

# Highly Contorted Rigid Nitrogen-Rich Nanographene with Four Heptagons

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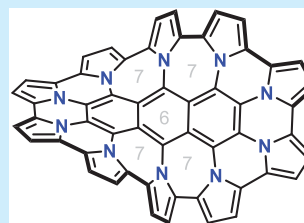


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Supporting Information

**ABSTRACT:** Nucleophilic substitution of 9,10-dichlorooctafluoroanthracene with 3,4-diethylpyrrole and subsequent Scholl reaction give the annularly fused decapyrrolyl anthracene. Single crystal X-ray analysis revealed a highly contorted geometry induced by a combination of adjacent heptagons, forming a unique 7–7–6–7–7 topology. The end-to-end twist angle along the acene moiety is 90°. Cyclic voltammetry studies reveal 6-electron oxidation waves. Density functional theory calculations provided further insights into the aromaticity and electronic properties of this highly twisted, nitrogen-rich nanographene. The structural rigidity and high racemization energy barrier have been studied theoretically and experimentally by VT-NMR.



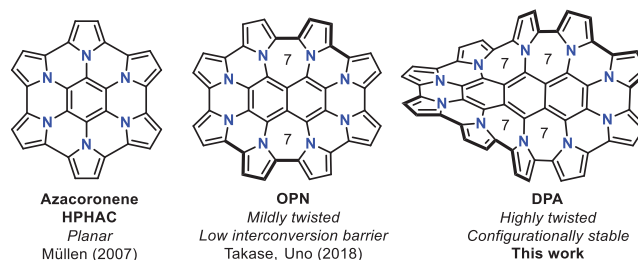
2-step synthesis  
X-ray structure  
4 heptagons  
6-electron oxidation  
stable configuration  
7-7-6-7-7 topology

The incorporation of seven-membered rings in flat nanographenes (NGs) induces contortion of the plane.<sup>1</sup> Contorted NGs possess chirality that generates a new set of optical, conductive, and magnetic properties, leading to potential applications in modern molecular electronics.<sup>2</sup> Numerous NGs containing isolated heptagonal rings have been synthesized.<sup>3</sup> The majority of them exhibit mild curvatures and low interconversion energy barriers, hindering their resolution into pure enantiomers—an essential feature for some applications.<sup>4</sup> NGs containing two or more adjacent seven-membered rings demonstrate higher inversion energy barriers.<sup>5</sup> However, only a limited number of structures with multiple adjacent 7-membered rings have been reported. Yamamoto's seminal work on [7.7]circulene<sup>6</sup> paved the way for the development of carbon-based NGs with three adjacent heptagons by Miao's group in 2023.<sup>7</sup> Additionally, Gryko and colleagues have recently achieved the synthesis of nitrogen-doped NGs with multiple odd-membered rings.<sup>8</sup> Despite their potential, NGs with multiple heptagonal rings often suffer from lengthy synthetic routes. Configurationally stable NGs with heptagons remain scarce.

In this work, we report an azacoronene-based NG with a highly contorted conformation induced by multiple adjacent heptagons, demonstrating exceptional thermal configurational stability.

Azacoronene, or hexapyrrolohexaazacoronene (HPHAC), is a polyaromatic compound accessible through a two-step synthesis involving hexafluorobenzene and pyrrole (Scheme 1).<sup>9</sup> HPHAC, a robust 2-electron donor,<sup>10</sup> has been studied in the context of materials<sup>11</sup> and radical chemistry.<sup>12</sup> An extended naphthalene analog-fused octapyrrolyl naphthalene (OPN) was reported by Takase and Uno in 2018 (Scheme 1).<sup>13</sup> OPN contains two seven-membered rings inducing mild curvature with low interconversion energy barrier. Uno's group later

## Scheme 1. Azacoronene and its Extended Analogs



synthesized an OPN derivative with bulky acenaphtho[1,2-*c*]pyrroles, but the configurational stability of this OPN variant remained low.<sup>14</sup>

