Supporting material for:

Carbon Networks Based on Dehydrobenzoannulenes.
3. Synthesis of Graphyne Substructures.

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EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were recorded using a GE QE-300 (^{1}H: 300.13 MHz, ^{13}C: 75.51 MHz) or a Varian Inova (^{1}H: 299.94 MHz, ^{13}C: 75.43 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual chloroform as internal standard (^{1}H: 7.26 ppm, ^{13}C: 77.0 ppm). Coupling constants are expressed in hertz. IR spectra were recorded using a Nicolet Magna FTIR 550 spectrometer. UV-vis spectra were obtained using a Hewlett-Packard 8453 UV-vis spectrophotometer. MS spectra were recorded using a Kratos MS50 spectrometer. Melting points were determined on a Meltemp II apparatus and are uncorrected. Dichloromethane, triethylamine, and pyridine were distilled from calcium hydride under an atmosphere of nitrogen prior to use. Tetrahydrofuran and benzene were distilled from sodium and benzophenone under an atmosphere of nitrogen prior to use. All other chemicals were reagent quality and used as obtained from manufacturers. Column chromatography was performed on Whatman reagent grade silica gel (230-400 mesh). Baker pre-coated silica gel plates were used for analytical (200 x 50 x 0.25 mm) thin layer chromatography. Reactions were carried out in an inert atmosphere (dry nitrogen or argon) when necessary.

General Aryl Diethyltriazene Formation Procedure. To a 1 M solution of the starting aniline in 1:1 (v:v) acetonitrile and water was slowly added 3.2 equivalents of conc. HCl solution. The addition was highly exothermic and rapidly produced precipitate; additional water and acetonitrile were added as required to maintain a homogeneous solution. When the HCl addition was complete, the dark brown solution was placed under argon and cooled to –5 °C. An ice-cold 0.05 M solution of sodium nitrite (1.45 equiv) in deionized water was added dropwise such that the temperature of the reaction mixture never exceeded 0 °C. After stirring for 30 min at -5 to 0 °C, the reaction mixture was added over 5 min to a rapidly stirring, ice-cold solution of potassium carbonate (5.2 equiv) and diethylamine (2.5 equiv) in a 2:1 (v:v) mixture of water/acetonitrile (ca. 100 mL of the solvent mixture for every 10 mmol of starting aniline). After stirring for 15 min, the reaction mixture was extracted with four times with ether. The organic layer were washed twice with brine, dried ($MgSO_4$), filtered, and concentrated by evaporation. The crude product was purified by flash chromatography over silica gel.

General Acetylene Coupling Procedure. An Ace-thred pressure tube was charged with an iodoarene (1 equiv), bis(triphenylphosphine)palladium(II)chloride (0.05-0.10 equiv), copper(I) iodide (0.10-0.20 equiv), and dry, deoxygenated triethylamine (0.1 M). After brief argon bubbling, the silyl-protected terminal acetylene (1 equiv) was added via syringe under an inert atmosphere. The reaction vessel was then filled with argon and sealed with a Teflon screw cap equipped with a pressure relief valve. The reaction mixture was stirred at 25-50 °C for 12-48 h. When TLC indicated completion of the reaction, the mixture was cooled and concentrated *in vacuo*. The dark residue was extracted into ether and washed sequentially with 10% HCl solution, water, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography.

General Methyl Iodide Deprotection Procedure. A 0.3 M solution of the diethyltriazene substrate in distilled iodomethane was stirred in a sealed pressure reactor under argon at 120 °C for 6-24 h. Upon cooling, the reaction mixture was diluted with hexanes, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography over silica gel.

General (Trimethylsilyl)acetylene Deprotection Procedure. The appropriate (trimethylsilyl)acetylene was vigorously stirred with anhydrous potassium carbonate (0.5 equiv) in a 5:1 (v:v) solution of methanol and diethyl ether (1.5 M). The reaction was followed by TLC and generally required 1 to 4 hours for completion. When the starting material had been consumed, the mixture was diluted with water and extracted into additional diethyl ether. After washing with water and brine, the organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford the desired terminal acetylene in sufficiently pure form for further elaboration.

