Heteroacenes

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Stable Hexacenes through Nitrogen Substitution**

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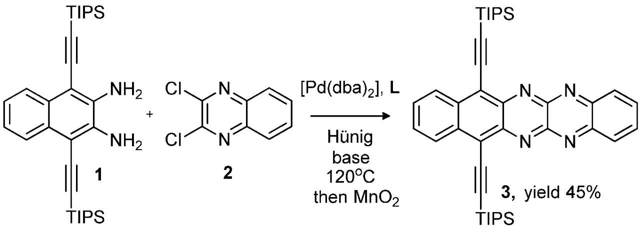
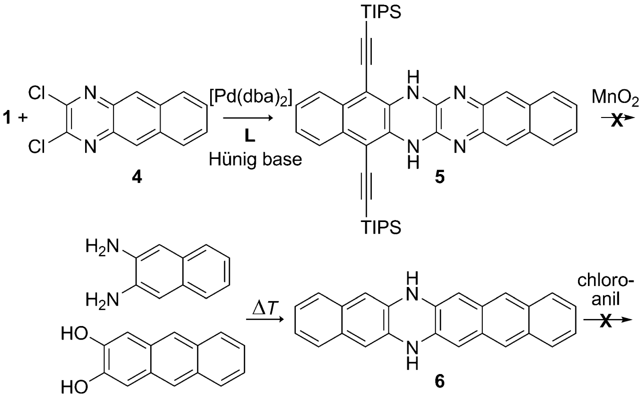
The stabilization of larger acenes is a demanding task both synthetically as well as conceptually to be solved in different ways.[1] Neither unsubstituted hexacene nor its higher homologues are stable, but their existence can be demonstrated in suitable matrixes.[2] In the case of pentacene, two strategically attached TIPS-ethynyl groups suffice to fully stabilize and solubilize this material (TIPS = triisopropylsilyl).[3] In larger acenes, however, two TIPS-ethynyl groups do not provide enough stabilization to furnish long-term persistent representatives.[4] Anthony et al. demonstrated that even sterically encumbered hexacenes (with two tris(trimethylsilyl)silylethynyl substituents) react in solution under butterfly dimerization with a half-life of around 20 minutes.[5]

Only the introduction of four more aryl groups in lateral positions increases the stability of higher acenes so far that the Wudl and Chi groups could obtain persistent heptacene derivatives with a half-life of up to one week in solution.[6,7] But even here, formation of endoperoxides is observed after some time. The laterally attached phenyl groups lead to isolation of the π systems with respect to their next neighbors, as evidenced by single-crystal structure analysis. We demonstrate herein that nitrogen atoms introduced into the acene skeleton give persistent disubstituted heterohexacenes, which are stable even when stored for longer periods of time. The palladium-catalyzed coupling of **1** with **2** in the presence of the ligand **L** gave the tetrazaacene **3** after oxidation with MnO_2 in good yields (Scheme 1).[8,9] The dichlorobenzoquinoxaline **4** also couples in good yields to give **5** (Scheme 2) However, attempts to oxidize **5** by MnO_2, IBX = 2-iodoxybenzoic acid, *N*-bromosuccinimide (NBS), potassium chromate, pyridinium chlorochromate (PCC), or $Cu(OAc)_2$ were fruitless. Difficult-to-separate product mixtures formed, but not the desired acene. This behavior was not entirely unexpected, as Kummer and Zimmermann had already unsuccessfully attempted to oxidize **6**, readily obtained by co-melting of diaminonaphthalene and dihydroxyanthracene at 220 °C, using chloroanil or PbO_2. Azahexacenes remained unknown.[10]



Scheme 1. Palladium-catalyzed synthesis of **3**. dba = dibenzylideneacetone.



Scheme 2. Synthesis of the *N*,*N*-dihydrodiazahexacenes **5** and **6**.

