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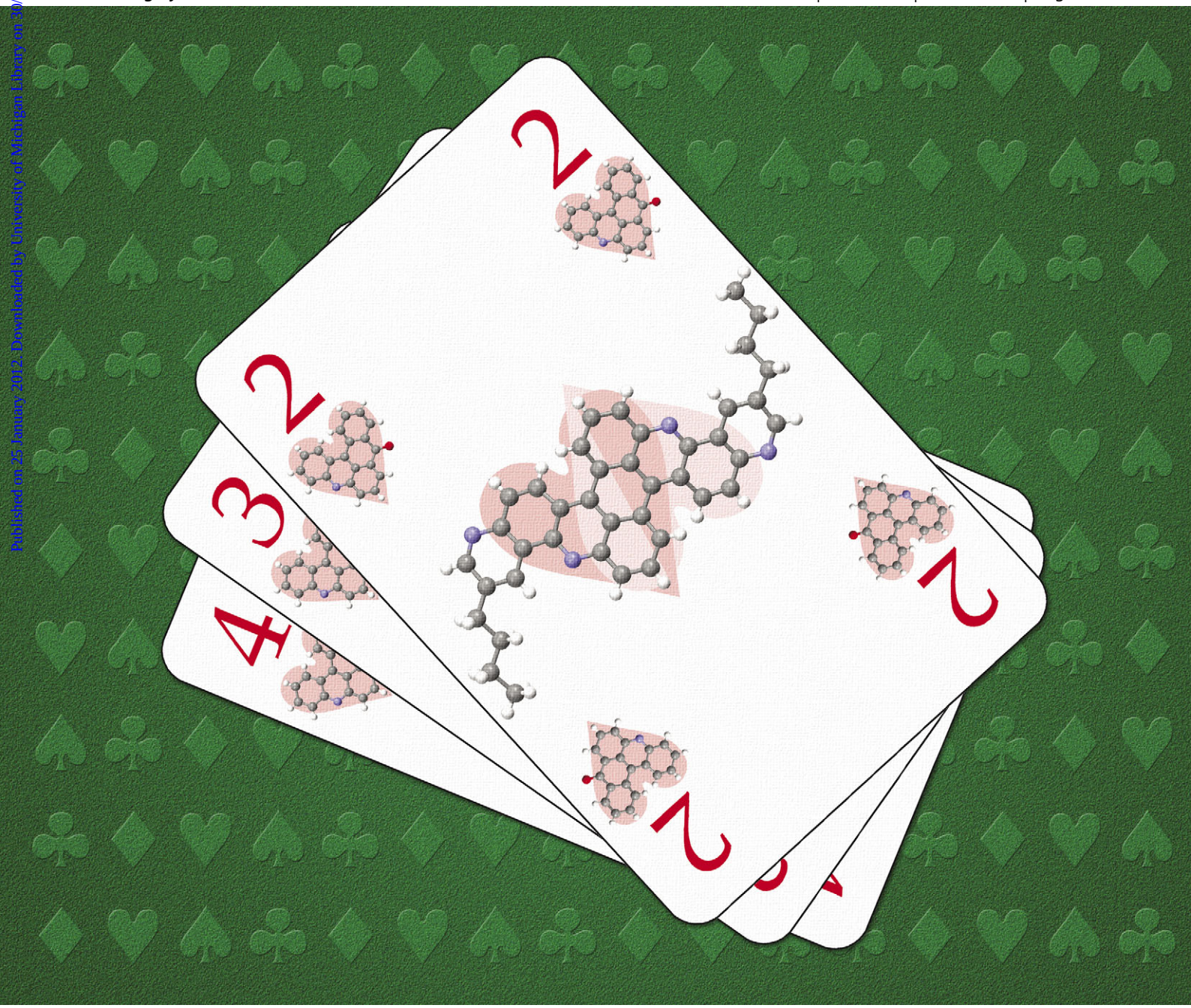

