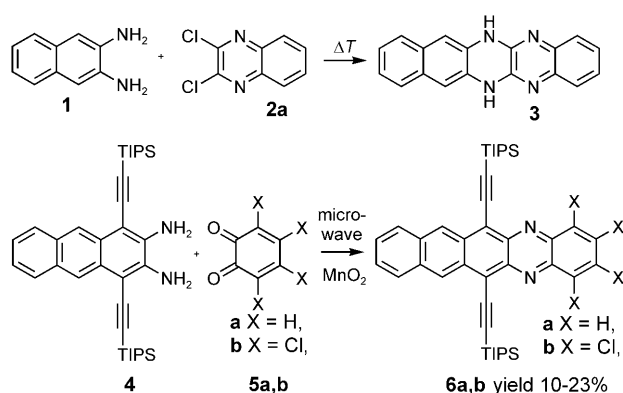


# An Efficient Synthesis of Tetraazapentacenes\*\*

Olena Tverskoy, Frank Rominger, Anastasia Peters, Hans-Jörg Himmel, and Uwe H. F. Bunz\*

Dedicated to Professor Günter Helmchen and Professor Rolf Gleiter

Azapentacenes, or better their *N,N*-dihydrocompounds, have been known since the end of the 19th century and they were first synthesized by Fischer<sup>[1]</sup> and by Hinsberg.<sup>[2]</sup> Hinsberg's synthetic approach, that is, condensation of an aromatic diamine with a suitable catechol or an activated *ortho*-dihaloarene (1,2-dichloroquinoxaline or 1,2-dichloropyrazine) is still used today. The starting materials are reacted in the melt at 130–160 °C to give the desired dihydrodiazacenes, such as **3**, in surprisingly good yields (Scheme 1). This method

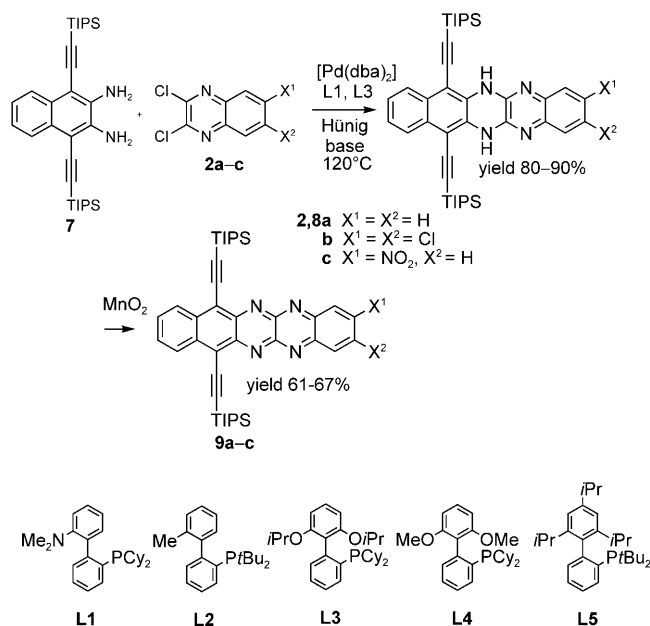


**Scheme 1.** Synthesis of azaacenes according to Hinsberg and Appleton et al.<sup>[1,3,4]</sup>

is however unsuitable for the pair **7** plus **2**, as substituents *ortho* to the amino groups apparently severely curtail reactivity. The condensation of **4** with **5a,b** gives the desired dihydrodiazapentacenes, however in relatively low yields (10–23 %). Oxidation with MnO<sub>2</sub> quantitatively transforms these products into the diazaacenes **6a,b** (Scheme 1).<sup>[3,4]</sup>

At temperatures above 250 °C, reaction mixtures of **7** with **2a**, with or without [(Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>] present, give rise to undefined, tarry decomposition products. Upon reaction of the mixture of **7** with **2a–c** in Hünig base in the presence of

Pd(OAc)<sub>2</sub> or [Pd(dba)<sub>2</sub>] (dba = dibenzylideneacetone) and the ligands **L1–L5** at 120 °C for 16 h, we obtained the desired coupling products **8a–c** (Scheme 2). All ligand/palladium-source combinations worked, but the yields of coupling



**Scheme 2.** Palladium-catalyzed synthesis of **9a–c** and the structure of the ligands **L1–L5**.<sup>[5]</sup> TIPS = triisopropylsilyl, dba = dibenzylideneacetone.

product **8** are heavily dependent upon L and the palladium source used. Best yields result when [Pd(dba)<sub>2</sub>] is combined with **L1**; **8a** is isolated in 82 % yield, while **8b** and **8c** were best produced with [Pd(dba)<sub>2</sub>] in the presence of **L3** in yields of 80 and 90 %, respectively (**7** plus **2b** or **2c**); [Pd(dba)<sub>2</sub>] is superior to Pd(OAc)<sub>2</sub>. It is however not clear what the cause is for the significant differences in coupling yields.

