Novel Dihydropyrazines and their Double *ortho*-Annulation to Hexaazapentacenes

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Dedicated to Professor Peter Metz, Dresden, on the occasion of his 60th birthday

The cycloacylation of oxalic amidines **7** with *bis*-imidoylchlorides **6** furnished the dihydropyrazine derivatives **8**. Due to their *vicinal* amino-imino substructures, they provide good preconditions for a double intramolecular ring closure reaction. An alternative synthesis for hexaaza-pentacenes **1** was developed using potassium carbonate as the base and lead tetraacetate as the oxidizing agent.

Key words: Hexaazapentacenes, Dihydropyrazines, *ortho*-Annulation, Amidines, Fluorophores

Introduction

Acenes, particularly pentacene, have attracted significant interest in organic electronic devices; however, they become increasingly unstable with increasing size [1]. Whereas one approach to the stabilization of higher acenes involves their substitution at selected positions, the other involves the exchange of CH atoms with heteroatoms, such as nitrogen. The resulting aza-acenes [2 – 5] are of particular interest since they possess different electronic and physical properties, and they also introduce new possibilities for chemical modification at the nitrogen atoms. Linear systems, such as "pyrazinacenes" **1** [6], offer by far the most opportunities for derivatization and applications have been reported as solvatochromic dyes [7, 8], redox-switchable chromophores/fluorophores [9, 10] and liquid crystalline materials [11]. Their most important application, as easily processable organic derivatives, is established in organic thin-film field effect transistors (OTFTs) [12 – 18]. Recent reviews [19] emphasize that aza-acenes are underrepresented in charge transport materials, and there is a high need for research activities in this field.

We recently reported syntheses of novel hexaazapentacenes **1** and **2**, *via* aminolysis reaction of tetrachloropyrazine **3** with 2-aminophenyl(phenyl)-amine [20] (Scheme 1). At the beginning, product **3** has only been available by a tedious chlorination of pyrazine-2,3-dicarboxylic acid or pyrazine itself, and an alternative synthesis is desirable. In addition, pyrazines such as **3** have a high oxidation potential and, therefore, are able to oxidize vicinal diamines to undesirable by-products very easily.

The starting point for a new synthetic approach was the observation of highly fluorescent octaazahexacenes **5** as by-products during the derivatization reactions of pyrazino[2,3-*b*]pyrazines **4** [21] (Scheme 2). For the formation of **5**, we first postulated a cycloaddition-redox sequence, however, this reaction is based on a different reaction type: an *ortho*-annulation reaction primarily *via* radical cations. Consequently, the prototropic form **4′**, which possesses a *vicinal* amino-imino substructure, plays the key role in

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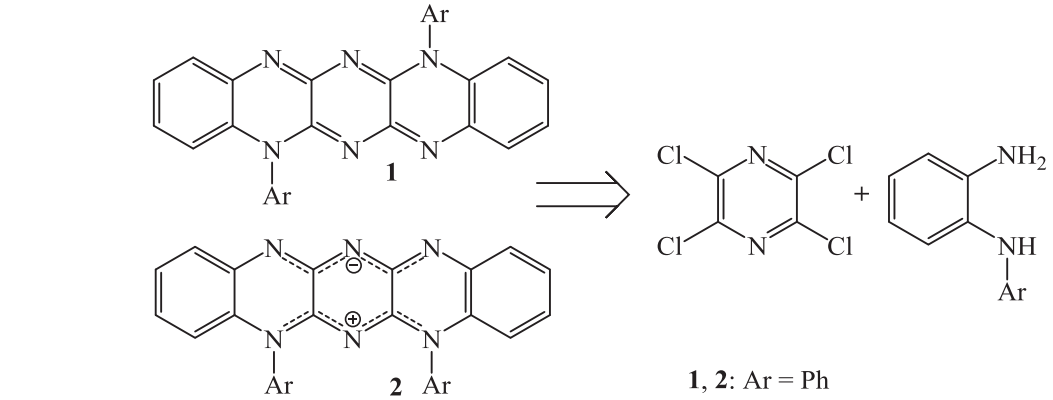
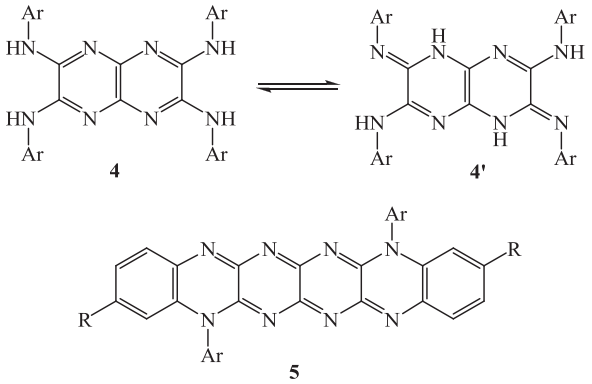


Scheme 1. Retrosynthetic approach to hexaazapentacenes of types **1** and **2**.



