DE GRUYTER DOI 10.1515/pac-2013-1211 — Pure Appl. Chem. 2014; 86(4): 483–488

Conference paper

Michaela Märken, Benjamin D. Lindner, Anthony L. Appleton, Frank Rominger
and Uwe H.F. Bunz*

Synthesis of tetraazatetracenes and -pentacenes: role of the substituents for their stability

Abstract: We report the synthesis of a series of novel tetraazaacene derivatives and compare their stability with respect to size, oxidation potential and position of the TIPS-ethynyl groups. The latter has the most pronounced effects on the stability. In case of azatetracenes where TIPS-alkynes are either attached laterally or in the *peri*-positions, the former ones dimerized while the latter are stable. Attempts to expand this concept to the corresponding tetrakis-*peri*-substituted heptacenes led to the isolation of the dimerized butterfly product.

Keywords: acenes; alkynes; heterocycles; ISNA-15; organic chemistry; organic electronics.

Cambridge Crystallographic Data Centre numbers: CCDC 989563; CCDC 989564; CCDC 989565; CCDC 989566.

***Corresponding author: Uwe H.F. Bunz,** Organisch-Chemisches Institut, Ruprecht-Karls-Universität, Im Neuenheimer Feld 270, 69120 Heidelberg, FRG, e-mail: uwe.bunz@oci.uni-heidelberg.de
Michaela Märken, Benjamin D. Lindner and Frank Rominger: Organisch-Chemisches Institut, Ruprecht-Karls-Universität, Im Neuenheimer Feld 270, 69120 Heidelberg, FRG
Anthony L. Appleton: Stanford University, Department of Chemical Engineering, Stauffer III, 381 North-South Mall, Stanford, CA 94305, USA

Article note: A collection of invited papers based on presentations at the 15th International Symposium on Novel Aromatic Compounds (ISNA-15), Taipei, Taiwan, 28 July–2 August 2013.

Introduction

We disclose here the synthesis of a series of novel N,N′-dihydroazatetracenes, -pentacenes and -heptacenes and the attempt to oxidize them into azaacenes. We observe significant structure dependent differences in stability of the targets. N-Heteroacenes have received increasing attention in the last few years [1]. Compounds of this type have been the subject of research for more than a century, and were first independently synthesized by Fischer and by Hinsberg at the end of the 19th and the beginning of the 20th centuries [2]. Hinsberg noted that in the case of tetraazatetracenes, both the azatetracenes but also the respective N,N′-dihydro compounds were stable and could be interconverted. In case of the azapentacene, Hinsberg noted that he could only obtain the N,N′-dihydro-derivatives, which are formally antiaromatic. More than sixty years later, Zimmermann and Leete independently synthesized the azapentacenes by oxidation of the corresponding dihydroazaacenes with Chloranil or copper(II)acetate [3]. Characterization of their targets was accomplished by UV-Vis spectroscopy, a state of the art technique at that time. Azaacenes were reinvigorated in 2003 when Nuckolls et al. [4] demonstrated that N,N′-dihydrodiazapentacene is an attractive alternative for pentacene in thin film transistors. The question for the use of the dehydrogenated versions, the “real azaacenes” was not investigated until several years later when we started to systematically develop synthetic strategies for the

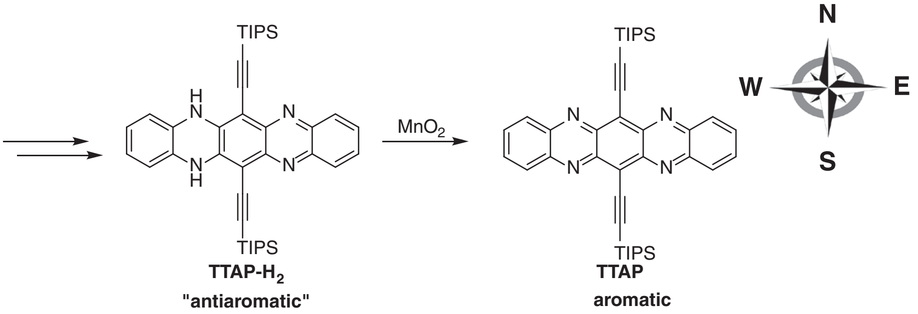


Fig. 1 Oxidation of dihydro compound TAPP-H_2 with manganese dioxide.

