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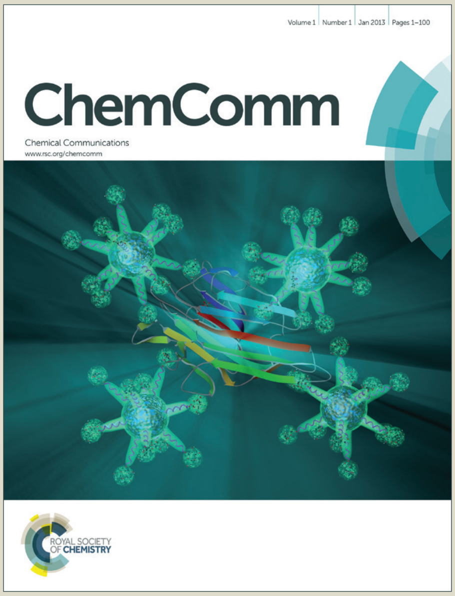

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A bisalkynylated 3,6-diiminocyclohexa-1,4-diene-1,4-diamine†

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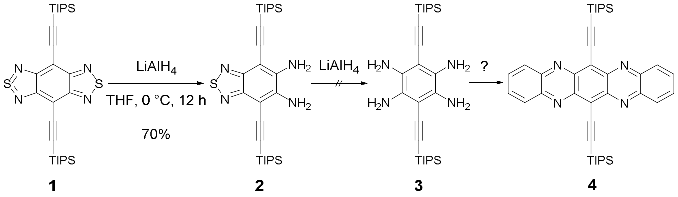
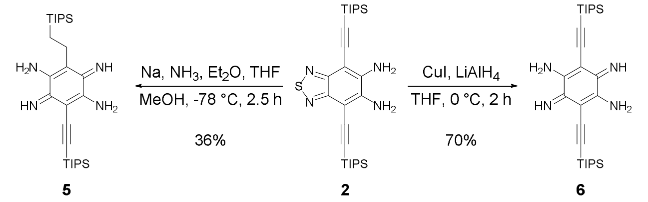
Reduction of a bis(benzothiadiazol) by $LiAlH_4$/CuI gives a diethynylated diaminobenzoquinoneimine. This building block accesses novel targets in a one step condensation reaction with different *ortho*-quinones, resulting in unexpected rearrangement products. The compounds are characterized by their photophysical and electrochemical data as well as quantum chemical calculations.

The synthesis of the larger azaacenes has made great strides in the recent past; the discovery that the azaacene **4** displays spectacular electron mobilities has further fanned the interest in this formerly forgotten area of organic chemistry.[1] While the history of the field has been reviewed several times,[2] the synthesis of substituted azaacenes is still complex and also, almost each new derivative necessitates new synthetic routes.[3] Our recent foray into Pd-catalyzed reactions[4] access substituted diaza- and unsymmetrical tetra- and hexaazaacenes. Yet, there is no simple and efficient way to prepare derivatives of **4** using late state functionalization methods. A retrosynthetic analysis identifies **3** as a critical and attractive, versatile intermediate. However, **3** is unknown. In attempts to reduce **1**, the diamine **2** forms,[5] but further reduction was unsuccessful, even with an excess of $LiAlH_4$ or $NaBH_4$. We therefore expanded the choice of reducing agents. Under Birch conditions we could isolate **5**, the first hint that it is possible to break up the second thiadiazole ring. However, the structure of **5** was puzzling, as the triple bond was fully reduced, but the tetraamine **3** did not form. Instead, a diaminoquinoneimine forms.



Scheme 1 Reduction of **1** by $LiAlH_4$ stops at the mono(thiadiazole) stage **2** (TIPS = triisopropylsilyl).[5]



Scheme 2 Conditions for the opening of the second thiadiazole ring into **6**.

