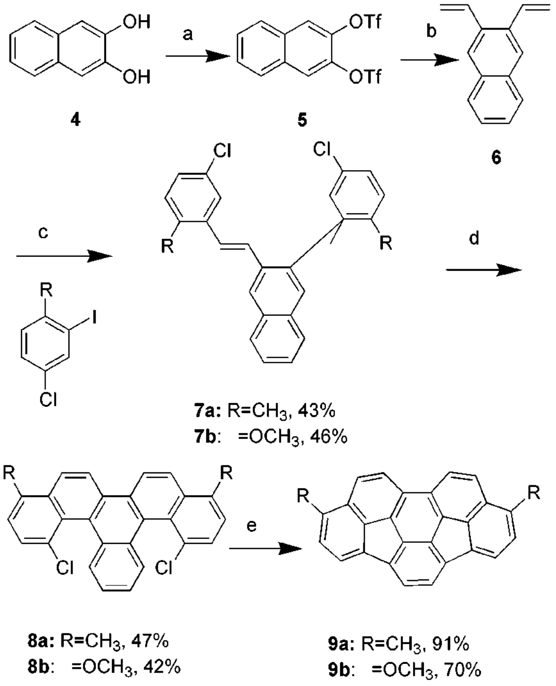
including polycyclic aromatic hydrocarbons.[8] Recently, we reported an efficient synthesis of benzo[*ghi*]fluroanthenes by palladium-catalyzed intramolecular coupling using bromides, triflates, and chlorides as leaving groups, eq 1.[9] These coupling reactions proceeded smoothly in the presence of various substitutients including strong electron donors. Our purpose in developing this palladium methodology was to use it as an alternative route to bowl-shaped molecules. We now wish to report here that we have successfully utilized this method to synthesize new curved molecules, the *as*-indaceno[3,2,1,8,7,6-*pqrstuv*]picenes **9a,b**, from dichlorobenzo[*s*]picenes **8a,b**. Reisch, Bratcher, and Scott have recently reported an elegant synthesis of dibenzo[*a,g*]-corannulene using palladium-mediated intramolecular coupling with bromide.[10]



(1)

The five-step synthesis of **9a,b**, via **8a,b** is shown in Scheme 1. Thus, 2,3-ditrifloxynaphthalene, **5**, was prepared from the corresponding 2,3-dihydroxynaphthalene **4**. 2,3-Divinyl-naphthalene, **6**, was synthesized by Stille coupling with **5** and tributyl-vinyl stannane in dixoane in the presence of tetrakis(triphenylphosphine)palladium.[11] The Heck reaction was then employed to make substituted *trans*-2,3-distyryl-naphthalenes **7a,b** from the corresponding iodides and 2,3-divinyl-naphthalene. The double photocyclization−oxidation successfully converted **7a,b** into dichlorobenzo-[*s*]picenes **8a,b** in the presence of iodine and propylene oxide.[12] This reaction was accompanied by a competing electrocyclization−oxidation to an anthracene derivative, which lowered the yields of **8a,b**. The bowl-shaped molecules **9a,b** were synthesized by a double palladium-mediated five-membered ring formation using bis(tricyclohexylphosphine-palladium(II) chloride, Pd$(PCy_3)_2Cl_2$, in good to excellent yields in the presence of the strong organic base DBU.[13] The dichlorobenzo[*s*]picenes **8a,b** were insoluble in common organic solvents such as methylene chloride as a result of $\pi-\pi$ stacking. However, they became quite soluble once they were cyclized and the $\pi-\pi$ stacking was reduced by the introduction of curvature.

Scheme 1[a]



[a] Reagents and conditions: (a) Tf_2O, Et_3N, CH_2Cl_2, −78 °C to rt, 90%; (b) tributyl-vinyl stannane, Pd$(Ph_3)_4$ (5%), LiCl, 1,4-dioxane, reflux, 4 h, 87%; (c) Pd(dppf)Cl_2 (5%), Et_3N, DMF, 100 °C, 20 h; (d) UV, I_2, 1,2-epoxypropane, $PhCH_3$, 2 h; (e) Pd$(PCy_3)_2Cl_2$, DBU, DMAc, 140 °C, 30 h.

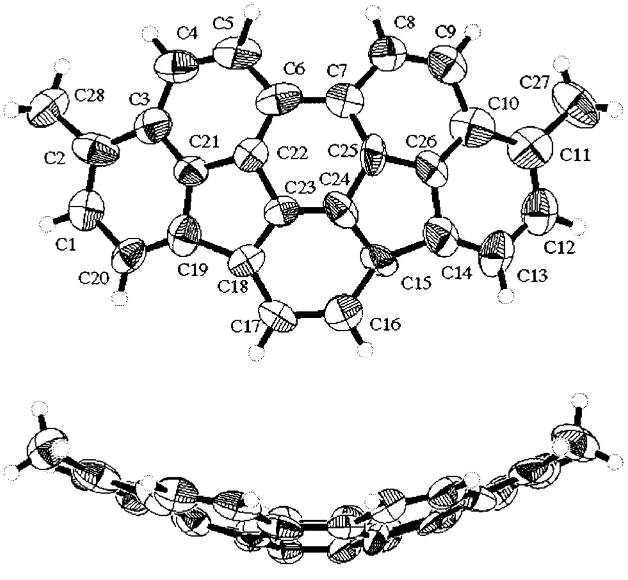


Figure 1. Crystal structure of **9a** (top, plan view; bottom, side view).

