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Large Azaacenes: Pyridine Rings Reacting Like Carbonyl Groups

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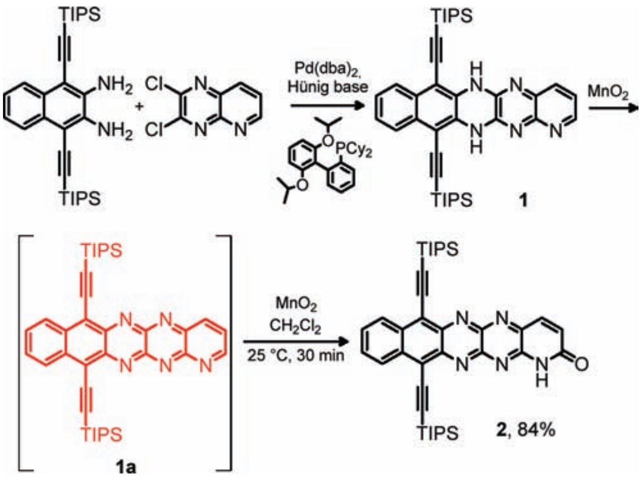
ABSTRACT

***N,N*-Dihydropentaazapentacenes and -hexacenes displaying terminal pyridine rings are surprisingly easily oxidized by MnO_2 into their corresponding pyridones.**

Azaacenes[1] have demonstrated potential in organic electronic applications, specifically as electron transporting materials for thin film transistors. The synthesis of such heteroacenes is often achieved by simple condensation of diamines with *ortho*-quinones, but we have recently[2] developed an alternative, Pd-catalyzed reaction that furnishes *N,N*′-dihydrotetraazapentacenes and -hexacenes when using 2,3-dichloroquinoxalines as coupling partners under mild conditions. If one employs 2,3-dichloropyrido[2,3-*b*]-pyrazine as a coupling partner, compound **1** is formed in good yield. However, attempts to oxidize **1** using MnO_2 into the corresponding heteroacene **1a** (7,12-bis((triisopropylsilyl)-ethynyl)benzo[*g*]pyrido[2′,3′:5,6]pyrazino[2,3-*b*] quinoxaline, Scheme 1) failed. Instead an unknown compound was isolated in 84% yield, of which we obtained a single crystal X-ray structure (Figure 1). Compound **1** was overoxidized, and the terminal, easternmost pyridine ring had been transformed into a pyridone ring to give compound **2**. This oxidation is surprising as pyridine rings do not react with MnO_2 under oxidation into pyridones, particularly not under these mild conditions. Oxidation of pyridines and quinolines is difficult and necessitates harsh conditions and temperatures around 300 °C either in water,[3] in the presence of copper, zinc or cadmium sulfates,[4] or by

Scheme 1. Synthesis of **2** by Oxidation of **1**



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deployment of aggressive reagents such as acetyl hypofluorite at lower temperatures.[5]

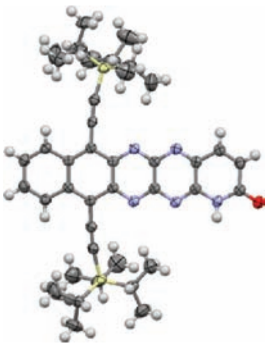


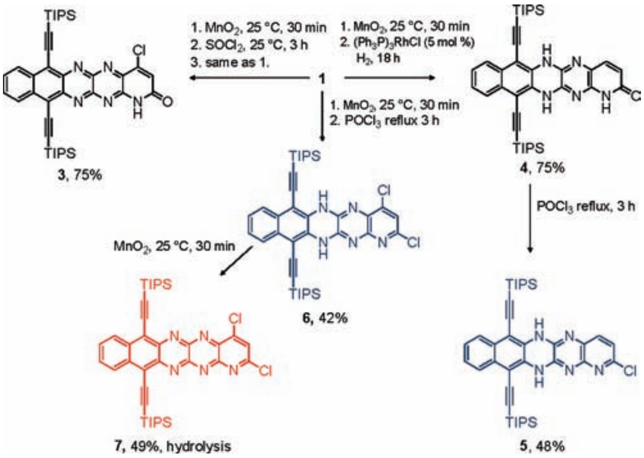
Figure 1. X-ray crystal structure of a suitable single crystalline specimen of **2**.