Scheme 2. Pyrazino[2,3-*b*]pyrazines **4** and **4′** as starting point for a cascade reaction to give octaazahexacenes **5**.

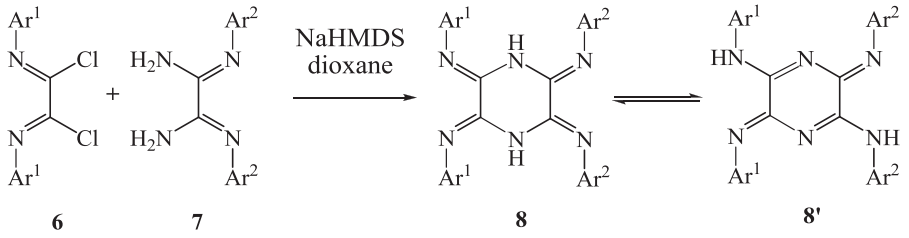
a double *ortho*-annulation reaction which finally leads to the hexacyclic derivative **5**. Similar annulations have been observed in previous work dealing with the reactivity of 2,3-diaminoquinoxalines [22]; however, the mechanism was interpreted as a rare example of a nucleophilic aromatic substitution of hydrogen (NASH) promoted by complexation of ruthenium. This type of quinoxaline later served as the starting material for the synthesis of novel bridged bis-benzimidazoles *via* oxidative cyclization [23]. On the other hand, derivatives of quinoxaline were also obtained in the synthesis of Ni-diazadiene complexes which contain additional diphenylphosphane groups. Since, in this case, the prototropic formation of *vicinal* amino-imino substructures is not possible, the authors postulated an intramolecular [4+2]-cycloaddition reaction in which the substituted benzene rings function as a dienophile in the initial step [24, 25].

Generally, benzannulation of aromatics and heteroaromatics forms an important basis for the syntheses of new molecules, mainly for material chemistry. Modern organic chemistry offers an arsenal of methods using [4+2]-cycloaddition reactions of *o*-quinodimethanes [26, 27] or appropriately structured heterocycles (isobenzofurans, isoquinolinium systems) [28, 29], benzynes/pyridynes [30 – 32], and 3,3-benzannulation reactions [33].

We have previously demonstrated that other *vicinal* amino imines also allow an oxidative ring closure reaction. Applying 4*H*-imidazoles [34] and 3,4-bis(arylamino)-substituted pyrroles as model compounds [35], new ring-fused derivatives were synthesized and characterized. Based on quantum-chemical calculations [35], we showed that a multi-step process with a radical cation as the key intermediate most likely takes place. The fact that during the formation of **5** from **4**, a double *ortho*-annulation process took place prompted us to re-examine this reaction. Derivatives **8** (Scheme 3) provide ideal conditions to test this hypothesis and are easily accessible starting from common C2 building blocks.

Results and Discussion

As depicted in Scheme 3, derivatives **8** were synthesized by simple cycloacylation of amidines **7** with *bis*-imidoyl chlorides **6**. The only weakly electrophilic, but selective C2 building blocks of type **6** have already been used frequently for syntheses which take place *via* cyclization-tautomerism sequences [36 – 39]. Accordingly, the dihydropyrazines **8** were successfully synthesized. The reaction was carried out by fast addi-



6 **7** **8** **8'**

8a: $Ar^1 = Ar^2 = 4\text{-tol}$
8b: $Ar^1 = Ar^2 = 4\text{-MeOC}_6H_4$
8c: $Ar^1 = Ar^2 = 4\text{-}n\text{BuC}_6H_4$
8d: $Ar^1 = 4\text{-BrC}_6H_4$, $Ar^2 = 4\text{-}n\text{BuC}_6H_4$
8e: $Ar^1 = \text{Ph}(^{15}\text{N})$, $Ar^2 = 4\text{-}t\text{BuC}_6H_4$

Scheme 3. Synthesis of dihydropyrazines **8**.

tion of one equivalent of **6** to a dioxane solution containing the deprotonated amidine **7** (base: NaHMDS). The new products, which contain two linked oxamidine substructures, were isolated as orange crystalline compounds in good yields. They form equilibria consisting of different prototropic forms in common solvents, as indicated by broad signals in their NMR spectra. Starting from the ^{15}N-labelled *bis*-imidoyl chloride **6e**, a doublet ($^1J = 89$ Hz, ^{15}N–H) was detected besides a singlet for the unlabelled NH in the NMR spectrum of its cyclization product **8e**. This experimental finding is a clear indication of the coexistence of at least one other prototropic isomer **8e′**. The structure of the latter, being a donor-substituted diaza-quinonediimine, easily explains the strong absorption bands ($\lambda_{max} = 430-450$ nm, lg $\varepsilon = 4.2$) in the UV/Vis spectra. We succeeded in obtaining single crystals suitable for X-ray structure analysis. The structure determined of the derivative **8b** confirms the preference of the prototropic form **8b′** (Fig. 1).