Single-crystal X-ray analysis of **9a** unambiguously establishes its structure (Figure 1) and reveals its nonplanarity.[15] The curvature of **9a** was evaluated by the simple and convenient method of π-orbital axis vector analysis (POAV1)[14] based on the geometry obtained from the X-ray analysis.

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(5) (a) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754−2755. (b) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804−7813.

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The local curvature at each internal sp^2 carbon is given a pyramidalization angle $\Theta_{\sigma\pi} - 90$. In this analysis, Θ is the angle between the vector that makes equal angles to the three σ-bonds and any one of the three σ-bonds that are assumed to lie along the internuclear axes (Figure 2). These pyramidalization angles are summarized in Table 1. Not surprisingly, the highest local curvature, 8.5°, was found on carbons 23 and 24 in the molecular center and observed to decrease toward the edge of the molecule. Although the local maximum curvature is slightly larger than that in corannulene (8.4°), it is about 3° smaller than that in C_{60}.[15d] The average pyramidalization angle for all of the carbons that only connect sp^2 carbons is 4.4°.

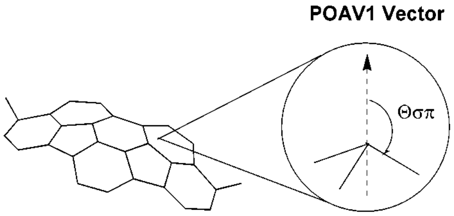

Figure 2. POAV1 π-orbital axis vector analysis method.

Table 1. Pyramidalization Angles (deg) Based on X-ray Analysis Geometry of **9a**

	C							
	23	22	18	21	6	19	3	2
$\Theta - 90$	8.5	6.3	4.9	4.0	3.7	2.6	1.0	0.9

In conclusion, we have successfully used palladium-mediated coupling to impose strain on simple polycyclic aromatic hydrocarbons by forming two five-membered rings with the production of two new bowl-shaped PAHs. X-ray crystallography of **9a** reveals its structure and nonplanarity. The presence of methoxy and methyl groups in the molecules demonstrates functional group tolerance and provides handles for further elaboration.

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(13) Analytical data are as follows. Compound **9a**: ^{1}H NMR (300 MHz, $CDCl_3$/MeOD) δ 8.04 (2H, d, $J = 8.8$ Hz), 7.81 (2H, d, $J = 8.8$ Hz), 7.53 (2H, m), 7.11 (2H, dd, $J = 7.4$, 1.1 Hz), 2.66 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$/MeOD) δ 138.09, 137.90, 137.46, 137.00, 136.65, 135.85, 129.12, 128.64, 128.43, 124.62, 123.89, 123.33, 123.30, 17.48; DCI/MS m/z 353 $(M + H)^+$, 370 $(M + NH_4)^+$. Anal. Calcd for $C_{28}H_{16}$: C, 95.42; H, 4.58. Found: C, 95.00; H, 4.97. Compound **9b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (2H, d, $J = 8.8$ Hz), 8.04 (2H, d, $J = 8.8$ Hz), 7.63 (2H, d, $J = 7.8$ Hz), 7.62 (2H, s), 6.66 (2H, d, $J = 7.8$ Hz), 4.02 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.48, 138.25, 138.00, 137.50, 137.45, 132.00, 129.86, 124.74, 124.34, 123.17, 122.33, 121.38, 106.29, 55.86; DCI/MS m/z 385 $(M + H)^+$. Anal. Calcd for $C_{28}H_{16}O_2$: C, 87.48; H, 4.20. Found: C, 87.17; H, 4.18.

(14) Crystal data for **9a**: $C_{28}H_{16}$, $M_r = 352.43$ g mol^{-1}; crystals from toluene; orange rod of dimensions $0.4 \times 0.10 \times 0.10$ mm^3; monoclinic; primitive; space group $P2_1/c$ (no. 14); $a = 21.140(4)$, $b = 3.84186(6)$, $c = 23.078(4)$ Å, $\beta = 115.388(3)°$; $V = 1693.3(4)$ Å^3; $Z = 4$, $D_{calc} = 1.38$ g cm^{-3}; F(000) = 736.00; μ(Mo Kα) 0.78 cm^{-1}.

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