(Aza)Pentacenes Clipped into a Ring: Stabilization of Large (Aza)Acenes

Lukas Ahrens, Olena Tverskoy, Svenja Weigold, Michael Ganschow, Frank Rominger, Jan Freudenberg,* and Uwe H. F. Bunz*

**Abstract:** A doubly alkylene bridged 6,13-diphenylpentacene and analogously bridged azapentacenes were prepared; they are persistent. The doubly bridged azapentacenes display superior photochemical, oxidative and thermal stabilities compared to azapentacenes protected by bis(TIPS-ethynyl)-substituents—clipping an azacene into a large ring is a viable complement in stabilization.

Stabilization and solubilization of larger acenes and heteroacenes, that is, ≥5 rings, is challenging, yet important to fully unlock their properties.[1] Aryl substituents attached at strategic positions of a large acene fulfills this need to a degree. Yet, the use of bis(trialkylsilylethynyl)-groups in 2001 changed the situation.[2] The silylethynyl substituents enjoy a near monopoly in the stabilization of larger (hetero)acenes—heptacene can be stabilized and solubilized with just two of them.[3] Additional auxiliary arene substituents are necessary for nonacenes to survive.[4] However, there should be alternative stabilization modes of similar efficiency. Kobayashi et al. demonstrated doubly alkylene bridged anthracenes as photoemitters with improved photostability when compared to 5,9-diphenylantracene.[5] Yet, these systems were not compared to their analogous 5,9-bis(trisopropylsilylethynyl)anthracenes to gauge relative stability. Double bridging was also employed to twist anthracene,[6] to ring perylenebisimides[7] and to shield polythiophene derivatives.[8]

Kobayashi’s encapsulation should be applicable to larger acenes. Herein, we present stable and soluble, modularly synthesized doubly bridged (aza)pentacenes 5–9 (Scheme 1).

Starting from 1, double Suzuki coupling furnishes 2. Removal of the methyl groups with BBr₃ is followed by transformation of the resorcinic intermediate with 1,7-dibromoheptane in DMF (K₂CO₃ as base) to furnish jacketed pentacene 5. The double cyclization was performed at concentrations of 5 mmol L⁻¹. For the azacenes 6 and 7, the bridged diaminoanthropentacene 4 was obtained from naphthothiadiazoloquinone. Addition of lithiated 1,3-dimethoxybenzene and reduction with sodium hypophosphite, followed by the opening of the thiazole ring by SmI₂, gives 4. Diamino-pentacene 4 couples under established Pd-catalyzed conditions[9-10,11a,b,12] with 2,3-dialkaoarcenes to give the azapentacenes 5 and 7. If the doubly bridged diaminoanthracene is employed, 8 results, while 9 is obtained by coupling of ortho-phenylenediamine with the encapsulated 2,3-diaminoanthracene. 6–9 form as N,N-diaphrag-compounds—these are oxidized by MnO₂ into the azacenes.

The consanguine TIPS-ethynyl(aza)acenes are literature known and were prepared as reference substances[11]. Figure 1 displays a photograph of dilute solutions of 5–9 and of 5TIPS·9TIPS. The visual colors are similar—slight variations (cf. 5 and 5TIPS) are due to the TIPS-ethyl group enlarging the conjugated π-system. The doubly alkylene bridged (aza)acenes display in general broader and blue-shifted features in the UV-vis spectra (Figure 2). This is not

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**Scheme 1.** Synthesis of doubly alkylene bridged (aza)pentacenes 5–9.

**Conditions:** i) ArB(OH)₂, KPO₄, Pd₂(dba)₃, XPhos, 1,4-dioxane, H₂O, 100°C, 7 d; ii) BBr₃, DCM, −78°C − r.t., 2 d → 7 d; iii) K₂CO₃, Br(CH₂)₇Br, DMF, 40°C → 80°C, 3 d; iv) 1) Cs₂CO₃, RuPhos Pd G1 (10 mol%), tolune, 110°C, 15 h; 2) MnO₂, DCM, r.t., 30 min.

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[1] M. Sc. L. Ahrens, O. Tverskoy, M. Sc. S. Weigold, Dr. M. Ganschow, Dr. F. Rominger, Dr. J. Freudenberg, Prof. U. H. F. Bunz Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
E-mail: freudenberg@oci.uni-heidelberg.de uwe.bunz@uni-heidelberg.de
Prof. U. H. F. Bunz Centre for Advanced Materials Im Neuenheimer Feld 225, 69120 Heidelberg (Germany)

[2] Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202015348.

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the case for assigned of is blue shifted, possibly due to an increased donor-acceptor character of in comparison to . The doubly bridged azaacenes appear non-emissive, similar to their TIPS-congeners, only fluoresces notably.