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LETTER

Tetraazaarenes by the ceramidonine approach†

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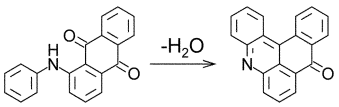
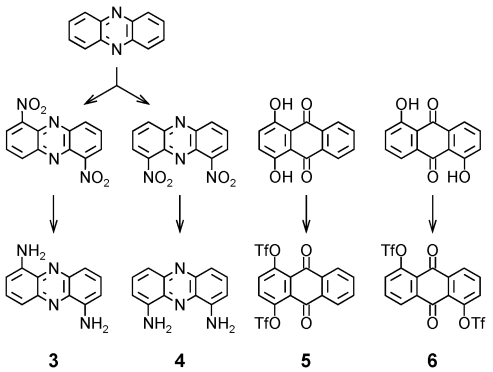
The synthesis of extended heteroarenes *via* the acid-promoted dehydrocyclisation of arylamino-anthraquinones is examined as an approach to highly conjugated electron-acceptor materials and eventually to heterographene nanoribbons. Whilst the latter perspective is found to remain challenging, the former is exemplified by the synthesis of extended tetraazaheterocycles bearing solubilising alkyl substituents.



2 **1**

Ceramidonine **1**, the heart-shaped cyclodehydration product of 1-phenylamino-anthraquinone **2**, is efficiently obtained by treatment of the latter in sulfuric acid at elevated temperature.[1,2] We assumed thus that oligo- and polymers with multiple 1-arylaminoanthraquinone fragments are convenient precursors of extended polycyclic heteroarenes. Such extended azaheterocyclic nanoribbons should exhibit pronouncedly electron-deficient and thus electron-acceptor type electronic character that may be of interest for organic electronics. They also are more stable against oxidation than their homoaromatic counterparts, and may represent novel chelating ligands for transition metal complexation, especially if further aromatic nitrogens are introduced by the choice of appropriate azaarylamine precursors. We deal here with the first stage on the path to ceramidonine based condensed polymers with high nitrogen content, *i.e.* the transformation of bifunctional azaaryl-diamines and bifunctional anthraquinones into tetraazaarenes with two heart-shaped pentacyclic fragments.

1-Arylaminoanthraquinones are most conveniently obtained by a condensation of an aminoarene with a 1-substituted anthraquinone such as 1-bromo- or 1-triflyloxyanthraquinone. A ceramidonine-based approach to oligomers requires bifunctional diaminoarenes and dianthraquinone bricks with substituents on opposing sides. As conveniently stable diaminoarenes with ring nitrogen atoms in vicinal positions to the amino groups for possible chelation, the 1,6- and 1,9-diaminophenazines **3** and **4** appear promising. They are accessible from phenazine *via* nitration[3] and separation of the two obtained dinitrophenazines by selective crystallisation.[4] As concerns bifunctional anthraquinones, the 1,4- and 1,5-dihydroxy derivatives are cheap and easily transformed into the corresponding triflates **5** and **6**.[5]



3 **4** **5** **6**

Replacement of the triflate leaving groups on **5** or **6** by the amino functions of **3** or **4** followed by loss of water leads to four hypothetical polymers; these ribbon-like polymers are linear in the cases of **poly35**, **poly36** and **poly46**, and helicoidal in the case of **poly45** (a hexameric macrocycle can also be imagined). It may anecdotically be noted that, if the three linear ribbons are classified in analogy to carbon nanotubes,[6,7] all three different basic types of hexagon orientations (with respect to any perpendicular cut through the ribbon) are present: zigzag (**poly35**), oblique (**poly36**) and armchair (**poly46**).

To obtain soluble ceramidonine dimers with these bifunctional bricks **3–6**, we aimed at condensing them with monofunctional counterparts bearing solubilising *n*-butyl chains, *i.e.* 4-butyl-1-triflyloxy-anthraquinone **7** and 3-butyl-5-aminoquinoline **8**. 4-Butyl-1-hydroxy-anthraquinone is available from the atypical reaction of butylamine with 1-hydroxyanthraquinone in the presence of $CoCl_2$ reported by M. Matsuoka *et al.*,[8] and we aimed at obtaining **8** from 3-bromoquinoline *via* nitration, alkylation and reduction.[9,10] To our surprise, when trying to obtain 3-butyl-5-nitroquinoline from 3-bromo-5-nitroquinoline with excess tetrabutyltin and catalytic $Pd(dppf)Cl_2$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] in DMF under argon, we isolated 3-butyl-5-aminoquinoline directly in 39% yield. This points to DMF acting as a reducing agent and a hydrogen source, in concordance with the recently reported reduction of nitro substituents to amino groups during the palladium-catalysed