Inspired by the studies of Müllen, Takase, and Uno, we set out to synthesize a novel  $\pi$ -extended azacoronene analog-fused decapyrrolyl anthracene (DPA) (Scheme 1).<sup>15</sup> Our objective was to further expand the family of these intriguing compounds with enhanced properties. We first prepared decapyrrole-substituted anthracene **1**, employing nucleophilic aromatic substitution reaction between 9,10-dichlorooctafluoroanthracene<sup>16</sup> and 3,4-diethylpyrrole sodium salt (Scheme 2). Surprisingly, full substitution has been achieved after 24 h in DMF at room temperature. The resulting decapyrrolyl anthracene **1** was isolated in 90% yield as a red crystalline solid. The product was characterized by <sup>1</sup>H, <sup>13</sup>C NMR, and

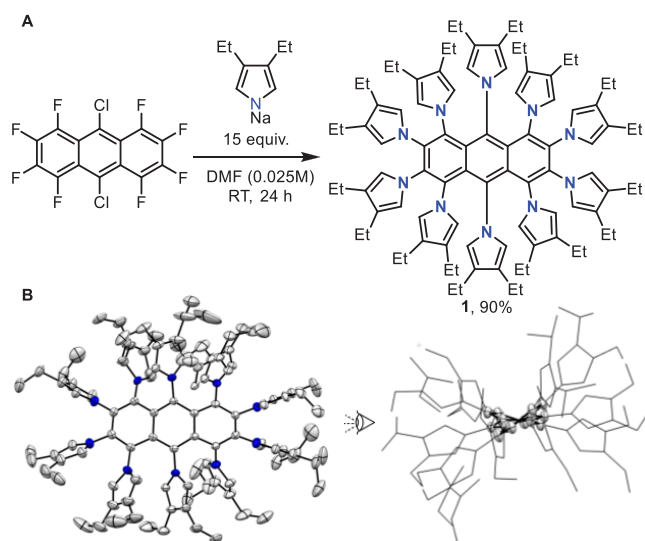
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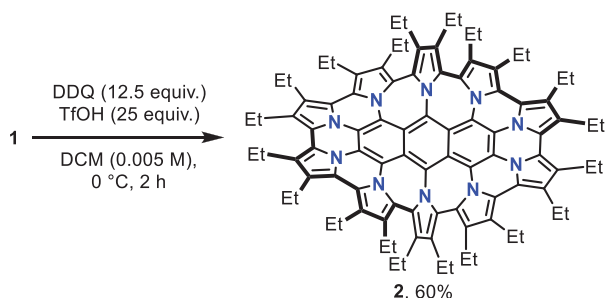


Scheme 2. Synthesis (A) and Crystal Structure (B) of **1**<sup>a</sup>

<sup>a</sup>Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

high-resolution mass spectrometry (HRMS). Variable temperature (VT) NMR studies disclosed restricted rotation of the nearly perpendicularly arranged pyrrole rings around C–N bonds. The molecular structure of **1** was established through single-crystal X-ray diffraction (SCXRD) analysis. The end-to-end twist angle of the anthracene core in **1** ( $58^\circ$ ) is comparable to analogous decaphenyl anthracene ( $63^\circ$ ) synthesized by Pascal and co-workers.<sup>17</sup>

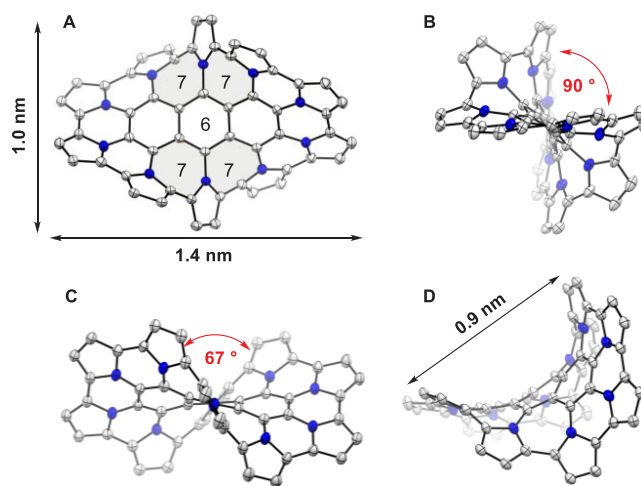
Subsequently, the Scholl reaction of **1** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and triflic acid (TfOH) in DCM at  $0^\circ\text{C}$  was performed (Scheme 3). The resulting

