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A Persistent Diazaheptacene Derivative

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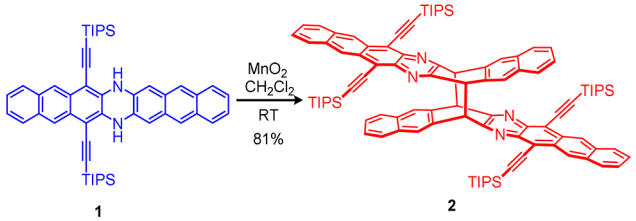
Supporting Information

ABSTRACT: We describe the synthesis of characterizable diazaheptacene derivatives. Diazaheptacenes need four silylethynyl protecting groups to be isolable. TIPS-ethynyl groups are not bulky enough to allow stabilization. Four Si(*sec*-Bu)$_3$-ethynyl groups symmetrically attached to the acene core sufficiently protect the formed diazaheptacene from dimerization through Diels–Alder reaction. It was characterized by NMR and UV–vis spectroscopies and cyclic voltammetry.

Synthesis, property evaluation, and applications of azaacenes are a rapidly developing field.[1] Most of the device and evaluative work is done on oligoazapentacene moieties, as synthetic approaches are developed and azapentacenes with up to four nitrogens are generally stable.[2] Azahexacenes are much more rare, and only very few are reported,[3] while azaheptacenes—if they do not contain pyrene or ovalene-substructures—are virtually unknown in contrast to higher all-carbon analogues.[4,5] Our recent attempts to generate diazaheptacene derivatives were unsuccessful. Oxidation of **1** led to the isolation of **2** in 81% as the sole product[6] (Scheme 1). The intermediate diazaheptacene must have formed before dimerization but could not even be detected as a fleeting intermediate using NMR or UV–vis spectroscopies.

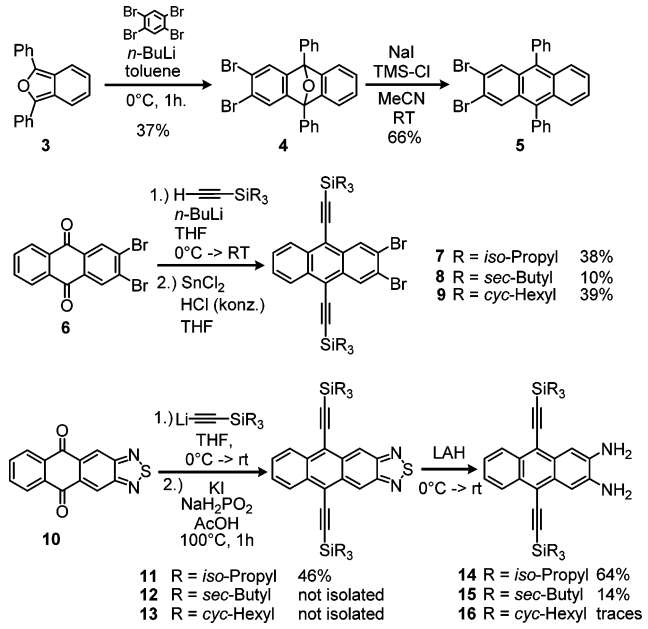
Scheme 1. Simple Azaheptacenes Immediately Form Dimers



1 2

Even though the stabilization of larger acenes through a single pair of bulky silylethynyl substituents is possible and practical,[7] this strategy was deemed less suitable for the diazaacenes, in which the pyrazine unit occupies the central ring. Here the employ of four silylethynyl substituents seemed to be a more promising approach. Scheme 2 shows the production of the necessary starting materials. The synthesis of **5** commences with the reaction of diphenylisobenzofuran **3** with the aryne formed from tetrabromobenzene and BuLi to give **4** in 37%. Deoxygenation yields the building block **5** in 66% yield. To prepare the dibromides **7**–**9**, the anthraquinone

Scheme 2. Synthesis of Diazaheptacene Precursors



derivative **6** was alkynylated and aromatized using $SnCl_2$. Yields are variable and at the lower end of satisfactory. The important coupling partners **14**–**16** are constructed by a similar strategy. The quinone **10** is treated with a lithium acetylide, and the resulting addition product is deoxygenated in situ using KI and phosphite in acetic acid at elevated temperatures. Only in the case of **11** the thiadiazole is isolated, as **12** and **13**, surprisingly, are too unstable to handle. After reduction with lithium aluminum hydride the coupling partners **14**–**16** are isolated; compound **16** unfortunately only in traces. **15** was used in the next step without characterization due to its low stability.