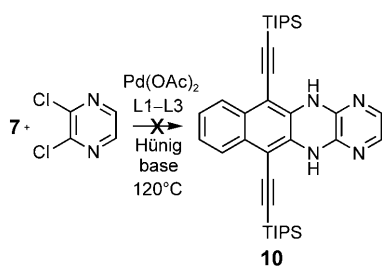
Compounds **8b–8c** are easily accessible functional derivatives, which, as was the case with **8a**, are oxidized by MnO<sub>2</sub> in yields ranging from 61–67 % into **9a–c**. Oxidation of the nitroarene **8c** is incomplete and furnishes 1:1 mixtures of **8c** and **9c**, which however are easily separated by chromatography. If the ring closure is attempted using **7** and 2,3-dichloropyrazine (Scheme 3), neither the expected product **10** nor the oxidized tetraazaacene congener is isolated. Compound **10** forms in traces, but it can only be detected by mass spectrometry. This observation may appear surprising, as the functionality of 2,3-dichloropyrazine is identical to that of **2**. The synthesis of **10** fails, perhaps as it might be a strongly

[\*] O. Tverskoy, Dr. F. Rominger, Prof. U. H. F. Bunz  
Organisch Chemisches Institut, Universität Heidelberg  
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)  
Fax: (+49) 6221-548-401  
E-mail: uwe.bunz@oci.uni-heidelberg.de

A. Peters, Prof. H.-J. Himmel  
Anorganisch-Chemisches Institut, Universität Heidelberg  
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)

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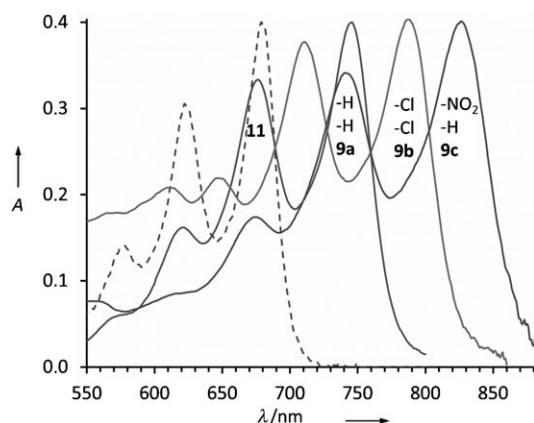
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**Scheme 3.** Attempted synthesis of **10**.

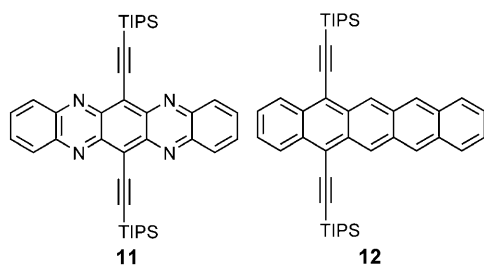
hydrogenating species, which could lead to a reductive poisoning of the palladium catalyst. Dihydrodiazatetracenes of similar structure spontaneously oxidize in air.<sup>[5]</sup> The intermediary  $\text{Pd}^{2+}$  species that is formed as part of the catalytic cycle would then be reduced to  $\text{Pd}^0$  and therefore be unavailable for further catalytic steps. Compounds such as **8** on the other hand are essentially non-reducing and can be stored in air for extended periods of time without oxidation and therefore can be formed by this coupling reaction efficiently.