Table 1 displays the electronic properties of the targets and their first reduction potentials. As expected, tetraaza-derivative is most easily reduced, while the other azaacenes display fairly similar reduction potentials ( to V vs. ) and electron affinities. This trend is echoed in the silylthynylated (aza)acenes, which are more readily reduced due to the electronnegative ethynyl substituents with reduction potentials ranging between to V for the diaza-derivatives.

Single crystalline specimen of , , and were obtained by slow diffusion of methanol into a chloroform solution of the (aza)acene (Figure 3). Bond lengths and angles of the aromatic cores are in agreement with calculated values. Both and contain chloroform in the crystal lattice. The packing is dominated by van der Waals contacts of the bridging rings with each other. - - -contacts are not observed for the (aza)pentacenes (packing diagram see SI), as the double bridges dominate the supramolecular structure.

Important is the relative stability under irradiation (Figure 4), performed under air and under argon ( mol L , DCM, ambient temperature).
Under argon, 5 is of comparable stability to 5TIPS, but in air, 5 is more easily oxidized than 5TIPS (Figure 4). We isolated 10, a rearrangement product of the endo-peroxide of 5, identified under mass spectrometric conditions and by its single crystal structure (Figure 5a). This rearrangement was previously described by Rigaudy et al. in the photolytic decomposition of anthracene.\cite{15} We propose predominant formation of an 5,14-endo-peroxide for 5 due to steric shielding, whereas for 5TIPS, the main product is the 6,13-endo-peroxide (98:2; 6,13- vs. 5,14-endo-peroxide).\cite{16}

6–9 are consistently more stable than their TIPS-ethynyl-congeners, both under argon but also under air. We note that the position of the pyrazine unit and to a lesser effect the position of the substituents influence the reactivity for the TIPS-ethynyl substituted azacenes. The bridged azacenes 6, 8 and 9 were still intact after 18 h irradiation under argon atmosphere. Irradiation in DCM under ambient conditions chlorinates the azacenes, as verified by mass spectrometry. 7 furnishes 11 as one of the photoproducts (Figure 5b) we could isolate. Generally, the mixtures formed during the photolysis of the azacenes are difficult to separate and to characterize.

To expand the clipping-and-jacketing concept, we reacted 12 (Pd-catalyzed) with 2,3-dichloroquinoxaline, treated the coupling-product with PbO2 and obtained the tetraazahexacene 13 in 53 % yield (Scheme 2, \(\lambda_{\text{max, abs}} = 946 \text{ nm}\)).\cite{12} An X-ray analysis proves the topology: 13 crystallizes without solvent and displays \(\pi-\pi\)-overlap involving the electron rich and electron poor parts of the hexacene, respectively (Figure 6).\cite{18} 13 is stable and can be handled without any problem, demonstrating the use of jacketing.

In large azacenes, Kobayashi’s double alkylene bridging, termed “clipping-and-jacketing”, is superior to TIPS-alkyne substituents with respect to stabilization. Tetraazahexacene

**Figure 4.** Time-dependent evolution of UV/Vis absorption intensities at \(\lambda_{\text{abs, max}}\) for 5–8 and 5TIPS-8TIPS (10⁻³ mol L⁻¹) after irradiation with a handheld UV lamp (\(\lambda_1 = 365 \text{ nm}\) and \(\lambda_2 = 254 \text{ nm}\)) in n-hexane at room temperature under argon atmosphere (left) and under ambient conditions (right). Distance to lamp was 5 cm for measurements under argon atmosphere and 20 cm under ambient conditions. 8 and 8TIPS show almost identical decomposition rates compared to 9 and 9TIPS (see SI, Figure S54), hence position of the sterically demanding group has less impact on stability compared to the position of nitrogen substitution.

**Figure 5.** Identified products of photolytic decomposition reactions: Solid state structures of a) 10 produced in photolysis of 5 under air and b) decomposition product 11 formed from 7.

**Scheme 2.** Synthesis of doubly alkylene bridged azahexacene 13. Conditions: i) 1.) Cs\(_2\)CO\(_3\), RuPhos Pd G1 (10 mol%), toluene, 110°C, 15 h; 2.) PbO\(_2\), DCM, 0°C, 30 min.
13 packs in the single crystalline state with π-π-stacking; it has not escaped our attention that molecules like 13 might be useful as n-channel semiconductors in thin-film transistors. Jacketing could emerge as powerful alternative to trialkylsilalkynylation, particularly as nature and steric demand of the alkylene bridges—the jackets—are easily varied.

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Conflict of interest

The authors declare no conflict of interest.

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