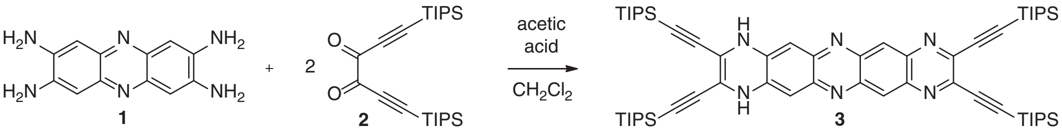
access of different azaacene topologies. Manganese dioxide oxidizes the dihydro compounds smoothly and in good-to-excellent yields into azaacenes (Fig. 1).

At that point Miao et al. started to investigate the electronic properties of substituted azaacenes and demonstrated that TIPS-tetraazapentacene (TTAP) [5] is an exceptional electron transporting material with impressive mobilities in excess of 3 $cm^2 V^{-1} s^{-1}$ [6]. At the same time, we developed a series of Pd-catalyzed coupling protocols to increase the number and type of azaacenes as these seem to be materials with attractive properties for applications in thin film transistors [7]. However, we had always restricted ourselves towards two TIPS-ethynyl groups attached to the azapentacene core either on the central or on the adjacent benzene ring. Here we give a full account about the synthesis of azaacenes with two or four TIPS-ethynyl groups either attached at the east/west or north/south positions. We also report some of the spontaneous dimerization reactions that are observed after oxidation.

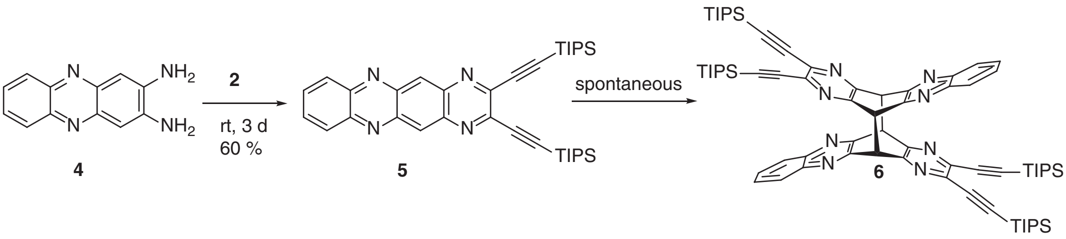
Results and discussion

In a first experiment (Scheme 1) we treated the literature known tetraaminophenazine **1** with Faust's dione **2** [8] but could never isolate pure **3**. Attempts to purify it by chromatography led to streaking and loss of product. Attempts to oxidize the mixture failed. Consequently we treated (Scheme 2) the commercially available diaminophenazine **4** with **2** and obtained the alkynylated tetraazaacene **5** in 60 % yield. The material is stable at –18 °C and under nitrogen atmosphere for several weeks and can be stored thusly.

Attempts to grow crystals under atmospheric conditions in solution were successful, but as shown in Fig. 2 it is not the X-ray crystal structure of **5** but of the butterfly-cycloaddition product **6**. This is an unusual



Scheme 1 Attempted synthesis of the hexaazapentacene **3**.



Scheme 2 Synthesis of azatetracene **5** and its spontaneous dimerization into **6**.

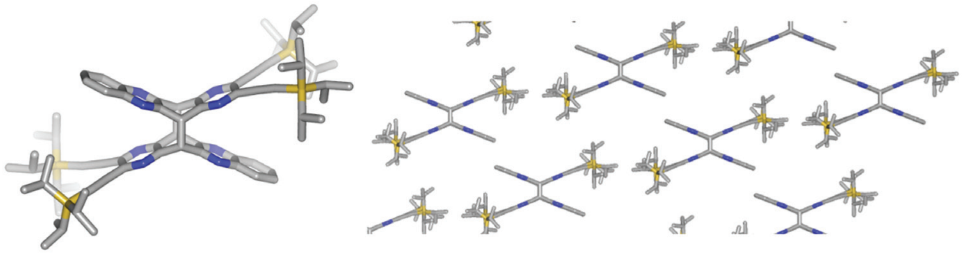


Fig. 2 Crystal structure of the dimerized product **6**.