Other reducing agents including $Hg(OAc)_2/LiAlH_4$ and $CuI/LiAlH_4$ were tested. The mercury based system gave **6,** but as main product the monodesilylated compounds **7** and **8**, with **9** and **10** as side products (Figure 1) form; some of those were isolated and X-ray crystal structures obtained‡ (Figure 2), some were evidenced by mass spectrometry (see ESI†). By far the cleanest and best method to prepare **6** was reduction of **2** in the presence of $CuI/LiAlH_4$. Here, **6** forms in 70% yield with the least amount of side products being present. The active reducing agent(s) are possibly copper metal and/or copper hydride species, due to the ratio of 1:4 of $CuI/LiAlH_4$ used in this reaction.[6] The structure elucidation of **6** was particular, as its ^{13}C-NMR spectrum at room temperature (Figure 3) did not show any of the signals for the imino and amino-carrying arene carbons. Only upon cooling to –40 °C the signals appear. The reason for the broadening at ambient temperature is probably the

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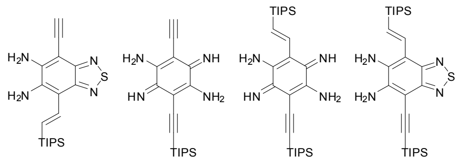


7 **8** **9** **10**

Figure 1 Isolated and characterized by-products of different reduction methods.

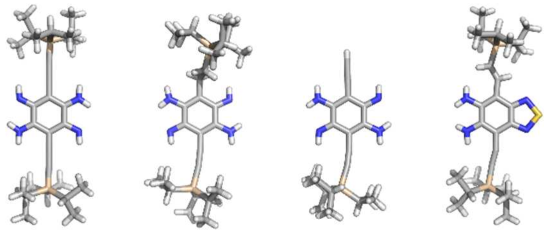


Figure 2 Single crystal structures of **6**, **5**, **8**, and **10**‡.

tautomerization of the imino and amino-functionalities, which apparently is slow on the NMR time scale at –40 °C. It surprises, that the tetraamine **3** does not form, only the quinoid form, **6**. Quantum chemical calculations show ($\Delta H_{f(\mathbf{6}+H2\rightarrow\mathbf{3})}$ = –26 kcal mol^{-1}) that the heat of hydrogenation of **6** into **3** is exothermic. Yet we never find analytical evidence for the tetraaminobenzene **3** in the reduction products but formation of compounds such as **6-10**. This behaviour has been reported previously for similar tetrasubstituted amines.[7] The diamino-quinoneimine **6** shows a strong acidochromicity (Figure 4). Upon addition of TFA, the yellow solution of **6** in THF deepens in colour, simultaneously losing its already weak fluorescence.

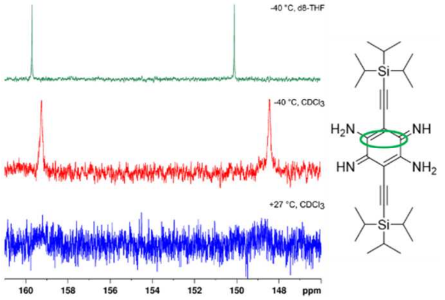


Figure 3 Tautomerization of the carbon atoms next to the nitrogens in **6** (^{13}C-NMR spectra).

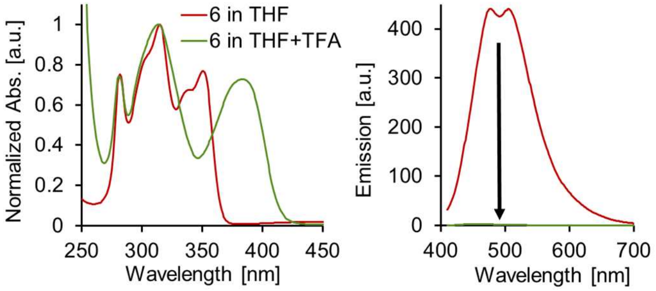
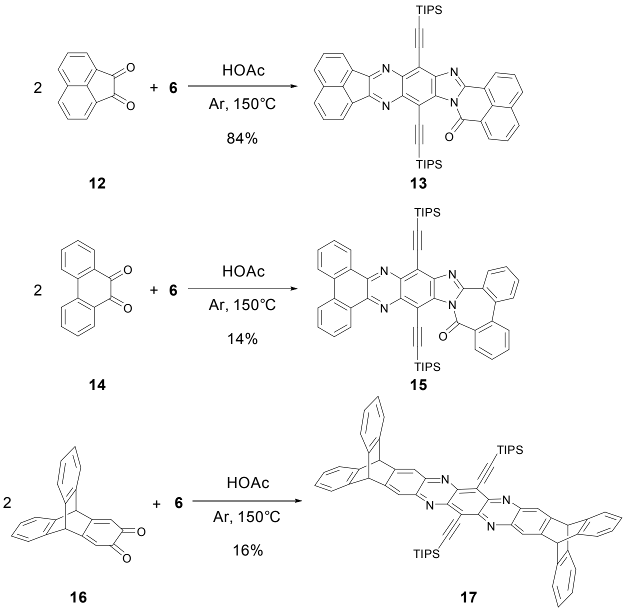