To maximize the shielding effect of the TIPS groups, it might be better to attach them in the center of the molecule. Consequently, **7a,b** were coupled to **2** (Scheme 3). The Pd-catalyzed coupling works very well in the presence of **L** and furnishes **8a,b** in good to excellent yields (92 %, 56 %). Both are dehydrogenated by MnO_2 into the azaacens **9a,b** in 56 % and 74 % yield, but it is not clear why this reaction does not work for **5**.

The heteroacenes **9a** and **9b** are greenish black crystalline powders, stable under laboratory conditions both as solids and in solutions, which display a green-yellow color. By NMR spectroscopy we could not detect endoperoxide formation or dimerization of **9** to butterfly cycloadducts.[5] In our case, triisopropylsilyl and even the triethylsilyl groups are sufficient to stabilize and solubilize the hexacene skeleton, but **9b** is considerably less soluble than **9a**. To extend this chemistry, we prepared **7c** in a multistep synthesis starting from diamino-

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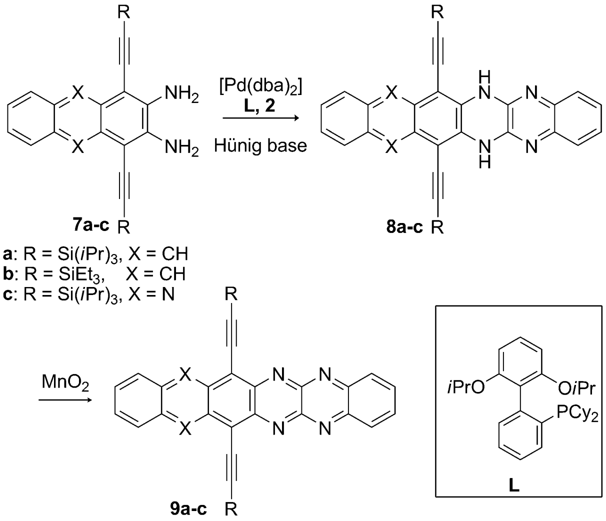

Scheme 3. Palladium-catalyzed synthesis of **9a–c** and structure of the ligand **L**.

phenazine (see the Supporting Information). Coupling of **7c** to **2** under standard conditions furnishes **8c** in 71 % yield, and oxidation with MnO_2 furnishes **9c** in 65 % yield. This material is somewhat sensitive and reacts in solution, but also in the solid state, in a mechanistically obscure reaction back to **8c** under laboratory conditions, testament to the facile reducibility of **9c**. Figure 1 displays the UV/Vis spectrum of **9b** and the long-wavelength range of the UV/Vis spectra of **9a** and **9c**. Spectra of **9a** and **9b** are, expectedly, superimposable.

The heteroacenes **9a–c** display the typical long-wavelength features, vibronically split bands with maxima for **9a** at 825 nm and for **9c** at 842 nm. Compared to the TIPS-ethynylhexacene ($\lambda_{max} = 790$ nm) prepared by Anthony et al., the bands are red-shifted, exactly as in the case for **3**, which also shows red-shifted absorption when compared to the structurally analogous pentacene. The ring nitrogen substituents lead to a partially disjunct frontier molecular orbital structure, stabilizing the LUMO considerably more than the HOMO, resulting in a lowered HOMO–LUMO gap.

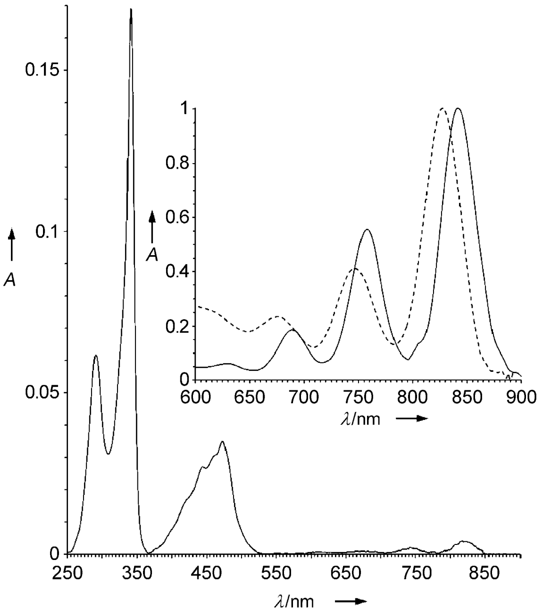

Figure 1. UV/Vis spectrum of **9b**. Inset: long-wavelength part of the UV/Vis spectra of **9a** (dotted, $\lambda_{max} = 825$ nm) and **9c** (solid line, $\lambda_{max} = 842$ nm) in hexanes.