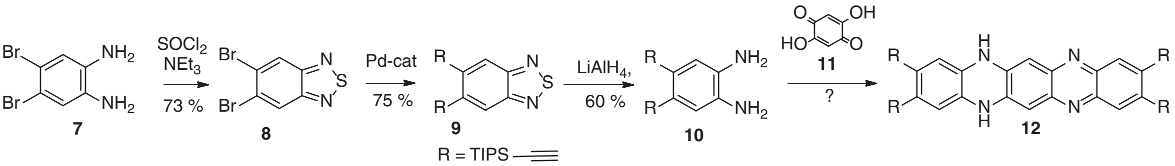
observation, as azatetracenes are normally stable and isolable without observation of any cycloaddition products, both substituted as well as unsubstituted cores as demonstrated in earlier works [9]. We interpret this result in that the two 2,3-TIPS-ethynyl groups orient the molecules of **5** in the solid state such that they immediately form the butterfly dimer by evading steric interaction of the two large substituents.

To better understand our observations, we prepared 4,5-bisTIPS-ethynylphenylenediamine **10** (Scheme 3) starting from **7**. Forming the thiadiazole ring **8** by thionyl chloride is followed by Sonogashira coupling to give **9**, in which the heterocyclic ring is reduced by $LiAlH_4$ to the diamine **10**. Attempts to couple to the quinone **11** to **10** were, however, met with little success, as **12** is unstable and decomposes during isolation (Scheme 3).

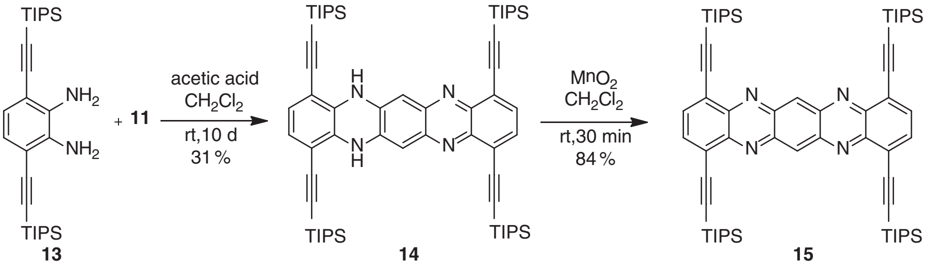
With these results in hand we investigated the reaction of **13**, the constitutional isomer of **10**, with **11** (Scheme 4). Here we form **14** in a slow reaction in a 31% yield; **14** is easily isolated, purified and characterized. Reaction with MnO_2 furnishes the fully aromatic tetraazapentacene **15** in almost quantitative yield. We were able to obtain suitable crystalline specimens for both **14** and **15** (Fig. 3).

Figure 3 shows the plots of the molecular structure and the packing of compound **15**. The packing is distinctly different from that of the 6,13-bisTIPS-ethynyl-substituted TTAP; π-π-interactions are not detected (for further information, see SI). The four TIPS-ethynyl groups are sufficiently bulky to insulate the tetraazapentacene cores from each other. The UV-Vis and emission spectra of **14** and **15** are shown in Fig. 4. The UV-Vis spectrum of **15** is similar but hypsochromically shifted with respect to that of the symmetrical TTAP.

As we were successful with the synthesis of the azapentacene **15** we also reacted the diamine **16** with **11** under similar conditions (Scheme 5), but **17** was obtained in relatively low yields. However, **17** is stable and could be isolated. We have recently reported its synthesis and single crystal X-ray structure [10]. Attempts to oxidize **17** did not result in the desired heptacene **18**, at least not in an isolated form, but furnishes the



Scheme 3 Synthetic route to the dihydrotetraazaacene **12**.



Scheme 4 Synthesis of the stable tetraazapentacene **15**.