Figure 4 Acidochromicity of **6**: Short wavelength absorption spectra (left) and emission spectra (right) in tetrahydrofuran (red) and after addition of trifluoroacetic acid (green).



Scheme 3 Condensation reactions and Pd-catalyzed coupling reaction of **6**.

As the building block **6** is available on the 100 mg-scale, we investigated its condensation reaction with a series of *ortho*-quinones (Scheme 3). Upon reaction with **12** or **14**, performed under "fire and sword" conditions, we find the formation of the rearranged coupling products **13** and **15**, featuring lactam rings on one side. As the nature of the condensation products **13** and **15** was unusual, we performed crystal structure analyses, corroborating their topology‡ (Figure 5). Concerning **13**, we cannot present the crystal structure, due to a heavily disordered crystal packing. Electron density distribution, however, indicates the presence of **13**. The formation of **13** and **15** (exemplarily for **15** in Scheme 4) probably proceeds via the spiroheterocycle **19**, followed by a rearrangement cascade.[8] In the case of the dione **16** the condensation (on a small scale) gave the desired adduct **17** in 16% as only isolable product, structurally characterized by a single crystal X-ray structure‡ (Figure 5). The oxidized specimen was directly isolated.

The rearrangement products **13** and **15** were fully characterized by NMR- and IR-spectra as well as their UV-Vis spectra, cyclic voltammetry (CV) and computed via DFT calculations (summarized in Table 1). While **15** exhibits a typical acene-like absorption spectrum with a maximum absorption band at 482 nm, the absorption spectrum of **13** allows only an estimation

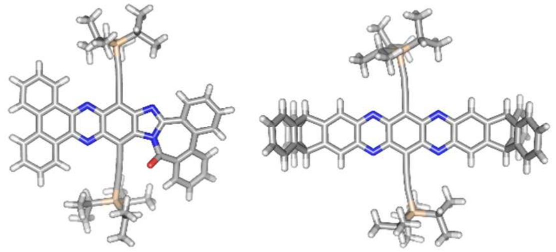


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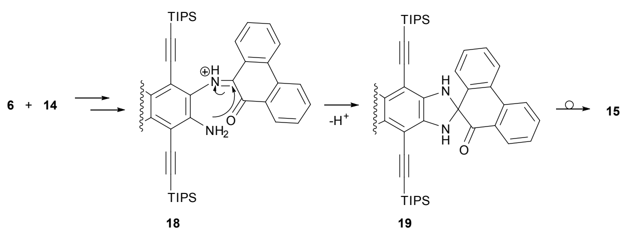
Figure 5 Crystal structures of condensation products **15** (left) and **17** (right)‡.

Table 1 Photophysical properties and DFT calculations for **13** and **15**.

Cpd	Abs_{max} [a] [nm]	Abs_{edge} [a] [nm]	Em_{max} [a] [nm]	Stokes-Shift [a] [nm]	$E^{(0/–)}$ [b] [V]	HOMO [c] [eV]	$LUMO_{CV}$ [d] [eV]	Gap_{UV} [e] [eV]	$HOMO_{DFT}$ [f] [eV]	$LUMO_{DFT}$ [f] [eV]	$E_{g,DFT}$ [f] [eV]
13	482	510	506	24	–1.01	–5.96	–3.53	2.43	–5.66	–2.97	2.69
15	482	496	493	11	–1.03	–6.12	–3.62	2.50	–5.68	–2.91	2.78

[a] Optical spectroscopy absorption maximum (Abs_{max}), absorption edge (Abs_{edge}), emission maximum (Em_{max}) and Stokes-Shift in hexane. [b] First reduction potential measured by cyclic voltammetry (CV) in tetrahydrofuran with Bu_4NPF_6 as electrolyte against Fc/Fc$^+$ as internal standard (–5.10 eV)[9] at 0.2 mV*s^{-1}. [c] $LUMO_{CV}$ – Gap_{UV}. [d] Calculated from CV measurement (–5.10 eV – $E^{(0/–)}$). [e] Calculated from Abs_{edge} in hexane. [f] Quantum chemical calculations performed with B3LYP/6-311++G**//B3LYP/6-311+G*.[10]



Scheme 4 Proposed mechanism for the rearrangement-product **15**.

