Synthesis of a Peralkynylated Pyrazino[2,3-g]quinoxaline

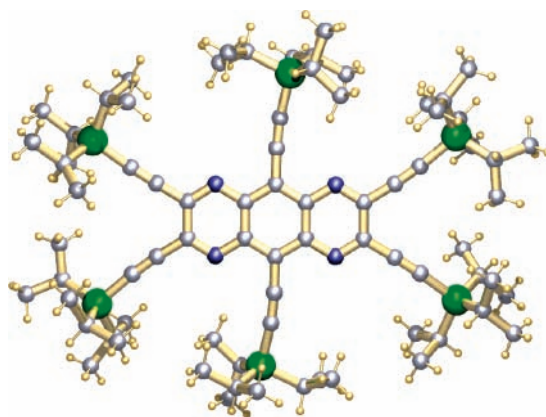**Shaobin Miao,[†] Mark D. Smith,[‡] and Uwe H. F. Bunz*,[†]**

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ABSTRACT

The synthesis of a hexaethynyl[2,3-g]pyrazinoquinoxaline and its crystal structure are reported. Starting from tetraaminobenzoquinone, condensation to bis(triisopropylsilyl)hexadiyne-2,3-dione affords 2,3,7,8-tetrakis(triisopropylsilylethynyl)pyrazino[2,3-g]quinoxaline-5,10-dione. Reaction with TIPS-CC-Li followed by reduction with hypophosphite in the presence of KI furnished the title molecule in a yield of 62%. Pd catalysis is not involved in any of these steps.

Peralkynylated arenes, "Vollhardt-perimeters" (VP), are aesthetically pleasing and structurally attractive synthetic targets. Vollhardt-benzene, -cyclobutadiene, -cymantrene, -cyclopentadiene, -thiophene, and -phenazine have been reported.[1−6] With exception of Vollhardt-phenazine and -triazine,[7] only few peralkynylated N-heterocycles are known.[8] One can speculate about the absence of these species. The

lack of broad synthetic access to the necessary perhalogenated N-heterocycles, electron-accepting arenes, has stunted the research in this area. Most of the VPs are prepared by Pd-catalyzed alkynylation of perhalogenated aromatic pre-

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cursors. Without these precursors, one has to resort to alternative synthetic strategies. Despite the scarcity of N-heterocyclic VPs and their lower alkynylated homologues, particularly of the heterooligoacene type,[9] these species may be attractive as both sensory materials and even more so as heterocyclic N-semiconductors. In this paper, we describe the synthesis and structural characterization of the first hexaethynyl-1,4,5,8-tetraazaanthracene derivative, **4**. Starting

Scheme 1. Synthesis of the Peralkynylated Heterocycles **3** and **4**
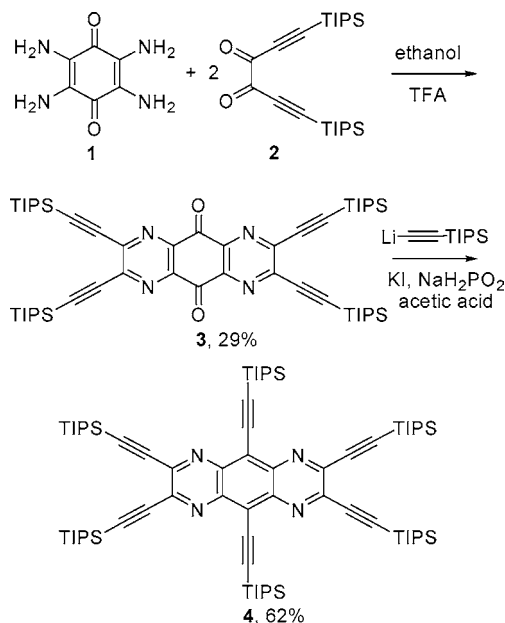
from tetraaminobenzoquinone **1**,[10] reaction with the dione **2**[11] in ethanol and trifluoroacetic acid as catalyst, furnished the tetraethynylated quinone derivative **3** in a yield of 29% as a light green solid after flash chromatography; **3** dissolves in common solvents under formation of green but nonfluorescent solutions.