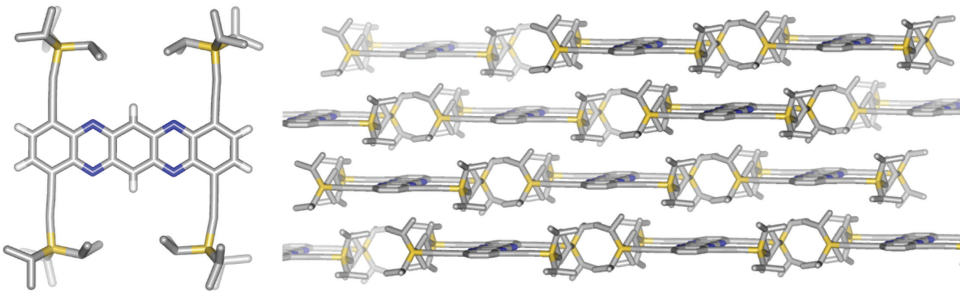


Fig. 3 Single crystal structures and packing of the tetraazaacene **15**.

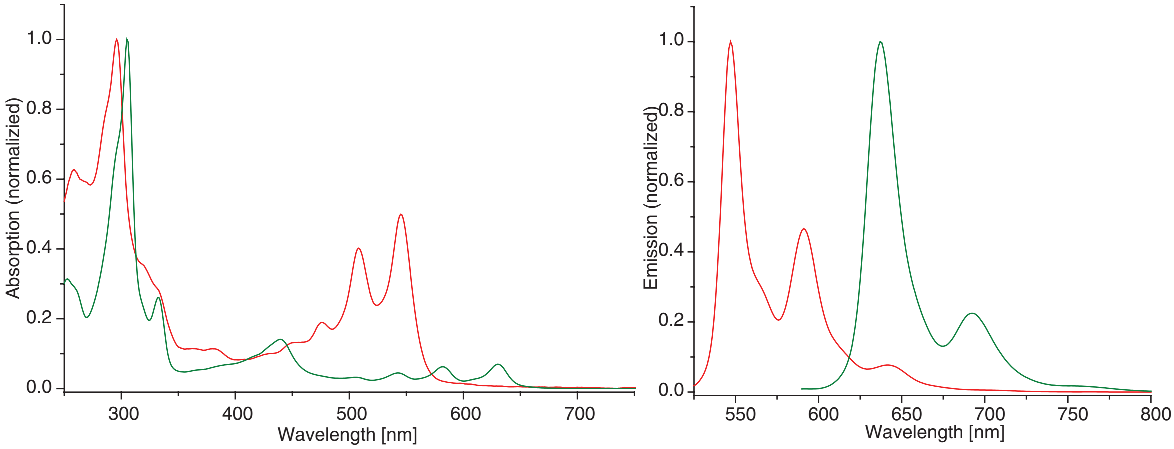
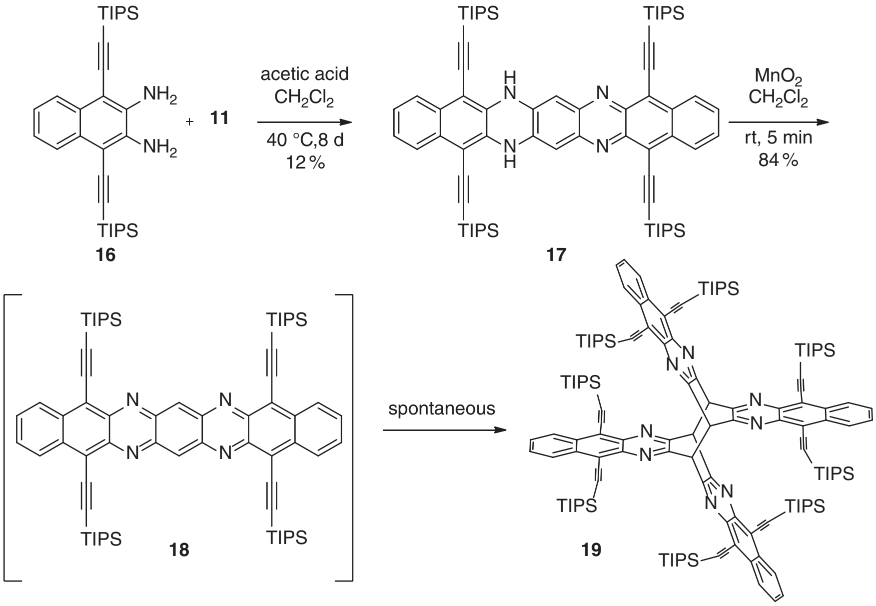


Fig. 4 UV-Vis spectra (left) of the N,N′-dihydro compound **14** (red) and the tetraazapentacene **15** (green). On the right hand side are the emission spectra of **14** (red) and **15** (green) shown.