Pd-catalyzed coupling of **17** to **5** furnishes **17** in 60% yield (Scheme 3), while the combination of **14** or **15** with **7**–**9** under microwave conditions gave **19**–**21** in yields ranging from 18 to 83%. The sterically more crowded dihydro-diazaacene **21** forms in lower yields. All the dihydro-diazaacenes **18**–**21** are stable. The oxidation of **18**–**21** (Scheme 4) was performed in $CDCl_3$; the solution was filtered after 40 s through a very small plug of silica gel into an NMR tube. A proton NMR spectrum was taken. The diazaheptacene **22** immediately reacted into a number of different species after generation (Figure S1). Figure

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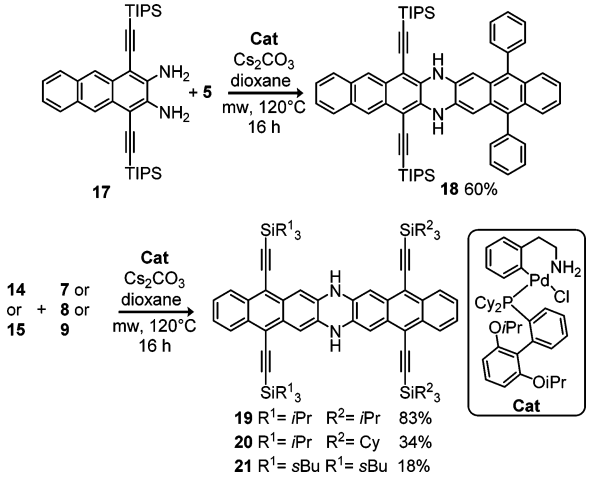
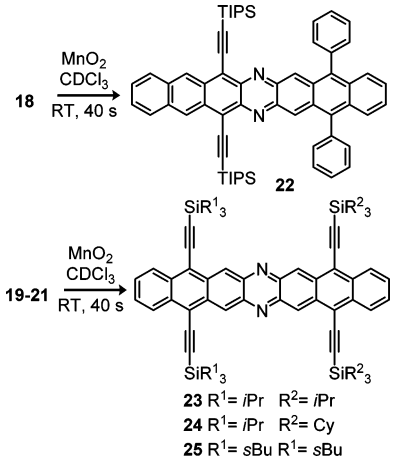
Scheme 3. Pd-Catalyzed Coupling to Dihydrodiazaheptacenes



Scheme 4. Oxidation of 18-21 into 22-25



1 shows that **23** forms but also slowly dimerizes into a mix of the two Diels–Alder adducts **26a** and **26b**. After 70 min there is still ~40% of **23** left, but the signals for the dimerization products **26a,b** have grown substantially. We have not found reduced or protonated azaheptacenes as degradation products (Figure S6–S8). The assignment of the respective stereochemistry of the isomers **26** is tentative and based on the hypothesis that **26a** is sterically less hindered and therefore forms more easily than **26b**. A separation of the dimers **26** was not possible due to identical polarity. The oxidation of **21** (Figure 1 bottom) exclusively forms **25**, which is stable in solution for a significant amount of time. After around 1 h, traces of the dimerization products **27a,b** of **25** are observed; one can easily obtain a UV–vis trace and a ^{13}C NMR spectrum of the diazaheptacene **25** (Figures 2 and 3). As comparison, the spectra of the NH-precursor **21** are also added. The UV absorption features a band at 870–920 nm indicative for an intact heptacene. Mass spectrometry shows a peak for $[M]^+$ at 1268.86083 m/z (1268.85286 calcd) with a correct isotope distribution, corroborating structure **25**. The UV–vis spectra prove a moiety similar to that observed for Anthony's heptacene; it shows an absorption band at 875 nm. The presence of the eight aromatic signals in the ^{13}C NMR spectrum of **25** are diagnostic of the formed diazaheptacene, with the expected nine signals (the feature at δ = 128 ppm