To obtain final proof of the structure and topology of **3**,[13] we grew a suitable specimen from dichloromethane/hexanes

as solvent. The aromatic nucleus of **3** (Figure 1) is planar as expected. The molecules pack in a brick layer-type motif, in which the TIPS groups of one layer are positioned over the aromatic core of the molecules in the layer above and below.[9b]
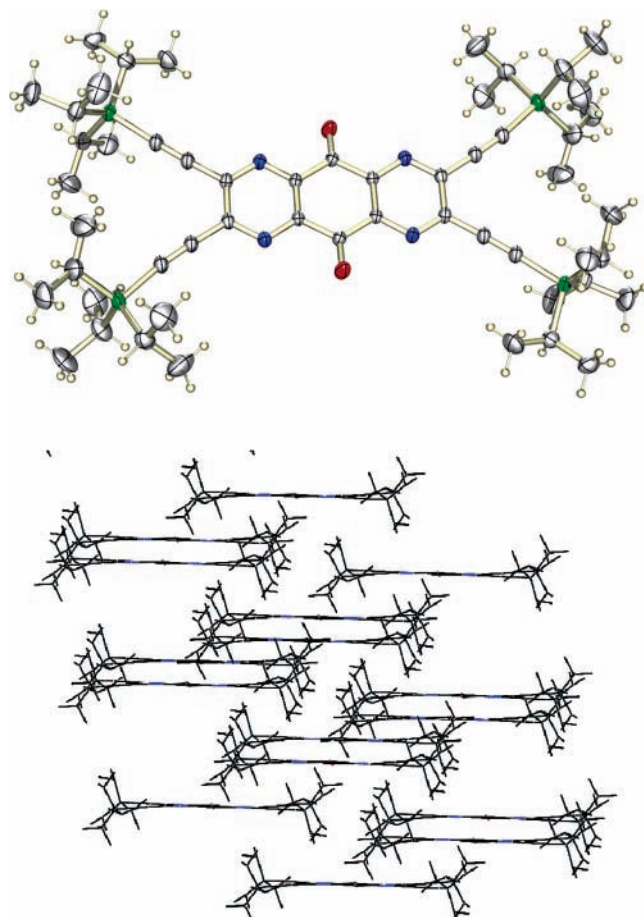

Figure 1. Single-crystal X-ray structure of **3**. Top: molecular structure of **3** (ORTEP). Bottom: packing of **3** in the solid state. Visible is the brick wall motif, in which the TIPS groups of one molecule are positioned over the arene nucleus of the one above and below.

The conversion of **3** into **4** proceeded by double nucleophilic attack of lithium (triisopropylsilyl)acetylide followed by treatment with tin dichloride after hydrolysis.[9] The hexaethynyl **4** was isolated after repeated chromatography over silica gel with hexane/dichloromethane as eluent,

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(13) **Synthesis of 3**: A mixture of **1** (0.200 g, 1.19 mmol), **2** (1.00 g, 2.39 mmol), and trifluoroacetic acid (2.0 mL) in ethanol (20 mL) was heated to reflux for 3 h. After evaporation of the solvent, the residue was chromatographed (silica gel, hexane/CH$_2$Cl$_2$, v/v, 1:2) to give **3** (0.321 g, 29%) as light green crystals from CH$_2$Cl$_2$/hexanes, mp = 258−260 °C; IR (KBr) ν 2943, 2864, 2359, 2162, 1711, 1504, 1464, 1350, 1312, 1261, 1184, 1059, 881, 783 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.18−1.17 (bs, 84 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 177.22, 144.75, 141.29, 107.76, 102.14, 18.67, 11.34. MS (MALDI) 935.6 (M$^+$). Accurate mass for C$_{54}$H$_{84}$N$_4$O$_2$-Si$_4$: *m/e* = 933.5769 (M$^+$), calcd *m/e* = 933.5744. **Synthesis of 4**: Triisopropylsilylacetylene (0.40 mL, 1.8 mmol) and dry THF (10 mL) were added to an oven-dried Schlenk flask, followed by BuLi (0.80 mL, 1.3 mmol) at 0 °C. The solution was stirred at 0 °C for 2 h, then **3** (0.300 g, 0.320 mmol) was added. After 12 h at ambient temperature, wet ethyl ether was added. After evaporation of the solvent, the residue was chromato-

graphed (silica gel, hexane/ethyl acetate, v/v, 5:1) to yield the crude diol, which was suspended in acetic acid (20 mL); KI (0.641 g, 3.86 mmol) and NaH$_2$PO$_2$ (0.340 g, 3.86 mmol) were added, and the mixture was heated to reflux for 1 h. After cooling, the red solids were collected by filtration, washed with water (3 × 20 mL), CH$_3$OH (3 × 20 mL), dried in vacuo and chromatographed (silica gel, hexane/CH$_2$Cl$_2$, v/v, 5:1) to give **4** (0.251 g, 62%) as orange crystals from CH$_2$Cl$_2$/MeOH, mp = 284 °C (dec); IR (KBr) ν 2961, 2864, 2361, 2158, 1529, 1462, 1306, 1261, 1095, 1020, 881, 802 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.25−1.12 (bs, 126 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.33, 140.91, 121.16, 110.83, 103.76, 101.16, 100.34, 18.88, 18.77, 11.48, 11.41. MS (MALDI) 1264.9 (M$^+$). Accurate mass for C$_{76}$H$_{126}$N$_4$Si$_6$: *m/e* = 1263.8599 (M$^+$), calcd *m/e* = 1263.8607.