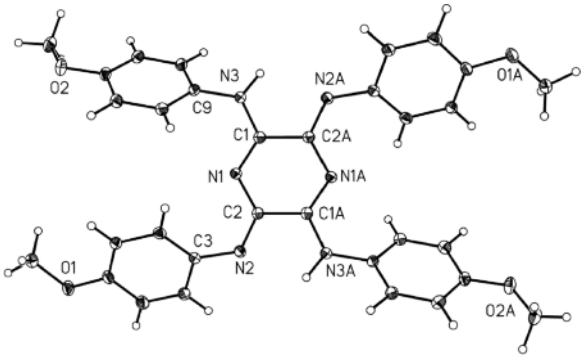
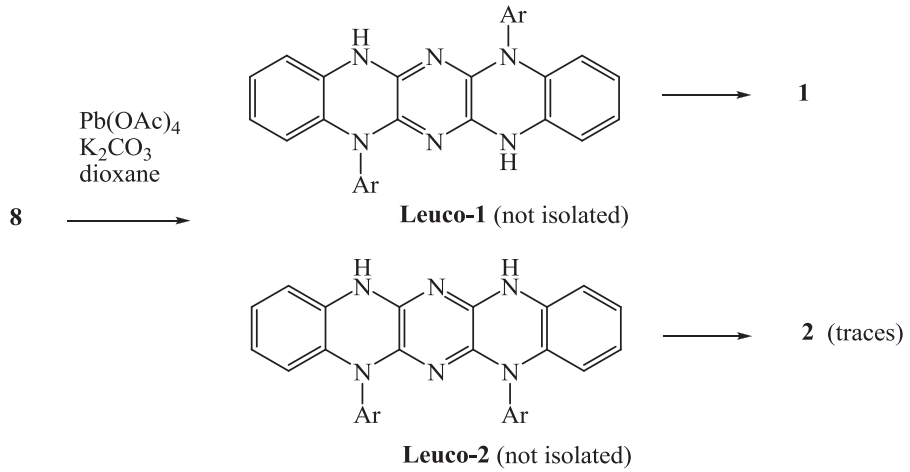


Fig. 1. Molecular structure of dihydropyrazine **8b** in the crystal. (Ellipsoids at the 50% probability level; H atoms as spheres with arbitrary radius). Selected bond lengths in Å: C9–N3 1.4230(19), N3–C1 1.3414(18), N1–C1 1.3132(17), N1–C2 1.3777(18), C2–N2 1.2944(17), N2–C3 1.4069(19).

The molecule crystallizes in space group $P2_1/m$ and has a twofold rotation axis perpendicular to the pyrazine ring, which, together with the nitrogen atoms, forms a plane. Both of the exocyclic imino substructures exhibit *Z*-configuration in the crystal. The aromatic rings bonded to the nitrogen atoms N2 and N3 are twisted out of the plane. The torsion angles between C2–C3–C8–N2 and between C1–N3–C9–C14 are 29.3° and 52.5°, respectively; the smaller torsion angle is caused by the double bond. The proton on the nitrogen atom N3 is connected *via* a hydrogen bond to a methoxy group of a neighboring molecule, thus forming a ladder-type structure. Compared to the bond between C1 and N3 (1.341 (2) Å), the bond length between N2 and C2 (1.294 (2) Å) is, therefore, significantly reduced – a further indication for the preference of the prototropic form **8′** in Scheme 3.

In the first oxidation test, derivative **8a** was reacted under the conditions (CAN in the presence of K_2CO_3 in acetonitrile) used successfully for *ortho*-annulation reactions already reported [34]. After a short time, the formation of a strongly yellow-fluorescent substance was detected by TLC. The chromatographic isolation yielded a black, amorphous substance; the MS data (M^+ $m/e = 494$) suggested the presence of structure **1a** (Ar = 4-tolyl). Optimization reactions for derivative **1a** showed that potassium carbonate as a base and lead tetraacetate as the oxidizing agent gave the best results



Scheme 4. Double oxidative *ortho*-annulation to give leuco forms of **1** and **2** which were immediately oxidized by air to give regioisomeric hexaazapentacenes **1** and **2**.