Hexacenes are of interest in organic electronics, similar to pentacenes as active materials in thin-film transistors. Heteroacenes such as **9** would be attractive as electron-transport materials but not as hole transporters, as the pyrazine-like structure makes their oxidation close to impossible, but facilitates reduction.[11] An important property is therefore the first reduction potential, which we obtained from **9a** and **9c** by cyclic voltammetry.

Compound **9a** is reversibly reduced at −0.58 V (standard ferrocene), while **9c**, with two additional nitrogen atoms in the ring system, is already reversibly reduced at −0.42 V. With these two azahexacenes we have investigated nine structurally different azaacenes (two tetracenes, five pentacenes, two hexacenes) electrochemically; their reduction potentials are dependent upon molecular structure and substituent pattern.[8,12] To investigate this issue more closely, we performed quantum chemical calculations on model systems of these heteroacenes (trimethylsilylethynyl instead of TIPS-ethynyl; see the Supporting Information for details). We plotted the LUMO energies versus the reduction potentials and found a linear correlation of the two quantities (Figure 2). The LUMO positions determined by the DFT calculations do not have a physical meaning per se, as the orbitals are not occupied, but the orbital positions can, empirically in a group

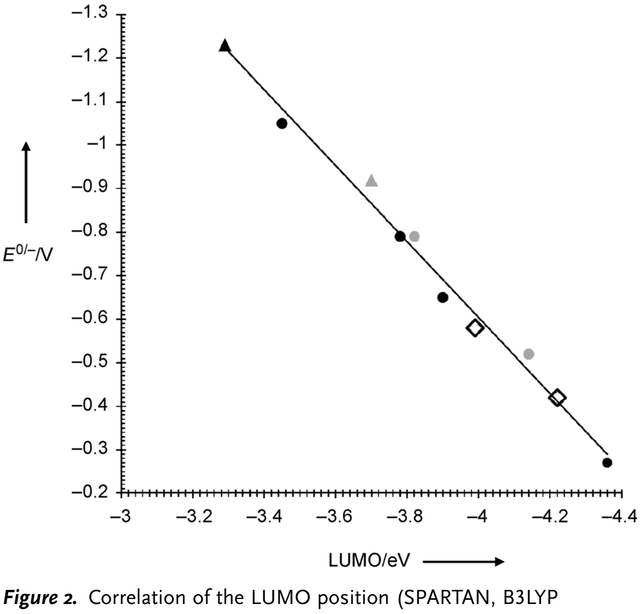

Figure 2. Correlation of the LUMO position (SPARTAN, B3LYP 6-311 + G**//B3LYP 6-311 + G**; citation see the Supporting Information) of TMS-ethynyl-substituted N-heteroacenes with experimentally determined reduction potentials (cyclic voltammetry, TIPS-ethynyl-substituted N-heteroacenes, ferrocene as standard). Triangles: azatetracenes, circles: azapentacenes, squares: azahexacenes. Light gray indicates halogenated azaacenes. Structures of the heteroacenes see Figure 15 in the Supporting Information.

of structurally related compounds, connect the reduction potentials with the molecular structure. The data points were connected using the linear relationship in Equation (1):

$$E^{0/-}\ [\mathrm{V}] = -0.87\, E_{\mathrm{LUMO}}\ [\mathrm{eV}] - 4.1 \qquad (1)$$

The slope is close to −1; LUMO energy and $E^{0/-}$ are well correlated, perhaps owing to the small reorganization energy of the heteroacenes, which suggests that structure and orbital positions of the radical anions and the neutral compounds are similar.[13]