however, in only 1% yield. Obviously, the introduction of the last two alkynes via $SnCl_2$ reduction was not satisfactory, even though it works well in the case of the higher acenes, as was demonstrated elegantly by Anthony for diethynyl-pentacene and diethynylhexacene.[9]

However, when the crude intermediate diol was treated with a mixture of KI and NaH_2PO_2 in acetic acid, the desired hexaethynyl **4** formed smoothly in 62% yield as orange−red crystalline material after aqueous workup.[12] Analytically pure material was obtained after chromatography utilizing a mixture of hexane and dichloromethane as eluent; **4** forms orange−red plate-shaped crystals that are weakly fluorescent
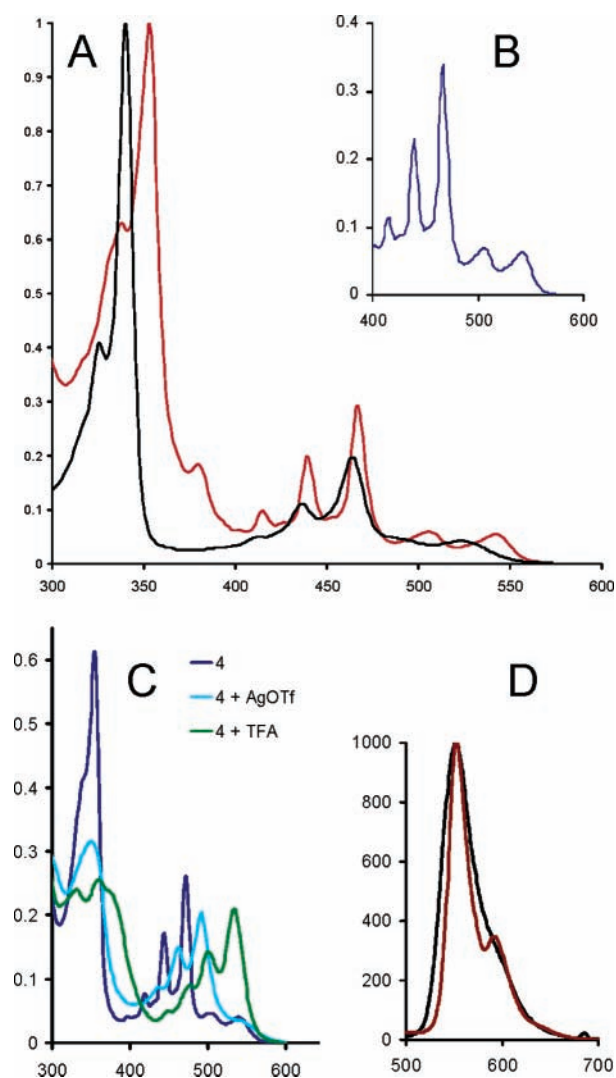

Figure 2. (a) UV−vis spectrum of **4** in hexane (353, 417, 439, 467, 506, and 544 nm; red) and of octaethynylphenazine (black). (b) Detail of the UV−vis spectrum of **4**. The vibronic progressions are 1311, 1314, and 1331 cm^{-1} for the two bathochromic absorptions. (c) Spectrum of **4** after addition of silver triflate and of trifluoroacetic acid. In both cases, a significant red shift is observed. (d) Emission spectrum of **4** (red, λ_{max} em = 553 nm) overlaid to that of octaethynylphenazine (black, λ_{max} em = 551 nm). Vibronic progression of the emission of **4**: 1248 cm^{-1}. Stokes shift of **4**: 299 cm^{-1}.