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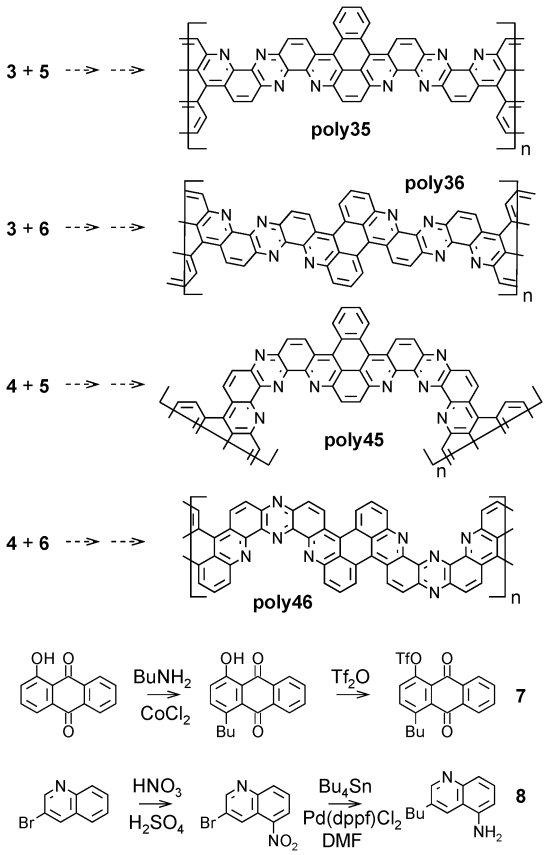


coupling of nitro-substituted 2-haloanilines with alkynes to amino-substituted indoles in DMF.[11,12]

Previous reports about the isomeric outcome of the mono-nitration of 3-bromoquinoline are ambiguous,[9,13] leaving some doubt about whether the main product is the 5- or the 8-nitro-derivative, both being poorly distinguishable by NMR. It was in this respect fortunate that we obtained single crystals of the derived amine **8** suitable for crystallographic structure determination, confirming that nitration predominately happens in position 5. 3-Butyl-5-aminoquinoline crystallises in the trigonal $R\bar{3}$ space group. Three molecules of the compound are arranged in a triangle held together by hydrogen bonds between one of the amino hydrogen atoms and the quinoline ring nitrogen of adjacent molecules (dotted lines in Fig. 1). The triangular units are arranged into a hexagonal geometry in the *ab* plane.

The four bifunctional and two monofunctional bricks **3–8** should yield the two quinones **737** and **747** and the two

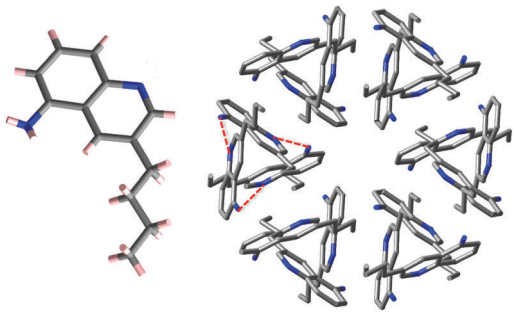
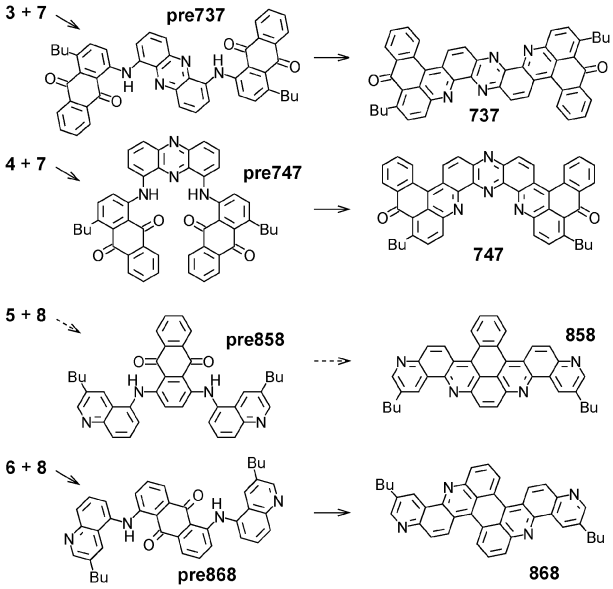
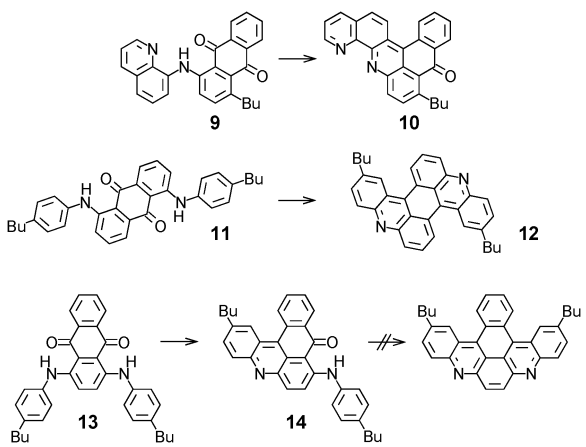