General Macrocyclization Procedure. A 0.01 M solution of the silyl protected acetylenic substrate in wet THF was treated with 2.1 equivalents of tetrabutylammonium fluoride (1M THF solution) at room temperature. The reaction was followed by TLC and was typically complete in less than 1 h. The mixture was diluted with diethyl ether (ca. 25 mL per mmol substrate), washed with water and brine, dried ($MgSO_4$), and then filtered through a short pad of silica gel (hexanes). After removal of the solvent, the crude product was redissolved in dry, deoxygenated triethylamine (0.05 M). This material was added dropwise to a stirring, 80°C solution of bis(dibenzylideneacetone)palladium(0) (1.5 equiv), copper(I) iodide (1.4 equiv), triphenylphosphine (6 equiv), and triethylamine (ca. 250 mL per mM of di-silyl starting material). The addition was done under argon over 16-20 h. When TLC indicated completion of the reaction, the mixture was cooled and concentrated *in vacuo*. The dark residue was extracted into ether and washed sequentially with 10% HCl solution, water, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography.

Selected spectroscopic data for compounds **4**-**6**, **8**-**13**, and **15**-**17**:

***N,N*-Diethyl-*N'*-[2-(trimethylsilylethynyl)phenyl]triazene (8).** ^{1}H NMR (CDCl$_3$): δ 7.47 (d, *J* = 7.9, 1H), 7.38 (d, *J* = 7.9, 1H), 7.24 (t, *J* = 7.4, 1H), 7.03 (t, *J* = 7.4, 1H), 3.79 (q, *J* = 7.1, 4H), 1.31 (t, *J* = 7.1, 6H), 0.24 (s, 9H). ^{13}C NMR (CDCl$_3$): δ 152.83, 133.26, 129.05, 124.54, 118.03, 116.83, 103.60, 97.82, 0.11.

***N,N*-Diethyl-*N'*-(2-ethynylphenyl)triazene (9).** ^{1}H NMR (CDCl$_3$): δ 7.50 (d, *J* = 7.5, 1H), 7.39 (d, *J* = 8.1, 1H), 7.28 (t, *J* = 7.7, 1H), 7.06 (t, *J* = 7.4, 1H), 3.79 (q, *J* = 7.1, 4H), 3.26 (s, 1H), 1.31 (t, *J* = 6.9, 6H). ^{13}C NMR (CDCl$_3$): δ 153.10, 133.48, 129.27, 124.54, 117.07, 116.96, 82.11, 80.68.

1-Iodo-2-(trimethylsilylethynyl)benzene (10).[1] ^{1}H NMR (CDCl$_3$): δ 7.83 (d, *J* = 7.8, 1H), 7.46 (d, *J* = 7.7, 1H), 7.28 (t, *J* = 7.7, 1H), 6.98 (t, *J* = 7.8, 1H), 0.29 (s, 9H). ^{13}C NMR (CDCl$_3$): δ 138.66, 132.70, 129.59, 129.52, 127.67, 106.49, 101.25, 98.77, –0.20.

Triazene 11. ^{1}H NMR (CDCl$_3$): δ 7.58 (d, *J* = 7.5, 1H), 7.48 (t, *J* = 7.5, 2H), 7.42 (d, *J* = 8.0, 1H), 7.31-7.19 (m, 3H), 7.10 (t, *J* = 7.4, 1H), 3.80 (q, *J* = 7.1, 4H), 1.32 (t, *J* = 7.1, 6H), 0.26 (s, 9H). ^{13}C NMR (CDCl$_3$): δ 152.32, 133.14, 132.22, 131.53, 129.99, 128.00, 127.31, 127.02, 125.44, 124.57, 118.26, 116.95, 103.74, 98.34, 92.52, 91.95, 0.02.

Triazene 12. ^{1}H NMR (CDCl$_3$): δ 7.60-7.48 (m, 5H), 7.43 (d, *J* = 8.1, 1H), 7.32-7.20 (m, 5H), 7.07 (t, *J* = 7.5, 1H), 3.76 (q, *J* = 7.1, 4H), 1.28 (t, *J* = 7.1, 6H), 0.25 (s, 9H). ^{13}C NMR (CDCl$_3$): δ 152.46, 133.23, 132.26, 132.13, 132.00, 131.66, 128.99, 128.11, 127.95, 127.79, 127.37, 126.81, 126.36, 125.72, 125.50, 124.63, 118.25, 117.06, 103.53, 98.62, 92.74, 92.60, 92.08, –0.03.

Annulene 4.[2] Mp 210-211 °C. ^{1}H NMR (CDCl$_3$): δ 7.36-7.31 (*AA'*m, 4H), 7.20-7.15 (*BB'*m, 4H). ^{13}C NMR (CDCl$_3$): δ 131.96, 128.48, 126.66, 92.83. IR (CHCl$_3$) *ν* 2206 cm^{-1}. UV-vis (CH$_2$Cl$_2$) λ (log ε) 271 (1.37), 282 (1.18), 295 (3.23) nm. MS (EI, 70 eV): *m/z* 302 (M$^+$+2H, 6), 301 (M$^+$+H, 35), 300 (M$^+$, 100).