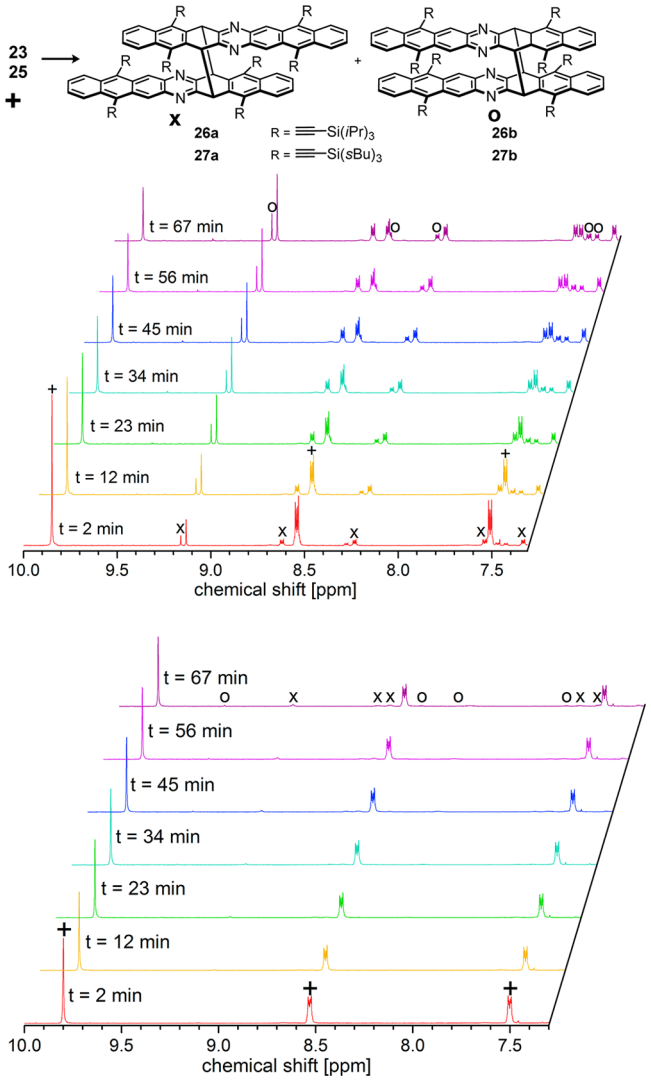


Figure 1. Formation of dimers (top) and the stability of the azaheptacenes **23** (middle) and **25** (bottom) in $CDCl_3$ solutions, investigated by ^{1}H NMR spectroscopy. For more detailed spectra including high field shifted bridgehead protons of the dimerization products see SI.

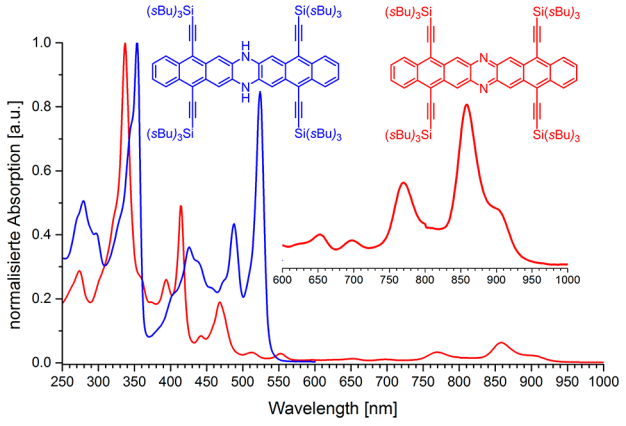


Figure 2. UV–vis spectrum of **21** (blue) and oxidized diazaheptacene **25** (red) in chloroform. The red-shifted feature indicates the formation of the diazaheptacene moiety.