Scheme 3. Synthesis of Fused Decapyrrollyl Anthracene **2**

product was isolated in 60% yield as an air-stable dark-brown solid. Remarkably, compound **2** is highly soluble in most apolar organic solvents including hexanes. A comparison of the  $^1\text{H}$  NMR spectra of **1** and **2** revealed the absence of pyrrolic C–H signals in **2**, confirming the successful fusion of all ten pyrrole rings. The elemental composition of  $\text{C}_{94}\text{H}_{100}\text{N}_{10}$  was confirmed by HRMS MALDI-TOF.

Further recrystallization of **2** from benzene/methanol yielded crystals suitable for SCXRD which revealed the twisted saddle structure of **2** (Figure 1). Both M and P enantiomers of **2** were identified in the crystal lattice “buffered” with cocrystallized  $\text{C}_6\text{H}_6$  solvent molecules (Figure S26).

The nanometer dimensions of the DPA core of **2** without ethyl groups correspond to the definition of nanographene ( $1.4\text{ nm} \times 1.0\text{ nm}$ , Figure 1A). Along the long axis, the end-to-end



**Figure 1.** X-ray diffraction crystal structure of **2**. (A) Top view. (B) Viewed along the anthracene long axis. (C) Viewed along the anthracene short axis. (D) Saddle view. Hydrogen atoms and ethyl groups are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

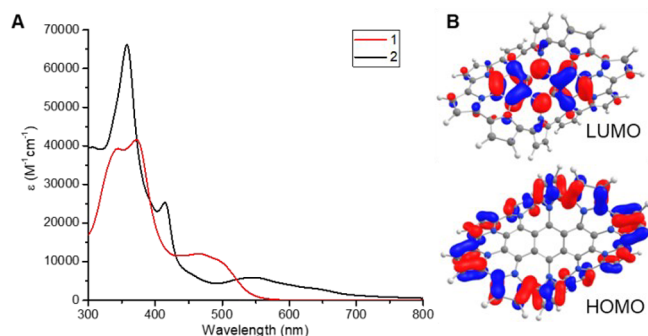
dihedral angle along the tetraazapentacene core ( $90^\circ$ ) is higher than that in the OPN ( $63^\circ$ ) (Figure 1B). Along the shorter axis, a figure-eight-shaped cyclo[10]pyrrole<sup>18</sup> embedded into anthracene can be viewed with  $67^\circ$  torsion angle induced by contiguous nonplanar seven-membered rings (Figure 1C). The average edge-to-edge distance between the carbon atoms of the saddle is  $0.9\text{ nm}$  (Figure 1D).

To better understand the configurational dynamics of **2**, we analyzed it by VT  $^1\text{H}$  NMR from  $8$  to  $80^\circ\text{C}$  in  $\text{C}_6\text{D}_6$  (Figure S14). Essentially no difference in chemical shifts and shapes of ethyl group signals was observed. It indicates that the rotation of densely arranged ethyl substituents is restricted, and the curved configuration of **2** is retained in this temperature range. We believe that dense ethylation enhances the configurational stability of the DPA core.

We also modeled the racemization dynamics of fused decapyrrollyl anthracene (DPA) by density functional theory (DFT) through the nudged elastic band method. The calculation was carried out using ORCA 5.0 at the B3LYP/def2-TZVP(-f) level of theory (Figure S28).<sup>19</sup> The calculated energy barrier of nonethylated DPA ( $19.4\text{ kcal/mol}$ ) going through a saddle-shaped transition state is more than three times higher than that of OPN ( $5.9\text{ kcal/mol}$ ). Notably, [7]circulene and [7.7]circulene fully surrounded with hexagons have lower inversion energy barriers ( $9$  and  $11\text{ kcal/mol}$  respectively) because of continuous wave-like pseudorotation.<sup>1c</sup> Such pseudorotation is not available to DPA because the seven-membered rings are only surrounded by six rings, making it more rigid.