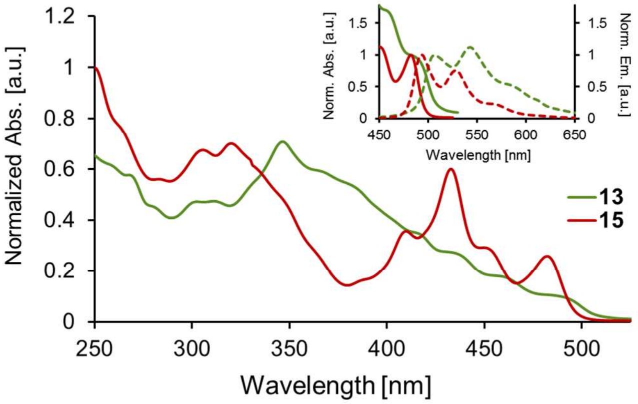


Figure 5 Absorption spectra of **13** (green) and **15** (red) in hexane. Inlay: Long wavelength absorption (solid) and emission spectra (dashed) of **13** (green) and **15** (red) in hexane.

of the absorption maximum, lying in the same range at about 482 nm, simultaneously showing a higher Stokes-shift than **15**. The onset gives an experimental HOMO-LUMO gap of 2.43 eV for **13** and 2.50 eV for **15**. CV measurements conducted in THF with NBu_4PF_6 as electrolyte against ferrocene/ferrocenium (Fc/Fc$^+$) as internal standard showed two reduction peaks in the solvent range (see ESI†). From the first reduction potentials relative to Fc/Fc$^+$ (using –5.10 eV)[9] we estimated the experimental LUMO levels of **13** (–3.53) and **15** (–3.62), calculating the HOMO levels to –5.96 and –6.12, with the LUMOs and gaps not unexpectedly lying in the range between those of phenazine- and diazatetracene-derivatives.[11] This trend is also visible in the absorption spectra, thus indicating that the central imidazoquinoxaline unit is determining the electronic properties of **13** and **15**.

In conclusion, among a variety of reducing agents, a system of CuI/$LiAlH_4$ is the best one to reduce benzobisthiadiazole **1** in high yields and with few side products. Instead of phenylenetetraamine **3**, the diaminobenzoquinoneimine **6** forms as stable product; **6** is reacted with acenaphthoquinone and phenanthrenequinone, leading to unexpected rearrangement products **13** and **15** with an imidazoquinoxaline core, determing their electronic structure. Condensation of **6** with triptycene-*o*-quinone leads to the symmetrical triptycene substituted tetraazapentacene **17**. Over all, a new building block opens additional reaction paths in the synthesis of soluble, symmetrical and unsymmetrical azaacenes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures and characterization data for all new compounds, full scaled photoluminescence spectra, cyclic voltammograms, DFT calculation details, further information about crystallographic data, copies of NMR spectra (^{1}H and ^{13}C), cartesian coordinates of computationally studied molecules, and Crystallographic Information Files (CIF). CCDC 1408361 (**1**), 1408362 (**5**), 1408363 (**6**), 1408364 (**8**), 1408365 (**10**), 1408366 (15), and 1408367 (**17**). See DOI: 10.1039/c000000x/

‖ These authors contributed equally to this work.