Scheme 5 Synthesis of the tetraazaheptacene **18** and its spontaneous dimerization into **19**.

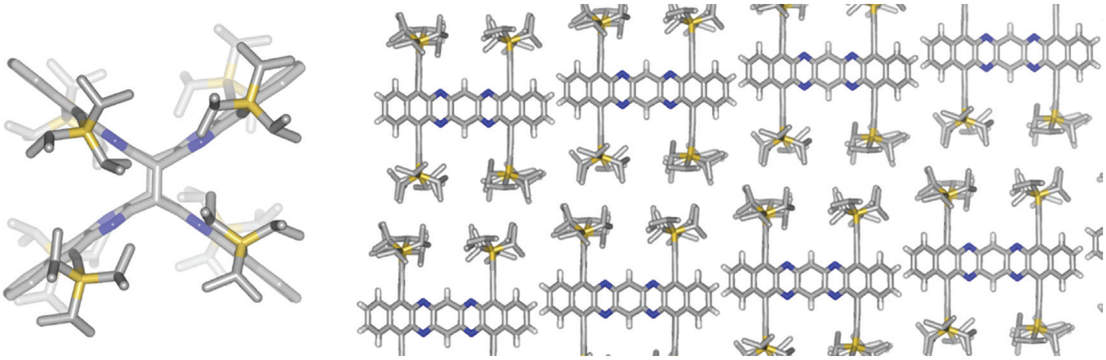
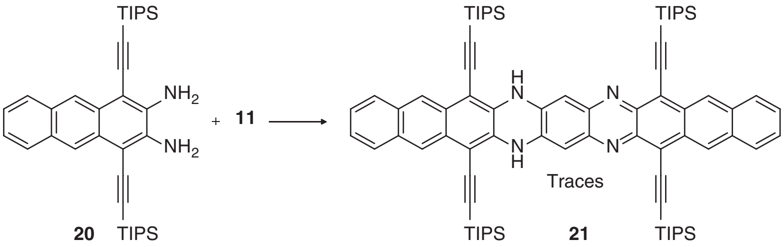


Fig. 5 Single crystal X-ray structure of compound **19**. The crystal contains hexanes as crystal solvent and are omitted for clarity.



Scheme 6 Attempted synthesis of the N,N′-dihydrotetraazanonacene **21**.

dimer **19** in 84 % yield after chromatography. The identification of **19** was achieved by NMR spectroscopy. We also obtained crystalline specimens (Fig. 5) suitable for determining the single crystal X-ray structure, thus confirming our NMR results. The bond distances and bond angles of **19** are inconspicuous (for further information, see SI). Synthesizing a nonacene derivative became our next priority. Disappointingly, attempts (Scheme 6) to couple the diaminoanthracene derivative **20** to **11** gave **21**, but only in traces, which shows the limit of utility to this synthetic approach.

Conclusions

In conclusion we have demonstrated that the position of the TIPS-ethynyl group in larger azaacenes plays a critical role for their stability. If the TIPS-eththynyl groups are located in the 2,3-position, even tetraaza*tetra*cenes are vulnerable towards dimerization in solid state, probably due to a preferred packing motif, in which the substituents force the stacking into oppositely aligned molecules that undergo thermal cycloadditions in the solid state. Attempts to prepare an azapentacene with 2,3,9,10-substituents (i.e. in the western and eastern positions) failed completely as even the typically stable N,N′-dihydroazaacene could not be isolated. On the other hand, for the azaacenes in which the 1,4,8,11-substitution pattern is present, the azapentacene **15** is stable, despite the central ring being unsubstituted. However, attempts to isolate the analogous heptacene **18** failed, as the azaacene apparently dimerizes *in situ* to the butterfly dimer **19**. Attempts to prepare the larger N,N-dihydrotetraazanonacene **21** failed, as the condensation yielded **21** only in traces. The overall stability of acenes, as previously determined by John Anthony [11], and their nitrogen-containing analogues, as demonstrated here, depend strongly on position and the size of the substituent attached to the core. Apparently the northern and southern positions of the azaacenes are more helpful in stabilizing these attractive materials than substituents attached to the eastern and western edges of the azaacenes.