Fig. 1 Crystal structure of 3-butyl-5-aminoquinoline.

oxygen-free azaarenes **858** and **868** *via* their precursors **pre737**, **pre747**, **pre858** and **pre868**.



Before using dearly obtained **8** in condensation attempts with bifunctional anthraquinones **5** or **6**, we investigated the condensation of commercial aminoarenes with mono- and bifunctional anthraquinones **7**, **6** and **5**. We achieved the coupling of singly triflate-substituted anthraquinone **7** with 8-aminoquinoline as monofunctional aminoarene to give **9** first in moderate yields (25%) with a combination of catalytic $Pd(dba)_2$ [dba = dibenzylideneacetone] and a dppf as a chelating ligand in the presence of sodium *tert*-butoxide as strong base.[14] The yields were significantly improved (57%) by addition of lithium chloride in order to deactivate the liberated triflate in the reaction medium which may poison the palladium catalyst, and slow addition of the triflate-substituted anthraquinones to the reaction in order to prevent base catalysed dissociation to hydroxyanthraquinones. Cyclisation of quinolinylamino-butyl-anthraquinone **9** in 70% H_2SO_4 (10 ml) at 130 °C for 8 min gave pyridino-ceramidonine **10** in about 50% yield. Having thus in hand a feasible method of condensation to obtain arylamino-substituted anthraquinones, we investigated the feasibility of double cyclisations in the presence of solubilising



alkyl chains, using the condensation products **11** and **13** of *p*-butylaniline with the bifunctional anthraquinones **6** and **5**.

Whereas 1,5-bis(*p*-butylphenylamino)-anthraquinone **11** yielded the corresponding bisceramidonine **12** upon double dehydration in hot sulfuric acid, the 1,4-isomer **13** did only give, depending on the reaction time and temperature, either the monodehydrated intermediate **14** or tar.[15] We thus abandoned **5** as a building block and did not attempt the synthesis of **pre858** and **858**. The three other cyclisation precursors **pre737**, **pre747** and **pre868** were obtained by our above-mentioned improved procedure with LiCl in 40%, 52% and 40% yield respectively. The three tetraazaarene targets **737**, **747** and **868** were obtained from their precursors by dehydration in 70% sulfuric acid at 170 °C in 53%, 41% and 64% as best yields, respectively. The yields proved to be strongly dependent on the reaction time, short times giving incomplete cyclisations and long times giving substantial degradation. Optimised reaction times were 8 minutes for **737** and **747**, and 30 minutes for **868**.

This synthetic approach appears to be practical for the synthesis of relatively small extended azaarenes that may offer potential for a variety of applications such as electron acceptor behaviour in organic electronics or double metal chelation for metal-to-metal spin–spin interactions. But it follows from the moderate yields accompanied by relatively fast decomposition under the necessary stringent reaction conditions that considerable further innovative effort may be needed to render this approach sufficiently efficient to lead to extended electron-deficient, potentially metal-chelating, heterographene nanoribbons such as **poly36** and **poly46**.