Attempts to obtain a crystalline specimen of **9c** were not successful, but we were able to determine the molecular structure of **9a**. Noticeable are the alternating bond lengths (Figure 3) in the outer rings of **9a**, which are also found in its calculated structure and which seem to be typical for larger acenes. The calculated structure of hexacene shows the same effects. An important property is the packing of heteroacenes in the solid state and the interaction of neighboring molecules as a prerequisite for a high transfer integral and the potential usefulness of these heteroacenes in organic electronics.[14] A molecule of **9a** has four nearest neighbors with which it forms strong diagonally symmetrical π–π interactions (green lines, 3.31–3.37 Å). Molecules of **9a** form a typical brickwork structure (Figure 4), also observed in TIPS-ethynylated pentacene, a material important for applications in organic electronics.[15] We hope that **9a–c** show promise for organic electronic applications as electron-transport materials.

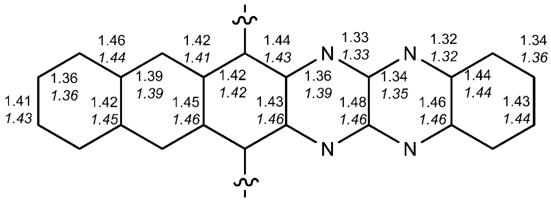

Figure 3. Bond lengths in **9a** determined by single-crystal structure analysis and calculated (with trimethylsilyl groups, SPARTAN'10, B3LYP 6-311+G**//B3LYP 6-311+G**, italics). Both the experimental and the calculated geometries display bond-length alternation in the outer rings. Calculated and experimental values are in excellent agreement.

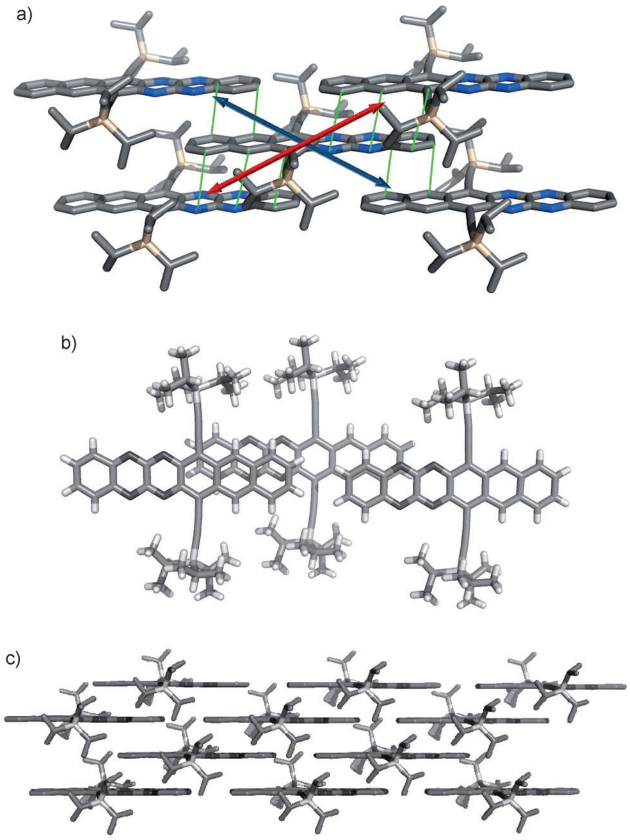

Figure 4. a) Each molecule of **9a** is surrounded by four next neighbors, green lines: 3.31–3.37 Å. b,c) Perpendicular view and packing of **9a** parallel to the crystallographic *ab* plane.

Three azahexacenes (**9a**–**9c**) were prepared by palladium-catalyzed coupling of substituted diaminoanthracenes or diamophenazines and subsequent oxidation with MnO_2; compounds **9** show, in comparison to the corresponding hexacenes, significantly increased stability. Particularly **9a,b** can be stored in solution and in the solid state for extended periods of time without any problems. In the future, we expect to prepare further functionalized heterohexacenes by this method and to use **9a–c** as electron-transport materials.

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