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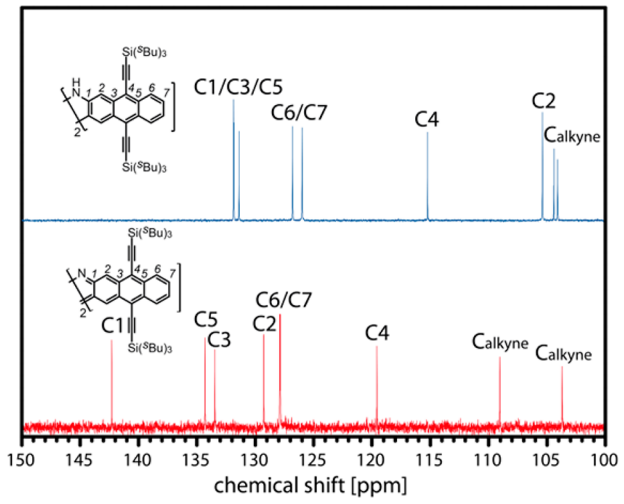

Figure 3. Aromatic regions of the ^{13}C NMR spectra of **21** (blue) and of **25** (red) are shown.

represents two signals), the alkyne units resonating at δ = 103 and 109 ppm. As **25** cannot be isolated in substance without substantial dimerization, we cannot obtain a precise yield for this oxidation reaction. However, the lack of side products and our experience with this reaction indicate the yield to be high.

Finally we performed cyclic voltammetry (Figure 4) and found, typical for azaacenes, two reversible reduction waves at

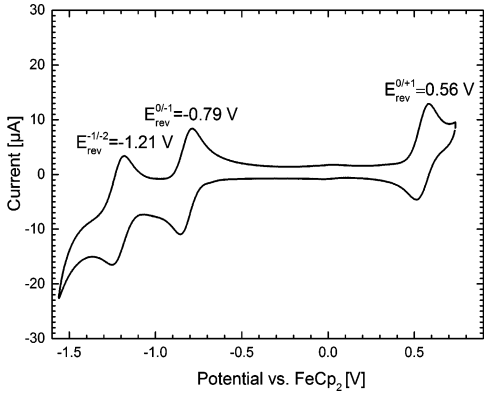

Figure 4. Cyclic voltammetry measurement of freshly oxidized **25** in dichloromethane (externally referenced against ferrocene/ferrocenium using a Pt working electrode and Bu_4NPF_6).

−0.79 and −1.21 V vs ferrocene. Also remarkable is the reversible oxidation of **25** into its cation. The electrochemical gap is 1.35 eV, which is in excellent agreement with the HOMO−LUMO gap obtained from the onset of absorption spectra (1.33 eV, 935 nm). The electrochemical data allow an estimate of the ionization potentials and electron affinities of **25**, by subtracting 3.8 (eV) from the numerical electrochemical potentials. This leads to an absolute ionization potential of −5.32 eV and an electron affinity of −4.01 eV for **25**.[8] These values are comparable to those obtained for more stable azahexa- and azapentacenes. Thus, the instability of the azaheptacenes does *not* arise from the FMO levels but is a consequence of decreased aromatic stabilization increasing the core size, as shown by us in previous publications.[9]

In conclusion we have prepared the first persistent diazaheptacene **25** by fast oxidation of an *N,N′*-dihydrodiazaheptacene **21** using MnO_2. The persistence of the azaheptacenes is dependent upon the substituent pattern. We find that the stability is **25** > **24** > **23** ≫ **22**. While even the most stable diazaheptacene **25** could not be isolated in substance, it forms dimers **27a,b** through cycloaddition, it is clearly stable enough to survive in solution for a sufficient amount of time to perform full characterization. In the future we will further expand the scope of this coupling reaction and expand the available structures to diaza- and tetraazaheptacenes of different topologies.

■ ASSOCIATED CONTENT

Supporting Information

Experimental data and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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