Alternatively, quinolones and pyridones can be obtained by Decker oxidation of the *N*-quaternized species by alkaline hexacyanoferrate(III).[6] The quite enhanced reactivity of **1** can be understood best if one assumes that the intermediate heteroacene **1a** is formed but reactive. Upon oxidation of **1a** into **2** the size of the aromatic system is reduced from a heteropentacene unit into a heterotetracene unit, which is energetically advantageous. In the case of the hitherto described heteroacenes, carrying internal pyrazine rings, overoxidation would not directly lead to a stable product, contributing to their persistence. In the presence of the terminal pyridine ring, oxidation into the pyridone allows the system to break up the heteropentacene structure. Instead a persistent tetracene substructure is formed.[7]

The oxidation of **1** with PbO_2 gives traces of an unknown compound (with a λ_{max} around 800 nm), which displays a comparable gap to that theoretically determined for **1a** (not isolated, Supporting Information (SI)). Further addition of MnO_2 to the reaction solution led to the formation of **2**. In a related experiment, we followed the oxidation of **1** with MnO_2 by UV–vis spectroscopy. The formation of **2** was immediately observed, and an additional weak feature at 800 nm was also visible. There was no trace of the strong band at 490 nm assigned to **4**. From these experiments we conclude that **1a** is probably formed and oxidized into **2**, and **4** is not an intermediate.

Having **1** available let us explore its unusual chemistry more fully. Scheme 2 displays the synthetic opportunities that arise from the transformation of **1** into chlorinated derivatives. Reaction of **1** with MnO_2 followed by thionyl chloride and subsequent reoxidation with MnO_2 furnished **3** in 75% yield, while reduction of **2** using Wilkinson's catalyst led to the more highly reduced compound **4**, which reacts with $POCl_3$ into the *N,N'*-dihydrocompound **5**. If **1** is oxidized and then immediately treated with $POCl_3$, one isolates the dichloride **6** in 42% yield. Both **5** and **6** are stable, fully characterized, and deeply yellow colored. Compound **6** can be oxidized to give the desired dichloropentaazapentacene **7** but only in 49% yield, as the material is exceedingly moisture sensitive and reacts like an active acid chloride.

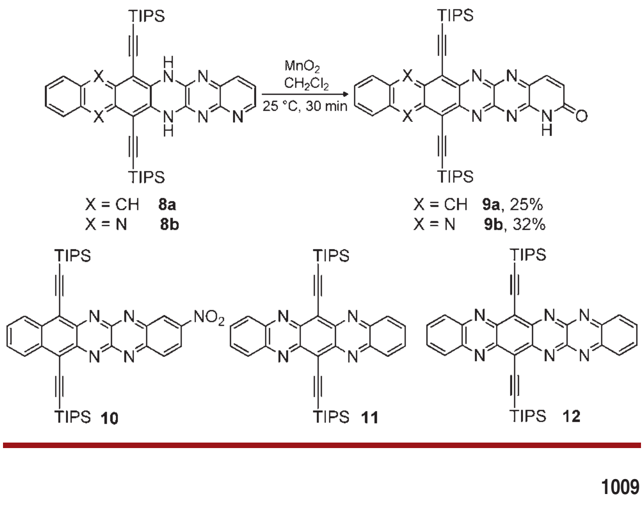
Scheme 2. Transformation of **1** into Chlorinated Derivatives



The exact position of dihydropyrazine moieties in compound **4** was assigned by two-dimensional NMR techniques (for more detailed information, see SI). Surprisingly that was not possible for compounds **5** and **6**. However, quantum chemical calculations in the gas phase indicate the same position of the *N,N'*-hydrogen atoms (Scheme 2).

The same type of MnO_2-based oxidation chemistry is observed for the larger heteroacenes **8a** and **8b** (Scheme 3), which are also oxidized into the corresponding pyridones

Scheme 3. Synthesis of Pyridones **9a** and **9b** and Structures of **10**–**12**



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9a and **9b**, and not into their heteroacenes. Here also, molecules carrying a pentacene unit and a lactam seem to be energetically more advantageous than the formation of a oligoazaheterohexacene unit. What are the electronic properties of these materials in dependence of their structure? Figure 2 displays the UV−vis and emission spectra of the *N*,*N*′-dihydro compounds **1**, **4**, **5**, **6**, **8a**, and **8b**. All of these display a robust fluorescence with a small Stokes shift as expected for rigid acene types and have absorption maxima in the range of 455−475 or 500 nm (**8b**, **4**). We note the influence of the pyridone ring, which shifts the absorption to the red as compared to that of the other derivatives.