(Scheme 4, **1a**: 24 % yield). Traces of a strongly red-fluorescent compound were always isolated as a by-product, the MS data of which were similar to those of compound **1a**. The ^{1}H NMR spectrum clearly showed two singlets for two different tolyl groups ($\delta = 2.11$ and 2.43 ppm). However, no exact assignment was possible in the region of aromatic protons; the integrals were consistent with the number of protons expected. The molecular structure of **2a** was confirmed by X-ray structure analysis. The poor quality of the crystals did not allow a satisfactory refinement. From these data, it is evident that, in this case, a double *ortho*-annulation also took place which led to the mesoionic regioisomer **2a**.

Because no single crystals could be obtained, the further characterization of **1a** proved to be problematic. Furthermore, all attempts to obtain suitable crystals by salt formation/*N*-methylation also failed. Suitable data could only be obtained from the UV/Vis fluorescence spectra. The absorption spectrum revealed a well-structured pattern with a maximum at 518 nm, while the emission spectrum is nearly congruent with an intense emission at 525 nm. The very small Stokes shift of only 7 nm comprises a very small difference between ground and excited state. The derivative **1c** was isolated in very low yields starting from **8c** and was characterized by MS ($[M]^+$, $m/e = 662$). All attempts to involve derivative **8b** in oxidative *ortho*-annulation led only to decomposition reactions with the formation of inseparable mixtures of polymeric products, obviously due to the strong influence of the donor methoxy groups. Derivative **8d** as a precursor gave better results. With a reaction time of 5 h, the derivative **1d** (yield up to 45 %) was obtained and characterized. Interestingly, the sequence cyclization/oxidation (starting from **6d** and **7d** *via* **8d**) was successfully realized in a one-pot synthesis, and gave comparable yields. The hexaaza-pentacene **1d** was obtained after purification by column chromatography as an amorphous, black solid, which showed decomposition upon heating above 400 °C. A molecular ion at $m/e = 708$ in its mass spectrum confirmed the proposed structure. The UV/Vis and the fluorescence spectra are almost identical to that of derivative **1a** and again show a very small Stokes shift of only 7 nm (Fig. 2).

Despite the testing of other oxidizing agents, the yields for derivatives **1** could not be increased; instead, a series of highly fluorescent substances was formed as by-products. An interesting result was found when potassium ferricyanide was used as an oxidant. In this case, a non-fluorescent iron complex was first formed, which decomposed after some time to give the starting material and small amounts of **1a** and **2a**. Further studies with metal complexes as oxidizing agents are planned, and the results will be the subject of a separate publication.

Based on our previous work and the findings of the present studies, we postulate the following mechanism (Scheme 5) for the formation of hexaaza-pentacenes of types **1** and **2**. First, the oxidation of the secondary amine group in **8** takes place under the intermediary formation of the radical cation **A**. A relatively strong

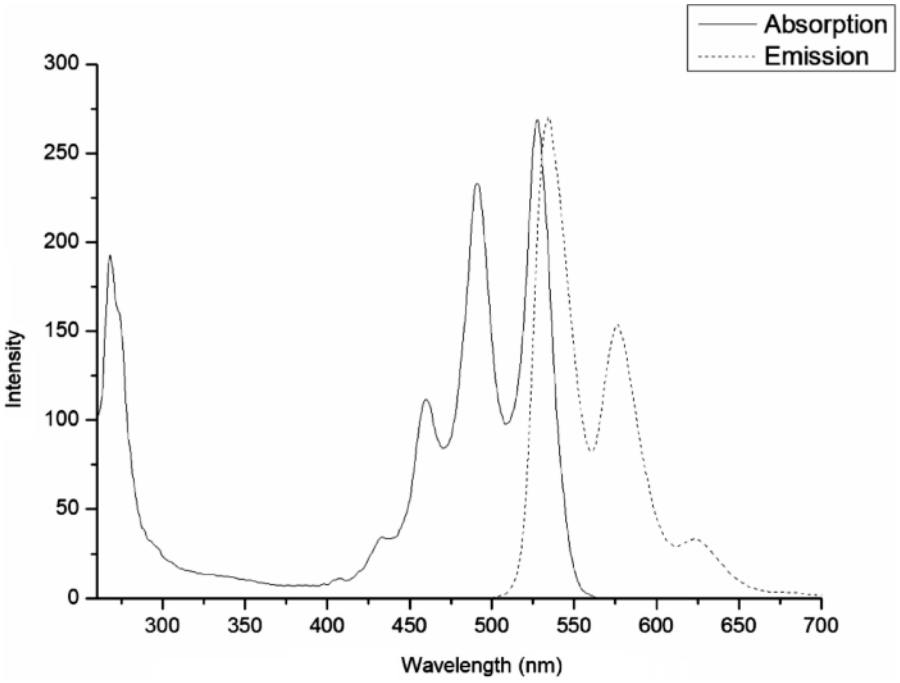
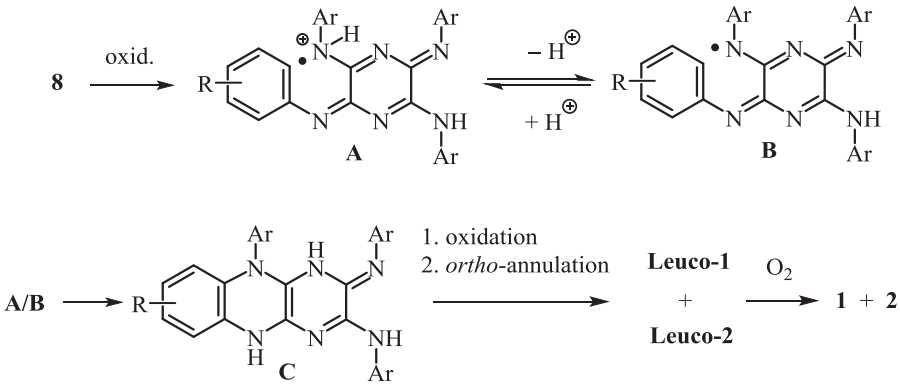