Figure 1 shows the UV/Vis spectra of compounds **9a–c** and for comparison the spectrum of the tetraazapentacene

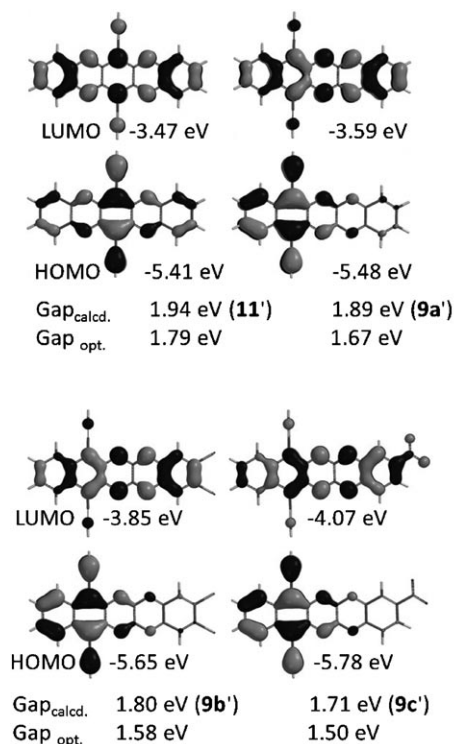


**Figure 1.** UV/Vis spectra of **9a–c** in hexane and the UV/Vis spectrum (dashed line) of **11** for comparison.

**11**.<sup>[6]</sup> Particularly noticeable is the significant red shift of the absorption maximum in the series **11**→**9a**→**9b**→**9c**, which is caused by an increased stabilization of the LUMO compared to that of the HOMO, and is induced by the electronegative



substituents. Similar effects were recently observed for halogenated diazapyrenes.<sup>[3]</sup> To clarify this issue, we performed quantum chemical calculations (B3LYP 6-31G\*\*//6-31G\*\*) on the nonsilylated model compounds **9a'–c'** and **11'**.<sup>[7]</sup> Compared to **11'**, **9a'–c'** have both stabilized HOMOs and LUMOs, but the HOMOs experience less stabilization than the LUMOs. This effect is particularly striking in **9c'**, where the LUMO is stabilized by 0.6 eV compared to that of **11'**, while the HOMO energy of **9c'** is lowered by only 0.37 eV. The reason for the lesser stabilization of the HOMO is its smaller orbital coefficients at the ring with the electronegative substituents (Figure 2).

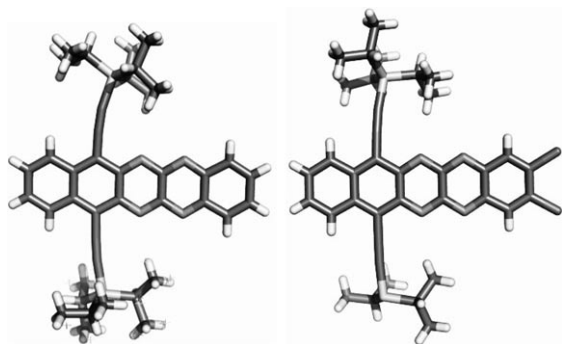


**Figure 2.** Molecular orbitals (HOMO and LUMO) of **11'** and **9a'–9c'**.

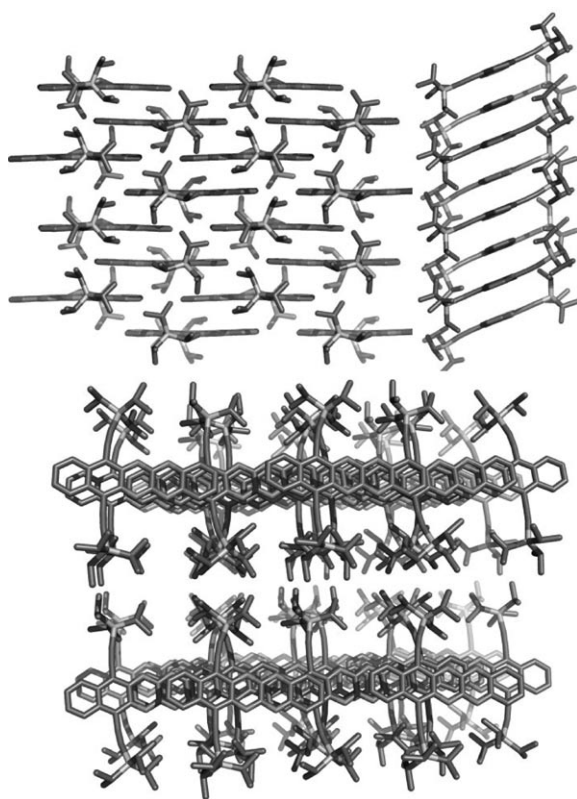
Heteroacene **9a** shows a reversible first reduction at  $E^{0/-} = -0.52$  V in cyclic voltammetry (acetonitrile, ferrocene as standard) and a second reduction at  $E^{-1/2-} = -1.0$  V, while the nitro-substituted compound **9c** shows reversible reduction waves at  $E^{0/-} = -0.27$  V and  $E^{-1/2-} = -0.80$  V (vs. ferrocene). Compound **9b** is too insoluble in acetonitrile under these conditions to allow cyclic voltammetry to be carried out. A comparison of the reduction potentials of **9a,c** with those of **11** and **6a,b** is instructive: **11**, **6a**, and **6b** are reduced at  $E^{0/-} = -0.79$  V,  $-1.05$  V, and  $-0.79$  V. Both tetraazapentacenes are more easily reduced than either **11** or **6b**, and the radical anions of **9a,c** should be stable in the presence of oxygen (reduction potential  $-1.3$  V vs. ferrocene). This point is important for the application of **9** as an electron-transport material, for example in thin-film transistors.