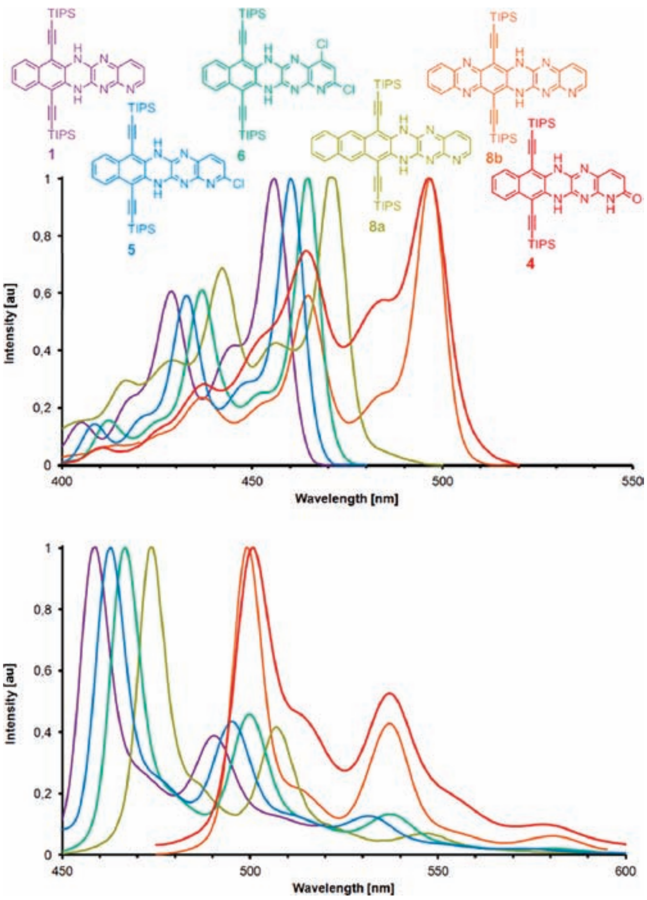

Figure 2. Absorption (top) and emission (bottom) spectra of dihydro compounds **1**, **4**, **5**, **6**, **8a**, and **8b**.

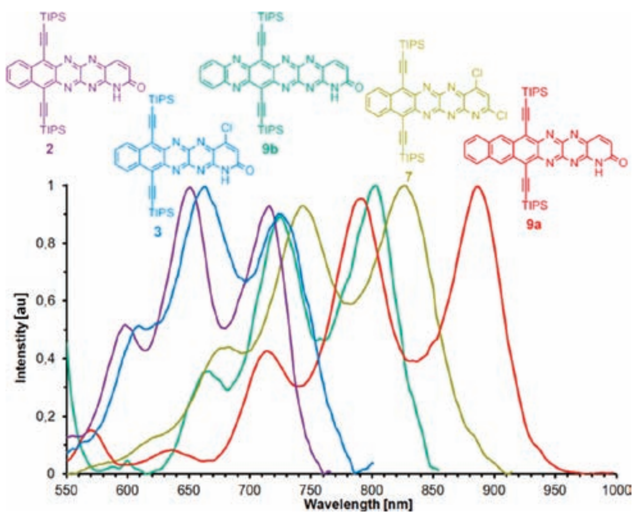

Figure 3. Absorption spectra of compounds **2**, **3**, **7**, **9a**, and **9b**.

This effect becomes more pronounced when the compounds **2**, **3**, **7**, **9b**, and **9a** are investigated (Figure 3). For **7** the red shift is expected, and its absorption maximum at 850 nm is in line with that of other acceptor-substituted tetraazaacenes, such as **10**, described in ref 2a. The pyridone derivatives also display absorption maxima that reach 750 nm for **2** and **3** and 800 or 940 nm respectively for **9b** or **9a**. The $\lambda_{\max\ \ \text{abs.}}$ of **2** is quite red-shifted as compared to the $\lambda_{\max\ \ \text{abs.}}$ of the symmetrical tetraazapentacene **11**. If one compares the optical spectra of **9a** with the absorption features of **12** ($\lambda_{\max} = 848$ nm) one can also see a significant red shift. The ε-values (and therefore the oscillator strengths) at $\lambda_{\max}$ of the investigated compounds (Table 1) are moderate and all around 5×10^3 L mol^{-1}cm^{-1}, for both the pyridones and the azacenes.