Fig. 2. UV/Vis and fluorescence spectrum of **1d** in THF (normalized).



Scheme 5. Proposed mechanism for the double *ortho*-annulation sequence.

acidity has been predicted for these types [40 – 42] and, consequently, deprotonation may result in the aminyl radical **B**. Radical cation **A** as well as radical **B** are able to substitute the attached aromatic ring intramolecularly to give the leuco-semi form **C**. Due to the bifunctionality of **10**, the same reaction subsequently can form **Leuco-1** and **Leuco-2**, which are transformed by oxygen from air in a final oxidation step into **1** and **2**, respectively. The mechanism, in which the key intermediates are radical cations/aminyl radicals **A/B**, is supported by the following experimental facts. Generally, anilines can easily be oxidized, and the radical cations thus formed tend toward a fast deprotonation. It is noteworthy, however, that kinetic studies revealed that cyclization reactions of aminyl radical cations are much faster than those of the corresponding neutral radicals [43, 44]. Despite the fact that some methods for the generation of aminyl radicals are described in the literature [45 – 48], reactions of nitrogen-centered radicals are less well developed than

those of the analogous carbon species. In addition, only a few data for intramolecular cyclization reactions with aminyl radicals/radical cations exist [43–45], among which the Hoffmann-Löffler-Freytag reaction is the oldest known reaction involving aminium cation radicals [49]. Whereas aminyl radicals are nucleophilic, aminium cation radicals and their metal complexes render the nitrogen atom more electrophilic. Because the interconversion of **A** to **B** is very fast, we are not able to determine the key intermediate.

The oxidative cyclization of aryl-substituted amidines, which have a similar substructure as **8**, was reported in 1996 [50, 51]. The authors suggest that aminyl cations are formed *via* oxidation processes and undergo a final cyclization reaction. Due to the presence of the potassium carbonate base in our experiments, however, the existence of aminyl radicals cannot be excluded. In contrast, proton-mediated redox processes on aromatic amines allow the synthetic entry to phenazines. Thus, prolonged heating of *N*-phenyl-*o*-phenylene diamine in 1 M $HClO_4$ finally resulted in tetraazapentacenes [52].

Conclusion

A new and alternative entry to hexaaza-pentacenes has been presented based on a double oxidative *ortho*-annulation sequence. Applying this method, the derivatives showing C_2 symmetry of type **1** can be preferably isolated, whereas the mesoionic regioisomers **2** were formed only in traces. The formation of **1** is strongly dependent on the nature of substituents on the aromatic systems. Whereas derivatives bearing alkyl groups (**1a**, **1d**) allow the isolation of hexaaza-pentacenes in moderate yields, the reaction fails completely in the presence of methoxy groups. The new azaacenes exhibit strong fluorescence with high quantum yields and very small Stokes shifts.