References

[1] U. H. F. Bunz, J. U. Engelhart, B. D. Lindner, M. Schaffroth. *Angew. Chem.* 52, 3810 (2013). U. H. F. Bunz. *Pure Appl. Chem.* 8**2**, 953 (2010). U. H. F. Bunz. *Chem.—Eur. J.* **15**, 6780 (2009). J. Mei, Y. Diao, A. L. Appleton, L. Fang, Z. Bao. *J. Am. Chem. Soc.* **135**, 6723 (2013). Q. Miao. *Synlett* 326 (2012). C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu. *Chem. Rev.* **112**, 2208 (2012). P. M. Beaujuge, J. M. J. Frechet. *J. Am. Chem. Soc.* **133**, 20009 (2011). A. L. Appleton, S. M. Brombosz, S. Barlow, J. S. Sears, J. L. Brédas, S. R. Marder, U. H. F. Bunz. *Nat. Comm.* **1:91**, DOI: 10.1038/ncomms1088 (2010). B. D. Lindner, M. Marken, J. U. Engelhart, O. Tverskoy, A. L. Appleton, F. Rominger, K. I. Hardcastle, M. Enders, U. H. F. Bunz. *Chem.-Eur. J.* **18**, 4627 (2012).

[2] O. Fischer, E. Hepp. *Chem Ber.* **23**, 2789 (1890). O. Fischer, E. Hepp. *Chem Ber.* **28**, 293 (1895). O. Hinsberg. *Liebigs Ann. Chem.* **319**, 257 (1901).

[3] F. Kummer, H. Zimmermann. *Ber. Bunsenges.* **71**, 1119 (1967). E. Leete, O. Ekechukwu, P. Delvigs. *J. Org. Chem.* **31**, 3734 (1966).

[4] Q. Miao, T. Q. Nguyen, T. Someya, G. B. Blanchet, C. Nuckolls. *J. Am. Chem. Soc.* **125**, 10284 (2003).

[5] S. Miao, A. L. Appleton, N. Berger, S. Barlow, S. R. Marder, K. I. Hardcastle, U. H. F. Bunz. *Chem.—Eur. J.* **15**, 4990 (2009).

[6] Z. X. Liang, Q. Tang, J. B. Xu, Q. A. Miao. *Adv. Mater.* **23**, 1535 (2011).

[7] O. Tverskoy, F. Rominger, A. Peters, H. J. Himmel, U. H. F. Bunz. *Angew. Chem. Int. Ed.* **50** 3557 (2011). B. D. Lindner, J. U. Engelhart, O. Tverskoy, A. L. Appleton, F. Rominger, A. Peters, H. J. Himmel, U. H. F. Bunz. *Angew. Chem. Int. Ed.* **50**, 8588 (2011).

[8] R. Faust, C. Weber. *Liebigs Ann.* 1235 (1996). R. Faust, B. Gobelt, C. Weber. *Synlett* **64**, (1998).

[9] S. Miao, S. M. Brombosz, P. V. R. Schleyer, J. I. Wu, S. Barlow, S. R. Marder, K. I. Hardcastle, U. H. F. Bunz. *J. Am. Chem. Soc.* **130**, 7339 (2008). J. I. Wu, C. S. Wannere, Y. Mo, P. V. R. Schleyer, U. H. F. Bunz. *J. Org. Chem.* **74**, 4343 (2009).

[10] A. L. Appleton, S. Barlow, S. R. Marder, K. I. Hardcastle, U. H. F. Bunz. *Synlett* **1983** (2011).

[11] B. M. Medina, J. E. Anthony, J. Gierschner. *ChemPhysChem* **9**, 1519 (2008). B. Purushothaman, S. R. Parkin, J. E. Anthony. *Org. Lett.* **12**, 2060 (2010).