‡ Crystal data for **1**: $C_{28}H_{42}N_4S_2Si_2$, M = 554.95, monoclinic, space group P2$_1$/n, a = 8.5203(3) Å, b = 15.4125(6) Å, c = 11.7589(5) Å, α = 90 °, β = 99.3033(9) °, γ = 90 °, V = 1523.86(10) Å^3, ρ = 1.209 g/cm^3, T = 200(2) K, Z = 2, 14317 reflections measured, 3094 unique (R_{int} = 0.0302), 2623 observed (I > 2σ(I)), θ_{max} = 26.449 °, final residual values $R_1(F)$ = 0.037, $wR(F^2)$ = 0.092 (observed reflections). Crystal data for **6**: $C_{28}H_{48}N_4Si_2$, M = 496.88, monoclinic, space group C2/c, a = 19.958(2)

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Å, b = 14.9301(16) Å, c = 14.7268(16) Å, α = 90 °, β = 132.098(2) °, γ = 90 °, V = 3256.1(6) Å^3, ρ = 1.014 g/cm^3, T = 200(2) K, Z = 4, 10051 reflections measured, 2866 unique (R_{int} = 0. 0500), 1938 observed (I > 2σ(I)), θ_{max} = 25.037 °, final residual values $R_1(F)$ = 0. 086, $wR(F^2)$ = 0. 239 (observed reflections). Crystal data for **8**: $C_{19}H_{28}N_4Si$, M = 340.54, monoclinic, space group C2/c, a = 37.446(8) Å, b = 7.8246(18) Å, c = 30.575(7) Å, α = 90 °, β = 116.744(5) °, γ = 90 °, V = 8000(3) Å^3, ρ = 1.131 g/cm^3, T = 200(2) K, Z = 16, 15868 reflections measured, 2428 unique (R_{int} = 0.1858), 1347 observed (I > 2σ(I)), θ_{max} = 17.222 °, final residual values $R_1(F)$ = 0.066, $wR(F^2)$ = 0.134 (observed reflections). Crystal data for **5**: $C_{28}H_{52}N_4Si_2$, M = 500.91, triclinic, space group P$\bar{1}$, a = 7.8130(18) Å, b = 12.886(3) Å, c = 15.976(4) Å, α = 102.557(5) °, β = 96.908(6) °, γ = 93.896(6) °, V = 1551.2(6) Å^3, ρ = 1.072 g/cm^3, T = 200(2) K, Z = 2, 10797 reflections measured, 3777 unique (R_{int} = 0.0627), 2334 observed (I > 2σ(I)), θ_{max} = 21.942 °, final residual values $R_1(F)$ = 0.059, $wR(F^2)$ = 0.122 (observed reflections). Crystal data for **10**: $C_{28}H_{48}N_4SSi_2$, M = 528.94, monoclinic, space group P2$_1$/c, a = 15.4408(14) Å, b = 13.9268(12) Å, c = 14.8221(13) Å, α = 90 °, β = 103.112(3) °, γ = 90 °, V = 3104.3(5) Å^3, ρ = 1.132 g/cm^3, T = 200(2) K, Z = 4, 24289 reflections measured, 3257 unique (R_{int} = 0.0758), 2347 observed (I > 2σ(I)), θ_{max} = 20.816 °, final residual values $R_1(F)$ = 0.054, $wR(F^2)$ = 0.107 (observed reflections). Crystal data for **15**: $C_{56}H_{59}N_4OSi_2$, M = 859.24, monoclinic, space group C2/c, a = 37.073(4) Å, b = 11.0554(13) Å, c = 26.576(3) Å, α = 90°, β = 118.358(3)°, γ = 90°, V = 9585.2(19) Å^3, ρ = 1.191 g/cm^3, T = 200(2) K, , Z = 8, 26024 reflections measured, 4224 unique (R_{int} = 0.1494), 2239 observed (I > 2σ(I)), θ_{max} = 19.588°, final residual values $R_1(F)$ = 0.075, $wR(F^2)$ = 0.152 (observed reflections). Crystal data for **17**: $C_{68}H_{66}N_4Si_2$, M = 995.47, monoclinic, space group P2$_1$/n, a = 18.0690(12) Å, b = 24.9858(17) Å, c = 29.3954(19) Å, α = 90°, β = 101.4712(17)°, γ = 90°, V = 13006.0(15) Å^3, ρ = 1.017 g/cm^3, T = 200(2) K, Z = 8, 78017 reflections measured, 13606 unique (R_{int} = 0.1000), 8280 observed (I > 2σ(I)), θ_{max} = 20.816°, final residual values $R_1(F)$ = 0.086, $wR(F^2)$ = 0.197 (observed reflections).

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