Experimental Part

Unless otherwise indicated, all reagents were purchased from commercial suppliers and used as received. Starting materials that were not commercially available were prepared according to literature procedures cited in the text. Reactions were monitored by TLC using SiO_2 (silica gel 60 F254) from Fluka. Melting points were measured with a digital detector system KSPS 1000 from Krüss and are uncorrected. The ^1H and ^{13}C NMR spectra were obtained on Bruker AC 250 (250/60 MHz) and DRC-400 (400/100 MHz) spectrometers, using residual solvent peaks as internal standards. Mass spectra were measured with a Finnigan MAT SSQ 710 Fison Trio 200 (EI) instrument. Elemental analyses were carried out with an automatic analyzer LECO, CHNS-932. The UV spectra were measured with a UNICAM UV500 spectrometer from Thermo Electron Corporation. For IR spectra a BIO-RAD FTS-25 instrument was used. Absorption spectra were recorded on a LAMBDA 16 spectrophotometer (Perkin Elmer). Fluorescence emission and excitation spectra were measured using an LS50B luminescence spectrometer (Perkin Elmer). Fluorescence quantum yields were calculated relative to quinine sulfate (purum; Fluka) in 0.1 N H_2SO_4 used as a standard ($\phi_f = 0.55$). The absorbance at the excitation wavelength was kept below 0.05 for the samples and the reference. The fluorescence lifetime was determined with a CD900 time-correlating single photon counting spectrometer (Edinburgh Instruments).

General procedure for the synthesis of dihydropyrazines ***8***

In a 100 mL two-necked flask 1 mmol of an oxalamidine **7** was dissolved in 5 mL of dioxane and heated to 80 °C. A 2 M solution (1.5 mL) of NaHMDS in dioxane was added, and the solution was stirred for 10 min followed by the addition of 1 mmol of the appropriate *bis*-imidoyl chloride **6** in 5 mL of dioxane. The mixture was stirred for 5 min at 80 °C. Then 50 mL of water was added to the hot reaction mixture. After cooling to r. t. the mixture was filtered. The red solid was washed with water, water-dioxane (1/1) and a small portion of toluene-heptane (1/10). The product thus obtained was used directly for further syntheses. An analytically pure sample was obtained by column chromatography (silica gel 60, $CHCl_3$).

*2,5-Bis(4-tolylamino)-3,6-bis(4-tolylimino)-3,6-dihydropyrazine (**8a**)*

Orange solid; yield 65 %. – M. p. 252–254 °C. – IR (KBr): $\nu(cm^{-1}) = 3293$ (NH), 2901, 2865, 1628 (C=N). – UV (CH_2Cl_2): λ_{max} (lg ε) = 268 (4.4), 281 (4.5) 383 br (4.4). – MS (EI): m/z (%) = 498 (30), 407 (8), 248 (38), 91 nm (100). – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 9.48$ (s, 2H, NH), 7.60 (d, $J = 8.3$ Hz, 8H, aryl), 7.17 (d, $J = 8.2$ Hz, 8H, aryl), 2.39 ppm (s, 12H, ar-CH_3). – $C_{32}H_{30}N_6$ (498.63): calcd. C 77.08, H 6.06, N 16.85; found C 77.28, H 6.20, N 16.51.

*2,5-Bis(4-methoxphenylamino)-3,6-bis(4-methoxyphenylimino)-3,6-dihydropyrazine (**8b**)*

Red crystals; yield 63 %. – M. p. 240–242 °C. – MS (EI): m/z (%) = 562 (100), 455 (6), 280 (30), 133 (84). – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 9.46$ (s, 2H, NH), 7.73 (d, $J = 9.0$ Hz, 8H, aryl), 6.91 (d, $J = 9.0$ Hz, 8H, aryl),

3.86 ppm (s, 12H, CH_3–O). – $C_{32}H_{30}N_6O_4$ (562.63): calcd. C 68.31, H 5.37, N 14.94; found C 68.28, H 5.29, N 15.01.

*2,5-Bis(4-n-butylphenylamino)-3,6-bis(4-n-butylphenylimino)-3,6-dihydropyrazine (**8c**)*

Orange solid; yield 15 %. – M. p. 103 – 106 °C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 272 (4.4), 282 (4.4) 385 nm br (4.2). – MS (EI): m/z (%) = 666 (42), 333 (14), 294 (46), 133 (100). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.39 (s, 2H, NH), 9.22 (s, 2H, NH), 7.48 (m, 8H, aryl), 7.12 (m, 8H, aryl), 2.57 (t, J = 7.4 Hz, 4H, CH_2), 1.53 (m, 4H, CH_2), 1.30 (m, 4H, CH_2), 0.88 ppm (t, J = 7.3 Hz, 6H, CH_3). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 157.4, 140.4, 139.9, 133.9, 130.0, 129.1, 128.6, 128.2, 122.5, 119.8, 35.2, 33.7, 22.3, 13.9 ppm.