A critical aspect for the potential usefulness of **9** in organic electronics<sup>[7,8]</sup> is their structure in the solid state.<sup>[9]</sup> It was possible to obtain single crystalline specimen of **9a** and

**9b** (Figures 3–5). The molecular structures of **9a** and **9b** are inconspicuous. Molecules of **9a** assume parallel packed stacks that are oriented in a brickwork motif (Figure 4), similar to the solid state structure of **11**. In contrast, the “isosteric”

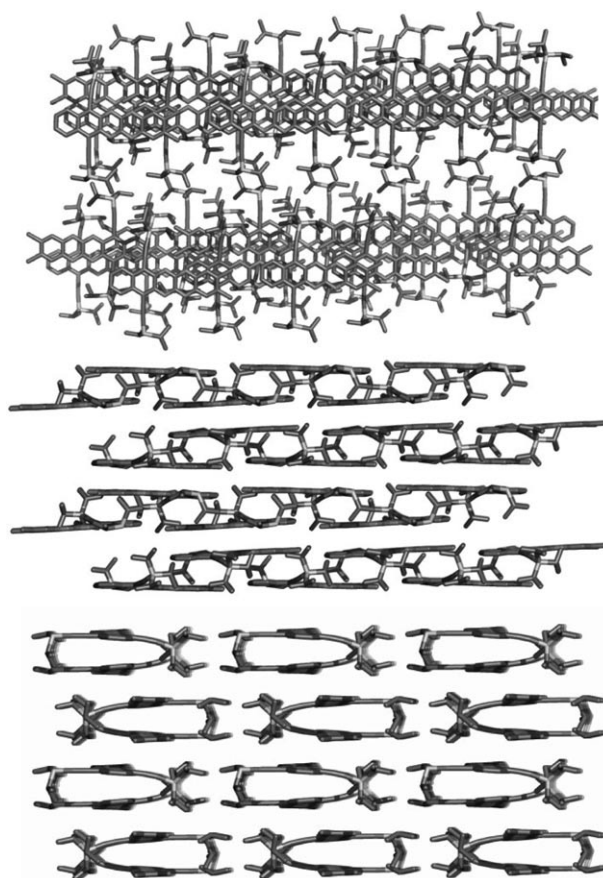


**Figure 3.** Single-crystal structure of **9a** (left) und **9b** (right). The picture was created in Pymol.



**Figure 4.** Packing of **9a** in the crystalline state. The offset stacking leads to a brickwork motif parallel to the crystallographic *b, c* plane. Top left: view perpendicular to the *b, c* plane; top right: view along the *b* axis; bottom: view of two parallel stacks from the top along the *c* axis.