Given the high configurational stability of **2**, we attempted the separation of M and P enantiomers using analytical chiral HPLC. We observed two peaks that were not fully resolvable due to the high solubility of **2** in hexanes (Figure S24).

Next, we measured UV–vis absorption spectra of **1** and **2** in hexane (Figure 2A). Compound **1** has absorption maxima at  $344\text{ nm}$  ( $\epsilon = 39300\text{ M}^{-1}\text{ cm}^{-1}$ ),  $372\text{ nm}$  ( $\epsilon = 41600\text{ M}^{-1}\text{ cm}^{-1}$ ), and  $465\text{ nm}$  ( $\epsilon = 12065\text{ M}^{-1}\text{ cm}^{-1}$ ). Due to the addition of 10 pyrrole substituents, the E2 absorption band of the anthracene core is red-shifted by about  $110\text{ nm}$  compared to the parent anthracene. The characteristic vibrational

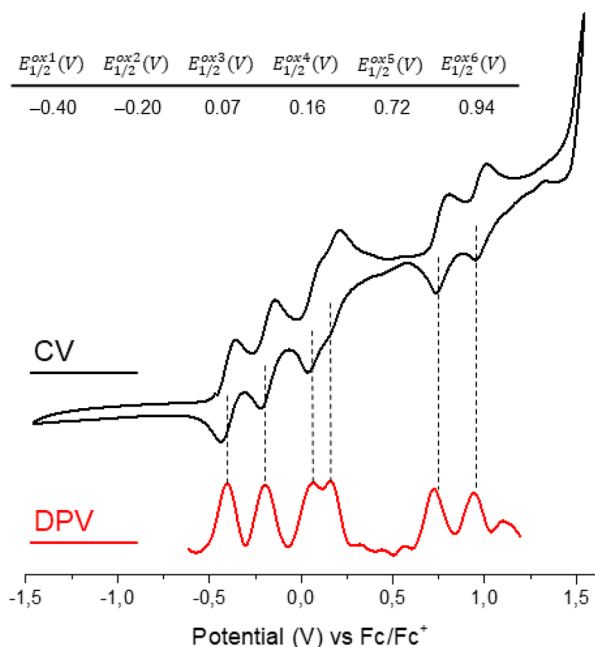


**Figure 2.** (A) Absorption spectra of **1** (red line) and **2** (black line) in hexane. (B) Frontier molecular orbitals of DPA calculated at the B3LYP/def2-TZVP(-f) level.

anthracene fine structure is still visible at 465 nm with an unresolved shoulder. Fused compound **2** has an absorption tail out to 800 nm with maxima at 358 nm ( $\epsilon = 66200 \text{ M}^{-1} \text{ cm}^{-1}$ ), 414 nm ( $\epsilon = 25300 \text{ M}^{-1} \text{ cm}^{-1}$ ), and 545 nm ( $\epsilon = 5900 \text{ M}^{-1} \text{ cm}^{-1}$ ). Compounds **1** and **2** are nonemissive under UV.

We calculated the frontier molecular orbitals of DPA using DFT. The HOMO is located on the outer double bonds of pyrrole rings, and LUMO is on the inner anthracene core (Figure 2B). The calculated energy band gap of DPA is 1.78 eV (Table S7).

We performed voltammetric studies to investigate the electrochemical properties of compound **2** (Figure 3). Cyclic



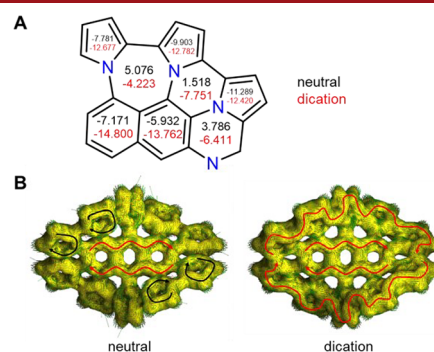
**Figure 3.** Cyclic voltammogram (black line) and differential pulse voltammogram (red line) of **2** in DCM/0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$  referenced to ferrocene/ferrocenium redox couple.