Bis(triazene) 13. ^{1}H NMR (CDCl$_3$): δ 7.75 (s, 1H), 7.69 (s, 1H), 7.59-7.51 (m, 6H), 7.36 (d, *J* = 7.8, 2H), 7.33-7.25 (m, 4H), 7.16 (t, *J* = 7.7, 2H), 7.01 (t, *J* = 7.2, 2H), 3.76 (q, *J* = 7.1, 8H), 1.27 (t, *J* = 7.1, 12H), 0.21 (s, 18H). ^{13}C NMR (CDCl$_3$): δ 152.18, 135.74, 135.52, 133.34, 132.04, 131.60, 129.00, 128.22, 127.25, 126.96, 125.90, 125.23, 124.84, 117.97, 116.79, 102.30, 100.96, 94.46, 93.17, 91.81, 90.90, –0.23.

Bisannulene 5. Mp 350 °C (dec). IR ($CHCl_3$) ν 2209 cm^{-1}. MS (EI, 70 eV): *m/z* 524 (M^++2H, 11), 523 (M^++H, 43), 522 (M^+, 100). UV-vis (CH_2Cl_2) λ 288, 296, 308, 325, 364 nm.[3] HRMS (FAB): calcd for $C_{42}H_{18}$ 522.1408, found 522.1411.

Arene 15. ^1H NMR ($CDCl_3$): δ 7.40 (s, 2H), 1.27 (s, 9H), 0.29 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 150.79, 130.33, 129.75, 107.26, 104.24, 98.10, 34.46, 30.88, –0.18. IR ($CHCl_3$) 2155 cm^{-1}. MS (EI, 70 eV) *m/z* 452 (M^+, 88), 437 (M^+–CH_3).

Bis(triazene) 16. ^1H NMR ($CDCl_3$): δ 7.54 (d, *J* = 7.2, 2H), 7.49 (s, 2H), 7.42 (d, *J* = 8.1, 2H), 7.27 (t, *J* = 7.4, 2H), 7.07 (t, *J* = 7.2, 2H), 3.79 (q, *J* = 7.1, 8H), 1.31 (br t, 12H), 1.28 (s, 9H), 1.08 (s, 21H). ^{13}C NMR ($CDCl_3$): δ 152.42, 150.31, 133.01, 128.88, 128.80, 127.05, 124.41, 124.25, 118.21, 116.78, 104.04, 98.49, 92.51, 91.49, 34.57, 30.90, 18.75, 11.33.

Bis(triazene) 17. ^1H NMR ($CDCl_3$): δ 7.64 (d, *J* = 7.5, 2H), 7.49 (s, 2H), 7.48 (s, 2H), 7.36 (d, *J* = 8.1, 2H), 7.22 (t, *J* = 7.2, 2H), 7.01 (t, *J* = 7.2, 2H), 3.80 (q, *J* = 7.1, 8H), 1.33 (s, 9H), 1.31 (s, 9H), 1.27 (br t, 12H), 0.03 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 152.28, 150.45, 150.25, 134.23, 129.35, 128.66, 128.28, 126.91, 126.70, 125.98, 125.04, 124.64, 118.68, 116.75, 103.69, 98.48, 94.84, 93.69, 93.00, 92.15, 34.72, 34.62, 31.03, 31.01, –0.30.

Bisannulene 6. Mp 340 °C (dec). ^1H NMR ($CDCl_3$): δ 7.35-7.30 (*AA'*m, 4H), 7.19-7.14 (*BB'*m, 4H), 7.16 (s, 4H), 1.28 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 151.95, 132.15, 129.19, 128.53, 126.76, 126.68, 95.87, 92.62, 92.30, 34.67, 30.74. IR ($CHCl_3$) ν 2208 cm^{-1}. UV-vis (CH_2Cl_2) λ (log ε) 286 (1.27), 295 (1.42), 305 (3.47), 323 (1.18), 360 (0.15) nm. MS (70 eV): *m/z* 536 (M^++2H, 13), 535 (M^++H, 47), 534 (M^+, 100), 519 (M^+–CH_3). HRMS (FAB): calcd for $C_{42}H_{30}$ 534.2347, found 534.2344.

REFERENCES

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2. Spectral data obtained at Oregon; original ^1H NMR data: Nicolaou, K. C.; Dai, W.-M.; Hong, Y. P.; Tsay, S.-C.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7944-7953.
3. The poor solubility of **5** precluded accurate determination of its molar absorptivity.