Table 1. Calculated and Measured HOMO−LUMO Gaps

	HOMO[a] (eV)	LUMO[a] (eV)	gap (eV) calcd	gap (eV/nm) opt[b]	ε (L mol^{-1} cm^{-1})
2	−5.82	−3.98	1.84	1.73/717	5083
3	−5.89	−4.09	1.80	1.70/729	5194
7	−5.89	−4.28	1.61	1.50/827	5892
9a	−5.49	−4.05	1.44	1.39/892	5493
9b	−5.85	−4.28	1.57	1.54/805	4236
12	−5.70	−4.22	1.48	1.46/842	n.a.

[a] Obtained by SPARTAN 10/windows using B3LYP method with the 6-31G*//6-311++G** basis set. Calculations were run on molecules, where TIPS groups were substituted for TMS groups. [b] Gap obtained from the $\lambda_{\max}$ of absorption.

What is the reason for this narrowing optical band gap in the pyridones? Quantum chemical calculations using the B3LYP 6-31G*//6-311++G** (Table 1 and Figure 4) method/basis set reproduce the optical gaps with good accuracy. Upon comparison of **9a** with **12**, however, the pyridone, even though an acceptor, is noted to be (relatively) more electron-rich than the corresponding acene structure. As a consequence **9a** displays both higher lying HOMO and LUMO but has a smaller HOMO−LUMO gap than **12**.

As an example we show the FMOs of **9a**. Here HOMO and LUMO display a disjunct character.[8] While the HOMO occupies the western part of the molecule, the LUMO is localized predominantly on the eastern part of **9a**, which

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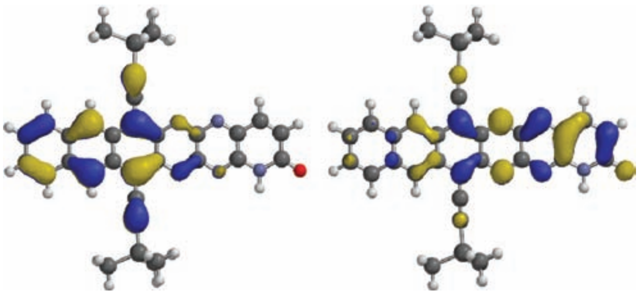

Figure 4. HOMO (left) and LUMO (right) of compound **9a′**. Visible is the disjunct nature of the FMOs.

contains all of the electron-accepting structural elements. This fact explains the decreased HOMO–LUMO gap. In compounds with disjoint FMO structures the influence of strategically placed substituents is particularly distinct on either HOMO or LUMO. Here the acceptor elements only stabilize the LUMO, but not the HOMO, which is localized on the opposite part of the molecule. The HOMO does not experience the stabilizing effect of the acceptor substituents, resulting in the decreased gap.

In conclusion, we have found an easy way to functionalize pentaazapentacenes and pentaazahexacenes. Starting from the coupling product **1**, oxidation with MnO_2 furnishes the pyridone derivative **2**, which can either be isolated or transformed *in situ* to give chlorinated *N,N′*-dihydropentaazapentacenes such as **5** and **6**. Oxidation of **5** is possible and furnishes the sensitive and reactive pentaazapentacene **7**. The facile oxidation of the heteroacene core is exceptional and might be best explained by the increase of reactivity through formation of an aromatic intermediate. The aromatization makes the terminal "pyridine" ring then vulnerable toward oxidation, just as if the —CH=N— unit of this embedded pyridine ring was an aldehyde. In the case of **7**, hydrolysis prevails, and the —CCl=N— unit correspondingly acts like a reactive acid chloride, while **4** is inert under the same conditions. This reactivity pattern, different from those observed for pyridines and quinolines, demonstrates that the incorporation of pyridine-like nitrogens into larger acenes produces materials with different properties and "turns on" alternative reactive pathways.

In the future we will improve our preparation of the compounds **6** and **7**, allowing investigation of these "armed" azaacenes.

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Supporting Information Available. Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.