The absorption spectra (Fig. 2) of the two tetraaza-diketones **737** and **747**, both of which can be seen as doubly benzoylene-substituted tetraaza-naphthopentaphenes, show very similar, relatively unpronounced spectra typical of kata-annellated arenes with relatively continuous absorption up to about 500 nm. In contrast, the tetraaza-dinaphthoperylene **868** exhibits the typical absorption features of a rylene, *i.e.* a gap zone of low absorption between a zone of intense short-wavelength absorption (below 350 nm) and intense three-peaked long-wavelength absorption (between 450 and 560 nm).[16]

To assess the electron-deficient character of the three materials, we tried to perform cyclic voltammetry on all three, but the still limited solubility in dichloromethane of the two diketones impeded the obtention of meaningful curves.

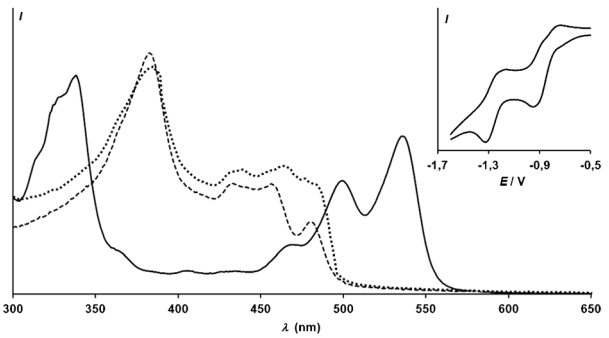


Fig. 2 Absorption spectra of **737** (dashed), **747** (dotted) and **868** (continuous) in chloroform. Inset: cyclic voltammogram against ferrocene of **868** in 1 mM solution in dichloromethane in the presence of 0.1 M tetrabutylammonium hexafluorophosphate (scan rate: 100 mV s^{-1}).

Azahydrocarbon **868** on the other hand showed two clearly discernable reversible reduction peaks at −0.85 V and −1.25 V *vs.* ferrocene (inset in Fig. 2). These values are closer than 0.1 V to the values for C_{60}, a prominent prototype acceptor material in organic electronics, whose reduction peaks are found at −0.92 V and −1.32 V *vs.* ferrocene under identical conditions.[17] This indicates that multiple azasubstitution in moderately long-wavelength absorbing (*i.e.* moderately low band-gap) arenes such as benzannellated perylenes leads to pronouncedly electron-deficient azaarenes of suitable reduction potentials for organic electronic applications.

We were able to obtain single crystals of **868**, which allowed us to assess the degree of non-planarity forced upon the arene system by the two [4]helicenic bay regions (Fig. 3). **868** crystallises in the centrosymmetric triclinic space group $P\bar{1}$, with two molecules per unit cell that are closely stacked by π–π interactions with shortest carbon–carbon distances of 3.44 Å (dashed lines in Fig. 3). The planes of the two diazatetraphene fragments (light and dark grey in Fig. 3), both of which are in themselves roughly planar, are tilted with respect to each other by an angle of 24° (when observed along the two central bonds between the two fragments).

In summary, we have explored an approach towards extended polycyclic azaarenes based on the acid-promoted cyclising dehydration of arylamino-anthraquinone fragments to ceramidonine fragments. The potential of this approach towards extended polycyclic azaarenes is found to be geometry-dependent with respect to anthraquinone disubstitution: 1,5-disubstituted anthraquinones yield the desired products, whilst 1,4-substituted ones do not. On the other hand, the approach is geometry-independent with respect to phenazine disubstitution, with both 1,6- and 1,9-disubstituted phenazines being similarly reactive. Whilst the yields observed do not allow an efficient access to polymeric nanoribbon structures, they are adequate for double cyclisations (of the order of 50%) leading to twisted tetraazaarenes such as **868** whose reduction potentials come close to those of C_{60}, the archetypal, but weakly absorbing and weakly soluble, acceptor material in organic electronics.