in the solid state and quite fluorescent when dissolved in hexanes. Figure 2a shows the absorption spectrum of **4** overlaid to the absorption spectrum of octaethynylphenazine, while Figure 2b shows an expansion of the high wavelength part of the spectrum as well as the overlaid emission spectra of **4** (Figure 2d) and octaethynylphenazine **6**. The absorption of **4** is structured, similarly to that of anthracene, but two different series of progressions (λ_{max}= 417, 439, 467 nm and 506, 544 nm) are observed. Both progressions (1311 and 1331 cm^{-1}) are smaller than those observed in anthracene (1495 cm^{-1}). The UV−vis spectra of **4** and of octaethyn-ylphenazine are almost superimposable, but that of **4** is considerably more structured. The emission of **4** shows a vibronic progression that is 1248 cm^{-1} separated from the main peak. Here again, anthracene shows a larger vibronic progression in its emission spectrum with a spacing of 1407 cm^{-1}. The Stokes shift in **4** is small (299 cm^{-1}), a testimony of the rigidity of **4**. To make sure that we did not record the spectrum of a protonated species, we added triethylamine to the solution of **4** in hexane and re-took the absorbance spectrum. We did not see any change.

Upon exposure to metal cations and to proton acids, we noted that silver salts and trifluoroacetic acid produce particularly large bathochromic shifts in **4** (see Figure 2c), while zinc, alkaline earth and alkali metals do not effect any change in the absorption spectra of **4**. Acetic acid, likewise, does not change the optical properties of **4**. We attribute this behavior to the reduced basicity of **4** when compared to that of pyridine or phenazine. The electron-accepting character of the four added nitrogen atoms in combination with the −I-effect of the alkyne groups explains this behavior without constraints.

To obtain final proof for the aesthetically pleasing topology of **4**, we obtained a suitable, single crystalline specimen from a dichloromethane/methanol mixture. Figure 3 shows an
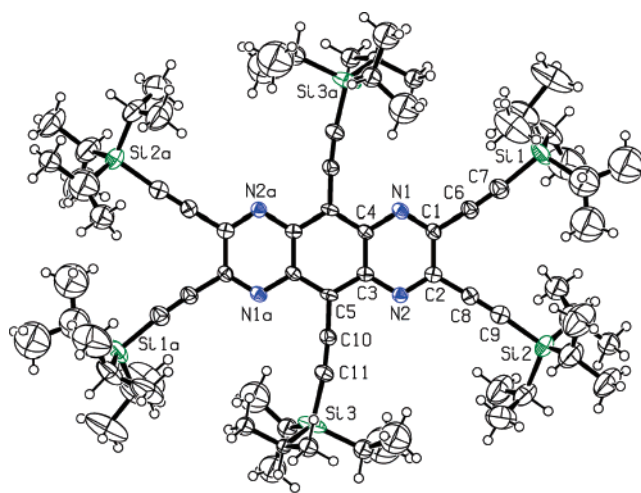

Figure 3. ORTEP of the hexaethynyltetraazaanthracene **4**. Bond lengths and bond angles are in excellent agreement with reported values.[1−3] The TIPS groups are highly disordered in the solid state. The packing is complicated and does not conform to a classic herringbone or brick wall packing motif.

ORTEP of **4**. The central alkyne units are somewhat bent, probably a crystal packing effect. In addition, all of the TIPS groups show significant disorder, as is not unexpected in such a structure, while bond lengths and angles are in agreement with literature values.[1b]

Attempts to desilylate either **3** or **4** utilizing tetrabutylammonium fluoride in THF were unsuccessful and led in both cases to the isolation of black tarry residues from which compounds with a defined structure could not be obtained.

Probably, the formed terminal alkynes are quite strong Michael systems. Under the conditions of the deprotection, not only the silyl groups are removed but other decomposition and polymerization reactions are also catalyzed by the fluoride ions. Partially or differentially silylated species may be more useful for the synthesis of free dialkynyl or tetraalkynyl pyrazinoquinoxalines.

In conclusion, we have demonstrated the synthesis of the first representative of hexaalkynylpyrazinoquinoxaline. The efficient two-step synthesis starts from tetraaminobenzoquinone that is condensed to the Faust-dione **2**. Addition of lithium acetylide furnishes the intermediate diol. We found that the classic tin chloride reaction did not work well in this case and gave **4** in approximately 1% isolated yield. If a mixture of sodium hypophosphite in the presence of potassium iodide in acetic acid as solvent was used, the yield increased to above 60%. We speculate that this method, described by Dehaen et al.[12] for the synthesis of diarylarenes, should be powerful and increase the relatively low yields that are often observed in the synthesis of acceptor-substituted diethynylacenes.

In the future, we plan to study the synthesis of differentially hexaalkynylated pyrazinoquinoxalines and will investigate their use as convenient *n*-semiconductors in thin film transistors and similar devices.

Supporting Information Available: Crystallographic CIF files and additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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