voltammetry (CV) and differential pulse voltammetry (DPV) measurements of **2** in DCM revealed six one-electron oxidation steps with the half-wave potentials of  $E_{ox1} = -0.40 \text{ V}$ ,  $E_{ox2} = -0.20 \text{ V}$ ,  $E_{ox3} = 0.07 \text{ V}$ ,  $E_{ox4} = 0.16 \text{ V}$ ,  $E_{ox5} = 0.72 \text{ V}$ , and  $E_{ox6} = 0.94 \text{ V}$ . Similar to HPHAC and OPN derivatives,<sup>9b,13</sup> the difference between  $E_{ox3}$  and  $E_{ox2}$  (0.27 V) is larger than one between  $E_{ox2} - E_{ox1}$  (0.20 V) and  $E_{ox4} - E_{ox3}$  (0.09 V), which implies that dication  $2^{2+}$  is electronically

stabilized. Repetitive CV measurements at different scan rates revealed that the first two oxidation steps are reversible, and the next four oxidation waves are pseudoreversible.

Chemical oxidation/titration of **2** into  $2^{2+}$  with  $\text{SbCl}_5$  in DCM was followed by UV-vis and NMR. The UV-vis spectrum of the dication has a red-shifted absorption band maximum (from 348 to 402 nm). On  $^1\text{H}$  NMR, methylene ( $\text{CH}_2$ ) peaks have shifted downfield from 3.08–2.63 ppm (**2**) to 3.37–2.83 ppm ( $2^{2+}$ ) and upfield from 2.27 ppm (**2**) to 2.00 ppm ( $2^{2+}$ ); methyl ( $\text{CH}_3$ ) peaks have downfield shift from 1.34–1.09 ppm (**2**) to 1.75–1.23 ppm ( $2^{2+}$ ) and upfield from 0.82 ppm (**2**) to 0.63 ppm ( $2^{2+}$ ) (Figure S15). Similar observations have been made for dication HPHAC and OPN derivatives.<sup>9b,13</sup> Our attempts to detect higher oxidation states of **2** ( $4+$ ,  $6+$ ) by NMR were not successful, likely due to their lower stability.

Nucleus-independent chemical shift (NICS) and anisotropy of the induced current density (ACID) calculations were carried out to determine the aromaticity of DPA in neutral and dication states (Figure 4).<sup>20</sup> NICS values together with the



**Figure 4.** (A) NICS values of DPA in the neutral (black) and dication (red) states calculated at the B3LYP/def2-TZVP(-f) level of theory. (B) ACID plots (B3LYP/6-31g(d)) of the neutral (left) and dication (right) of DPA.

ACID plot calculated for neutral DPA show aromaticity only in anthracene rings and isolated pyrrole rings. The dicationic state of DPA has higher aromaticity according to negative NICS values of all rings. The ACID plot of the dication shows conjugation between pyrrole rings with a 38-electron  $\pi$ -system which corresponds to the Hückel aromaticity rule ( $4n+2$ ) (Figure 4B).

To conclude, we have synthesized fused decapyrrollyl anthracene (DPA) **2** by a simple two-step procedure using commercially available starting materials in good yield. The single crystal X-ray structure of **2** revealed highly contorted geometry induced by a combination of two pairs of adjacent seven-membered rings linked through a benzene ring forming a unique 7–7–6–7–7 topology.<sup>21</sup> VT-NMR and DFT modeling studies show **2** as configurationally stable up to 80 °C in solution. Rigid chirality in combination with the multielectron redox behavior of fused DPA is interesting for applications in chiral-induced spin selectivity (CISS).<sup>22</sup> Related studies are currently underway in our laboratories. We hope our work will inspire the development of the next generation of extended azacoronene analogs based on tetracene and pentacene systems.<sup>23</sup>



## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its [Supporting Information](#).

### ■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.4c00588>.

Experimental details, analytical data of the new compounds, DFT calculations, and crystallographic data for compounds **1** and **2** (PDF)

### Accession Codes

CCDC 2320320–2320321 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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