*2-(4-Bromophenyl)amino-3-(4-bromophenyl)imino-5-(4-n-butylphenyl)amino-6-(4-n-butyl-phenyl)imino-3,6-dihydropyrazine (**8d**)*

Orange solid; yield 43 %. – M. p. 148 – 150 °C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 270 (4.4), 282 (4.4) 380 nm br (4.3). – MS (EI): m/z (%) = 712 (16), 355 (6), 218 (100), 155 (40). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.48 (s, 2H, NH), 9.40 (s, 2H, NH), 7.49 (m, 12H, aryl), 7.19 (d, J = 8.4 Hz, 4H, aryl), 2.64 (t, J = 7.5 Hz, 4H, CH_2), 1.65 (m, 4H, CH_2), 1.40 (m, J = 7.2 Hz, 4H, CH_2), 0.97 ppm (t, J = 7.3 Hz, 6H, CH_3). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 140.4, 131.7, 128.7, 124.0, 122.3, 117.9, 35.2, 33.7, 22.3, 14.0 ppm. – $C_{36}H_{36}Br_2N_6$ (712.53): calcd. C 60.68, H 5.09, Br 22.43, N 11.79; found C 60.48, H 5.14, Br 22.20, N 11.88.

*2-(^{15}N-Phenylamino)-3-(^{15}N-phenylimino)-5-(4-t-butylphenyl)amino-6-(4-t-butylphenyl)-imino-3,6-dihydropyrazine (**8e**)*

Orange crystals; yield 42 %. – M. p. 226 – 227 °C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 267 (4.4), 278 (4.4) 374 br (4.3). – MS (CI): m/z (%) = 557 (25), 484 (10), 353 (100), 337 (30), 297 (50). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.46 (d, ^1J = 89 Hz, ^{15}N–H), 9.45 (s, NH), 7.60 (m, 8H, aryl), 7.34 (m, 8H, aryl), 7.16 (t, J = 7.4 Hz, 2H, aryl), 1.34 ppm (s, 18H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 128.6, 126.0, 125.4, 124.8, 122.0, 118.9, 34.4, 31.3 ppm.

*Transformation of derivatives **8a** and **8d** to hexaazapentacenes **1a** and **1d***

In a 100 mL two-necked flask, a mixture consisting of 1 mmol of a dihydropyrazine **8**, 1.4 g (10 mmol) of potassium carbonate and 3.6 g (12 mmol) of $Pb(OAc)_4$ in 10 mL of dioxane was heated at 80 °C. The temperature was maintained for 5 h, and then unreacted $Pb(OAc)_4$ was reduced to $Pb(OAc)_2$ by adding 2 mL of ethylene glycol. The crude product was precipitated by adding 50 mL of water and filtered off. The solid was washed with 100 mL of dioxane-water (1/10), 10 mL of dioxane-water (1/1) and finally, 10 mL of diethyl ether. The azaacene was extracted with methylene chloride, then the extract was evaporated *in vacuo* and finally, the product was purified by column chromatography (silica gel 60, $CHCl_3$-acetone).

*5,12-Bis-(4-tolyl)-3,10-dimethyl-5,12-dihydro-[5,6,7,12,13,14]hexaazapentacene (**1a**)*

Black solid; yield 25 %. – M. p. > 400 °C (dec.). – UV (CH_2Cl_2): λ_{max} (lg ε) = 272 (4.8), 403 (3.3), 428 (3.9), 454 (4.4), 486 (4.8), 520 nm (4.9). – Emission ($CHCl_3$): λ = 528, 570, 617 nm, fluorescence quantum yield (ϕA) = 0.95($\pm$0.05). – ^{1}H NMR (250 MHz, $CDCl_3$+ CF_3COOD): δ = 7.53 (m, 8H, aryl), 7.17 (d, J = 8.1 Hz, 4H, aryl), 6,9 (s, 1H, aryl), 6,78 (s, 1H, aryl), 5,05 (s, 2H, NH), 2.54 (s, 6H, CH_3), 2.11 ppm (s, 6H, CH_3). – $C_{32}H_{26}N_6$ (494.60): calcd. C 77.71, H 5.30, N 16.99; found C 77.54, H 5.20, N 16.85.

