Twisted Pyrene-fused Azaacenes

Sandeep More,\textsuperscript{a,b,c} Sunil Choudhary,\textsuperscript{b,c} Alexander Higelin,\textsuperscript{d} Ingo Krossing,\textsuperscript{b,d} Manuel Melle-Franco\textsuperscript{e} and Aurelio Mateo-Alonso\textsuperscript{a,f}* \\
\textsuperscript{a} POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, E-20018 Donostia-San Sebastian, Spain. E-mail: amateo@polymat.eu  
\textsuperscript{b} School of Soft Matter Research, Freiburg Institute for Advanced Studies (FRIAS), Albert-Ludwigs-Universität Freiburg, Albertstraße 19, 79104 Freiburg, Germany  
\textsuperscript{c} Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg, Germany  
\textsuperscript{d} Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg, Germany  
\textsuperscript{e} Centro de Ciências e Tecnologias de Computação, CCTC Universidade do Minho, 4710-057 Braga, Portugal  
\textsuperscript{f} Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Supporting Information

Reagents, Solvents and Equipment
Reagents for synthesis were, if not otherwise specified, purchased from Aldrich, Fluka or Acros. All reactions were carried out under argon, with magnetic stirring. Commercial chemicals and solvents were used as received. Petrol ether refers to the fraction that distills between 40-60 °C. Anhydrous solvents were dried using a MB SPS Solvent Purification System. In the case of dry THF the first and second column is charged with molecular sieves (2Å) type II. Compounds 4, 1a, 6a, 6b, 3a and 3b were prepared according previously reported procedures.\textsuperscript{1}

Chromatographic Methods
Column chromatography was carried out using silica gel 60 (40-63 μm) from Fluka. Analytical thin layer chromatography (TLC) was done using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck, aluminum foils (20x20 cm) covered with nano-silica gel from Fluka. Column chromatography was carried out by using Merck silica gel with particle size 40-63 μm. UV-active compounds were detected with a UV-lamp from CAMAG at wavelength $\lambda = 254$ or 366 nm.

UV-Vis-NIR and Emission
Spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer, and a LS55 Perkin-Elmer Fluorescence spectrometer, respectively.

Cyclic Voltammetry.
Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with Pt disc working electrode (Ø = 0.5 mm), a platinum wire counter electrode (Ø = 0.5 mm) and a silver wire pseudoreference electrode. The cell and the electrodes were custom made. The reduction potentials were referred to SCE using ferrocene (Fc) as internal reference ($E_{1/2}^{Fc\ SCE} = +0.48$ V) after the measurements. Anhydrous THF were dried using a MB SPS Solvent Purification System.
**X-Ray Diffraction.**

Data for the crystal structures were collected on a Bruker SMART APEX2 CCD area detector diffractometer with Mo-Kα radiation. The single crystals were coated at room temperature with perfluoroether oil and mounted on 0.1 mm micromounts. The structures were solved by direct or dual space methods in SHELX\(^4\) and OLEX2\(^5\) and refined by least squares on weighted F\(^2\) values for all reflections. All hydrogen atoms were included in the refinement in calculated positions by a riding model. The graphical representations were prepared with mercury.
Compound 5b

Compound 4 (100 mg, 0.14 mmol) was added to a degassed solution of i-Pr₂NH (10 mL) and dry THF (10 mL) and the solution was degassed. Subsequently CuI (2.061 mg, 0.0108 mmol) and [Pd(PPh₃)₂Cl₂] (7.70 mg, 0.0108 mmol) were added and degassed. Then triisobutylsilyl acetylene (0.129 mL, 0.57 mmol) was added, the solution was once again degassed and heated at 80 °C under Argon overnight. The resulting mixture was filtered over celite and washed with 200 mL of CH₂Cl₂. Removal of the solvent under vacuum and purification of the crude product by column chromatography (petrol ether : ethyl acetate = 20 : 1) yielded 5b as white solid (80 mg, 62 %).

\[ \text{δ ppm = 7.78 (s, 4H); 4.18 (br s, 8H); 3.65 (br s, 8H); 1.90 (m, 6H); 1.01 (d, 36H, J=10Hz); 0.68 (d, 12H, J=10Hz).} \]

\[ \text{MS: Found 883.3 [M]\text{\textsuperscript{+}}. Calculated Mass: 883.31} \]

Compound 2b

A solution of 5b (100 mg, 0.125 mmol) in a mixture of TFA-H₂O (9:1, 10 ml) was stirred at room temperature for 8 hrs and reaction was monitored by TLC. After completion, the reaction mixture was poured in ice cold water and the precipitate was filtered then the solid was washed with water, which after drying purified by column chromatography (petrol ether : CH₂Cl₂; 7 : 3) offered 2b as dark orange solid (64 mg, 80% yield).

\[ \text{δ ppm = 8.37 (s, 4H); 1.85 (m, 6H); 0.95 (d, 36H, J=15Hz); 0.70 (d, 12H, J=15Hz).} \]

\[ \text{MS: Found 707.6 [M]\text{\textsuperscript{+}}. Calculated Mass: 707.10} \]
Compound 1b