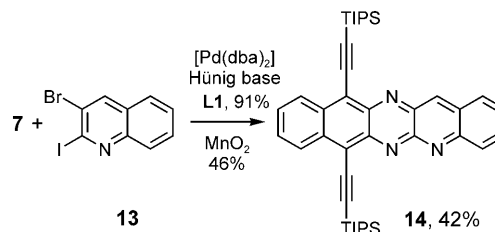
compound **12**<sup>[10]</sup> packs in a herringbone motif in the single crystal. Compound **9b** also forms offset stacks in the single crystal (Figure 5). Again, a brickwork motif runs parallel to the *b, c* plane with laterally offset double rows. If the packing motifs in **9a** or **9b** make them suitable as electron transport



**Figure 5.** Packing of **9b** in the single crystal. Bricklayer motif with lateral offset. Top: view from the top along the *b* axis; middle: top view on the brick-wall motif in the *b, c* plane; bottom: side view of the stacks along the *c* axis; the lateral offset of the double rows is clearly visible.

materials, they might be potentially useful in the fabrication of thin-film transistors. This issue is not clear but is currently under investigation. The facile reducibility of the heteroacenes **9** is clearly advantageous, as their radical anions should be environmentally stable.

To test synthetic extensions of this concept, we coupled **7** to 3-bromo-2-iodoquinoline (**13**) under palladium catalysis (Scheme 4). The intermediate was immediately oxidized by  $\text{MnO}_2$  to give the triazapentacene **14** in 42% yield, which is a good indication that the title coupling reaction is generally applicable. We expect to generate other heteroacenes applying this exciting methodology.



**Scheme 4.** Synthesis of **14**.

The palladium-catalyzed amination described herein forms substituted dihydrotetraazapentacenes easily and in good to excellent yields. Oxidation with  $\text{MnO}_2$  furnishes the respective novel tetraazapentacenes, which we foresee to have exciting applications in organic electronics.

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- [1] a) O. Fischer, E. Hepp, *Ber. Dtsch. Chem. Ges.* **1890**, 23, 2789; b) U. H. F. Bunz, *Pure Appl. Chem.* **2010**, 82, 953; c) U. H. F. Bunz, *Chem. Eur. J.* **2009**, 15, 6780; d) Q. Miao, T. Q. Nguyen, T. Someya, G. B. Blanchet, C. Nuckolls, *J. Am. Chem. Soc.* **2003**, 125, 10284.
- [2] O. Hinsberg, *Justus Liebigs Ann. Chem.* **1901**, 319, 257.
- [3] A. L. Appleton, S. M. Brombosz, S. Barlow, J. S. Sears, J.-L. Bredas, S. R. Marder, U. H. F. Bunz, *Nat. Commun.* **2010**, 1, Article 91.
- [4] a) F. Kummer, H. Zimmermann, *Ber. Bunsen-Ges.* **1967**, 71, 1119; b) E. Leete, O. Ekechukwu, P. Delvigs, *J. Org. Chem.* **1966**, 31, 3734.
- [5] a) D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, 120, 6438; *Angew. Chem. Int. Ed.* **2008**, 47, 6338.
- [6] S. Miao, S. M. Brombosz, P. von R. Schleyer, J. I. Wu, S. Barlow, S. R. Marder, K. I. Hardcastle, U. H. F. Bunz, *J. Am. Chem. Soc.* **2008**, 130, 7339.
- [7] S. Miao, A. L. Appleton, N. Berger, S. Barlow, S. R. Marder, K. I. Hardcastle, U. H. F. Bunz, *Chem. Eur. J.* **2009**, 15, 4990.
- [8] a) M. Winkler, K. N. Houk, *J. Am. Chem. Soc.* **2007**, 129, 1805; b) S. Z. Weng, P. Shukla, M. Y. Kuo, Y. C. Chang, H. S. Sheu, I. Chao, Y. T. Tao, *ACS Appl. Mater. Interfaces* **2009**, 1, 2071; c) Y.-Y. Liu, C.-L. Song, W.-J. Zeng, K.-G. Zhou, Z.-F. Shi, C.-B. Ma, F. Yang, H.-L. Zhang, X. Gong, *J. Am. Chem. Soc.* **2010**, 132, 16349.
- [9] a) J. E. Anthony, *Chem. Rev.* **2006**, 106, 5028; b) J. E. Anthony, *Angew. Chem.* **2008**, 120, 460; *Angew. Chem. Int. Ed.* **2008**, 47, 452; c) P. T. Herwig, K. Müllen, *Adv. Mater.* **1999**, 11, 480.
- [10] J. E. Anthony, D. L. Eaton, S. R. Parkin, *Org. Lett.* **2002**, 4, 15.
- [11] J. E. Anthony, J. S. Brooks, D. L. Eaton, S. R. Parkin, *J. Am. Chem. Soc.* **2001**, 123, 9482.
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