*3-(n-Butyl)-5-(4-n-butylphenyl)-10-bromo-12-(4-bromophenyl)-dihydro[5,6,7,12,13,14]hexaazapentacene (**1d**)*

Black solid; yield 45 %. – M. p. > 400 °C (dec.). – UV (CH_2Cl_2): λ_{max} (lg ε) = 272 (4.8), 431 (4.0), 458 (4.5), 488 (4.9), 524 nm (5.0). – Emission ($CHCl_3$): λ = 535, 576, 623 nm, fluorescence quantum yield (ϕA) = 0.95($\pm$0.05). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.41 (m, 14H, aryl), 2.27 (m, 4H, CH_2), 1.63 (m, 4H, CH_2), 1.03 (t, J = 7.3 Hz, 6H, CH_3), 0.88 ppm (q, J = 7.3 Hz, 4H, CH_2). – MS (EI): m/z (%) = 708 (50), 665 (10), 398 (100), 171 (93), 132 (24). – $C_{36}H_{32}Br_2N_6$ (708.50): calcd. C 61.03, H 4.55, Br 22.56, N 11.86; found C 60.95, H 4.46, Br 22.40, N 11.71.

*5,7-Bis-(4-tolyl)-3,9-dimethyl-5,12-dihydro[5,6,7,12,13,14]-hexaazapentacene (**2a**)*

In a 25 mL flask a mixture consisting of 100 mg (0.2 mmol) of dihydropyrazine **8a**, 111 mg (0.8 mmol) of potassium carbonate and 263 mg (0.8 mmol) of $K_3[Fe(CN)_6]$ in 5 mL of DMSO was heated at 75 °C. After 5 h the reaction was complete and the crude product was precipitated by addition of 10 mL of water. The precipitate was filtered off and washed with 10 mL DMSO-water (1/3). The product was purified by column chromatography (silica gel 60, $CHCl_3$-ethanol).

Bluish-black crystals; yield 5 %. – M. p. > 400 °C (dec.). – UV (CH_2Cl_2): λ_{max} (lg ε) = 375 (4.2), 409 (4.0), 525 (4.2), 564 (4.1), 609 nm (4.5). – Emission ($CHCl_3$): λ = 644 nm, fluorescence quantum yield (ϕA) = 0.55($\pm$0.05). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.0 Hz, 4H, aryl), 6.88 (d, J = 7.9 Hz, 8H, aryl), 6.16 (s, 2H, aryl), 2.43 (s, 6H, CH_3), 2.11 ppm (s, 6H, CH_3). – MS (EI): m/z (%) = 494 (66), 403 (10), 247 (14), 133 (35), 106 (100). – $C_{36}H_{32}Br_2N_6$

(708.50): calcd. C 61.03, H 4.55, Br 22.56, N 11.86; found C 60.89, H 4.50, Br 22.52, N 11.78.

Crystal structure determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromatized MoK_α radiation. Data were corrected for Lorentz and polarization but not for absorption effects [53, 54]. The structures were solved by Direct Methods (SHELXS-97 [55]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [55]). The hydrogen atoms of **8b** were located by difference Fourier synthesis and refined isotropically. All non-disordered, non-hydrogen atoms were refined anisotropically [55].

Crystals of **2a** were extremely thin and of low quality, resulting in a substandard data set (triclinic, space group $P\bar{1}$, $a = 8.7540(4)$, $b = 12.0801(9)$, $c = 14.6555(11)$ Å, $\alpha = 84.264(3)$, $\beta = 87.387(4)$, $\gamma = 81.701(4)°$, $V = 1525.14(18)$ Å^3, $Z = 2$). The structure refinement was sufficient, however, to confirm the connectivity and overall geometry despite high final R values. For the latter reason the crystallographic data will not be deposited at The Cambridge Crystallographic Data Centre.

XP (Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin (USA)) was used for structure representations.

Crystal data of ***8b***: $C_{32}H_{30}N_6O_4$, $M = 562.62\,g\,mol^{-1}$, red-brown prisms, size $0.05 \times 0.05 \times 0.05\,mm^3$, monoclinic, space group $P2_1/n$, $a = 6.3256(3)$, $b = 10.8267(4)$, $c = 19.9198(7)$ Å, $\beta = 92.302(2)°$, $V = 1363.11(9)$ Å^3, $T = -140\,°C$, $Z = 2$, $\rho_{calcd.} = 1.37\,g\,cm^{-3}$, $\mu(MoK_\alpha) = 1.9\,cm^{-1}$, $F(000) = 592\,e$, 9389 reflections in $h(-7/8)$, $k(-14/13)$, $l(-25/25)$, measured in the range $3.42° \le \theta \le 27.45°$, completeness to $\theta_{max} = 99.7\%$, 9389 measured reflections, 3112 independent reflections, $R_{int} = 0.0574$, 2189 reflections with $F_o > 4\sigma(F_o)$, 250 refined parameters, no restraints, $R1_{obs} = 0.0429$, $wR2_{obs} = 0.1018$, $R1_{all} = 0.0716$, $wR2_{all} = 0.1146$, GoF = 1.024, largest difference peak and hole $0.18/-0.23\,e\,Å^{-3}$.

CCDC 974508 (**8b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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