In a dry argon flushed Schlenk flask the compound 2b (50 mg, 0.07 mmol) and amine 3b (156.43 mg, 0.28 mmol) were suspended in the mixture of acetic acid (3 ml) and ethanol (10 ml). The reaction mixture was heated at 80°C overnight. After completion the reaction, mixture was allowed to cool down to room temperature. Then filtered and the solid was washed with ethanol, which after drying purified by column chromatography (petrol ether : CH₂Cl₂; 7 : 3) under vacuum yielded compound 1b (56 mg, 78%) as yellow solid. ¹H NMR: (300 MHz, CDCl₃) δ ppm = 9.72 (s, 4H); 7.97 (s, 4H); 2.08 (m, 18H); 1.14 (d, 108H); 0.90 (d, 36H). ¹³C NMR (125 MHz, CDCl₃): δ ppm = 142.60, 141.97, 134.01, 131.64, 130.08, 124.28, 103.87, 103.30, 26.44, 25.27, 25.13. MS: Found 1740.9 [M]+ Calculated Mass: 1741.08. UV-Vis (THF, nm): 269, 320, 335, 408, 432

Compound 5c

Compound 4 (100 mg, 0.144 mmol) was added to a degassed solution of i-Pr₂NH (10 mL) and dry THF (10 mL) and the solution was degassed. Subsequently Cul (1.37 mg, 0.007 mmol) and [Pd(PPh₃)₂Cl₂] (5.14 mg, 0.007 mmol) were added and degassed. Triphenylsilyl acetylene (164 mg, 0.57 mmol) was added, the solution was once again degassed and heated at 80 °C under Argon overnight. The resulting mixture was filtered over celite and washed with 200 mL of CH₂Cl₂. Removal of the solvent under vacuum and purification of the crude product by column chromatography (CHCl₃ : MeOH = 20 : 1) yielded 5c as white solid (30 mg, 20 %). ¹H NMR (300 MHz, CDCl₃): δ ppm = 7.96
(s, 4H); 7.7 (m, 6H); 7.43 (m, 24H); 4.22 (br s, 8H); 3.68 (br s, 8H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm = 135.76, 133.75, 133.42, 130.95, 130.14, 128.21, 128.16, 124.50, 101.36, 92.23. MS: Found 1002.9 [M-1]$^+$ Calculated Mass: 1003.24

**Compound 2c**

A solution of 5c (20 mg, 0.009 mmol) in a mixture of TFA-H$_2$O- CH$_2$Cl$_2$ (5:1:4, 10 ml) was stirred at 40$^o$C for 24 hrs and reaction was monitored on TLC. After completion, the reaction mixture was poured in ice cold water and extracted with CH$_2$Cl$_2$ (10 ml) 2-3 times the organic layer was dried over Na$_2$SO$_4$. After removal of solvent under reduced pressure yielded 2c as orange solid (12 mg, 72% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ ppm = 8.61 (s, 4H); 7.69 (m, 6H); 7.46 (m, 24H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm = 176.94, 139.77, 135.72, 132.39, 131.00, 130.5, 128.35, 128.28, 126.84, 104.79, 97.28. MS: Found 897.1 [M + 2NH$_4$OH]$^+$ Calculated Mass: 827.03

**Compound 6c**

To an oven-dried Schlenk flask was added dry THF (20 mL) and triethylamine (20 mL), which was then vacuum degassed three times. 4,7-dibromobenzo[c][1,2,5] thiadiazole (0.5 gm, 1.70 mmol), triphenylsilylacetylene (1.065 gm, 3.74 mmol), copper (I) iodide (9.26 mg, 0.05 mmol), and bis(triphenylphosphine)palladium(II) chloride (35.10 mg, 0.05 mmol) were all added at room temperature. The Schlenk flask was sealed and heated to 80$^o$C, whereupon the solution was stirred for 12 h. After the reaction was cooled to room temperature, water (200 mL) was added to the mixture and the aqueous solution was extracted with dichloromethane (2 x 100mL). The combined organic layers were washed with water (3 x 200mL), dried with sodium sulfate, filtered, and dried in vacuo. The residue was purified by column chromatography on silica gel using pure hexane. Compound 6c (0.900 g, 75% yield) was isolated as yellow crystals. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.805 (s, 2H); 7.792-7.769 (m, 6H), 7.477-7.362 (m, 24H). $^{13}$C
NMR (100 MHz, CDCl₃): δ 155.201, 136.409, 133.847, 133.683, 130.804, 128.780, 118.145, 104.959 and 99.477. ESI-MS calcd. For C₄₆H₃₂N₂Si₂ (M⁺) 701.2, found 700.2

**Compound 3c**

To a solution of 6c (0.5 g, 0.714 mmol) in THF (20 mL) was added LiAlH₄ (108.38 mg, 2.856 mmol) at 0 °C and the mixture was stirred at room temperature for 12 h. The mixture was quenched with saturated NH₄Cl solution and extracted with diethyl ether (3 x 200 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed *in vacuo* to give a light yellow solid (0.920 g, 96%). ¹H NMR (500 MHz, CDCl₃): δ 7.708-7.688 (m, 6H), 7.465-7.368 (m, 24H), 6.925 (s, 2H), 3.639 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 135.867, 135.272, 133.640, 130.426, 130.340, 128.506, 128.371, 128.345 and 128.227. ESI-MS calcd. For C₄₆H₃₆N₂Si₂ (M⁺) 672.6, found 672.2

**Compound 1c**

In a dry argon-flushed Schlenk flask, compound 2c (40 mg, 0.04 mmol) and amine 3c (92.4 mg, 0.13 mmol) were dissolved in the mixture of acetic acid (3 ml) and ethanol (10 ml). The reaction mixture was heated at 80°C for overnight. After completion the reaction, mixture was allowed to cool down to room temperature. Then filtered and the solid was washed with ethanol. The obtained product was purified by column chromatography (CH₂Cl₂ : petrol ether = 4 : 1) which gave compound 5c (52 mg, 51%) as yellow solid.

¹H NMR: (500 MHz, CDCl₃) δ ppm = 10.06 (s, 4H); 7.91 (m, 24H); 7.26 (m, 48H); 7.14 (m, 6H); 5.98 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ ppm = 142.54, 135.89, 135.78, 135.65, 135.34, 133.37, 133.04, 132.42, 130.34, 130.19, 129.74, 128.35, 128.32, 128.00, 124.19, 108.24, 106.30, 99.68, 93.45. MS: Found: 2101.654 [M + 3] Calculated Mass: 2098.64. UV-Vis (THF, nm): 280, 334, 348, 411, 436.
Fig. S1: $^1$H NMR and $^{13}$C NMR of compound 5b in CDCl$_3$. 
Fig. S2: $^1$H NMR and $^{13}$C NMR of compound 2c in CDCl$_3$. 

S8
Fig. S3: $^1$H NMR and $^{13}$C NMR of compound 1b in CDCl$_3$. 
**Fig. S4:** $^1$H NMR and $^{13}$C NMR of compound 5c in CDCl$_3$. 
Fig. S5: $^1$H NMR and $^{13}$C NMR of compound 5c in CDCl$_3$. 
Fig. S6: $^1$H NMR and $^{13}$C NMR of compound 6c in CDCl$_3$. 
Fig. S7: $^1$H NMR and $^{13}$C NMR of compound 3c in CDCl$_3$. 
**Fig. S8:** $^1$H NMR and $^{13}$C NMR of compound 1c in CDCl$_3$. 
Computer modelling

The geometry of compounds 1a-c was optimized with Spartan10 and Gaussian09 with a B3LYP 6-31g* basis set yielding similar results.

Fig. S9. HOMO, LUMO y LUMO+1 orbitals for 1a-c.

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO+1</td>
<td>-2.7</td>
<td>-2.7</td>
<td>-2.8</td>
<td>eV</td>
</tr>
<tr>
<td>LUMO</td>
<td>-2.7</td>
<td>-2.7</td>
<td>-2.8</td>
<td>eV</td>
</tr>
<tr>
<td>HOMO</td>
<td>-5.8</td>
<td>-5.8</td>
<td>-5.9</td>
<td>eV</td>
</tr>
<tr>
<td>HOMO-1</td>
<td>-5.7</td>
<td>-5.7</td>
<td>-5.8</td>
<td>eV</td>
</tr>
<tr>
<td>HOMO/LUMO gap</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>eV</td>
</tr>
<tr>
<td>LUMO(B_{1g})/LUMO(B_{3u}) ΔE</td>
<td>4</td>
<td>9</td>
<td>-2</td>
<td>meV</td>
</tr>
</tbody>
</table>

Table S1. B3LYP energy levels for 1a-c.
Twist effects

Fig. S10. HOMO, LUMO y LUMO+1 orbitals for S1 with varying twist angles.
<table>
<thead>
<tr>
<th>Twist angle</th>
<th>0º</th>
<th>12º</th>
<th>24º</th>
<th>36º</th>
<th>48º</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO</td>
<td>-5.919</td>
<td>-5.917</td>
<td>-5.914</td>
<td>-5.907</td>
<td>-5.896</td>
<td>eV</td>
</tr>
<tr>
<td>HOMO-1</td>
<td>-6.046</td>
<td>-6.045</td>
<td>-6.040</td>
<td>-6.033</td>
<td>-6.022</td>
<td>eV</td>
</tr>
<tr>
<td>HOMO/LUMO gap</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>eV</td>
</tr>
<tr>
<td>LUMO(B₁g)/LUMO(B₃u) ΔE</td>
<td>15</td>
<td>12</td>
<td>2</td>
<td>-16</td>
<td>-41</td>
<td>meV</td>
</tr>
</tbody>
</table>

**Table S2.** B3LYP energy levels for S1 with different twist angles.

**References**