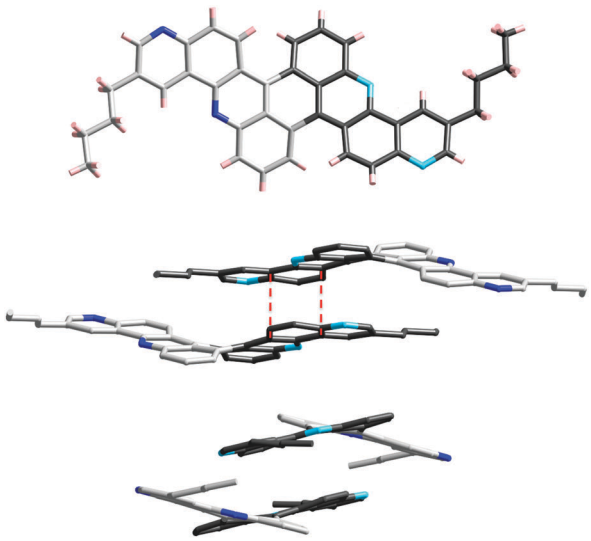


Fig. 3 Crystal structure of nonacyclic dialkyl-tetraazaarene **868**.

Experimental

Syntheses of key compounds 8, 737, 747 and 868

8: nitration of 3-bromoquinoline (Alfa Aesar) and separation of 3-bromo-5-nitroquinoline from small quantities of 3-bromo-8-nitroquinoline by crystallization were performed following the procedure of Crowley *et al.*,[9] which is identical to the procedure of Doherty *et al.*,[13] with the sole exception that Doherty *et al.* misassigned the main product, isolated by recrystallisation from ethyl acetate, as being the 8-nitro isomer. 3-Bromo-5-nitroquinoline (1.1 g, 4.3 mmol), $PdCl_2$(dppf) (630 mg, 0.86 mmol) and LiCl (360 mg, 8.6 mmol) were stirred in DMF (20 ml) for 10 min. Tetrabutyltin (6 g, 17.2 mmol) was added dropwise to the reaction mixture, which then was refluxed under argon for 24 h. The solvent was removed under reduced pressure. Column chromatography through silica in pentane elutes unreacted tetrabutyltin, and 1 : 1 DCM : EtOAc elutes the product. Yield: 340 mg (39%) of brown oil which formed needle shaped crystals in the freezer that were adequate for X-ray crystallography. ^{1}H NMR (400 MHz, $CDCl_3$): ∂ = 8.72 (s, 1H), 8.08 (s, 1H), 7.65 (d, 1H, J = 8 Hz), 7.49 (t, 1H, J = 8 Hz), 6.84 (d, 1H, J = 8 Hz), 4.27 (broad s, 2H), 2.81 (t, 2H, J = 8 Hz), 1.69 (m, 2H), 1.38 (m, 2H), 0.94 (t, 3H, J = 7 Hz) ppm; MS (m/z (%)): 202.2 (100, $[M + 2H]^+$), 201.2 (15, $[M + H]^+$).

737: 1,6-diaminophenazine (**3**) (200 mg, 0.96 mmol), $Pd(dba)_2$ (150 mg, 0.26 mmol), dppf (450 mg, 0.81 mmol), sodium ^{t}butoxide (200 mg, 2.0 mmol), LiCl (160 mg, 3.8 mmol) were stirred in toluene (10 ml) at 100 °C for 10 min under argon. Then a suspension of **7** (790 mg, 1.92 mmol) in toluene (10 ml) was added dropwise. The deep red mixture was refluxed overnight under argon, cooled and chromatographed through silica in chloroform to elute first a trace amount of unreacted **7**, followed by **pre737** and finally unreacted amine **3**. **pre737** was recrystallised from butanol. Yield: 280 mg (40%) of deep red crystals; ^{1}H NMR (400 MHz, $CDCl_3$): ∂ = 11.04 (broad s, 2H), 8.28 (m, 2H), 8.21 (m, 4H), 7.96 (d, 2H, J = 8 Hz), 7.79 (d, 2H, J = 8 Hz), 7.73 (m, 4H), 7.62 (t, 2H, J = 8 Hz), 6.59 (d, 2H, J = 8 Hz), 2.73 (t, 4H, J = 8 Hz), 1.63 (m, 4H), 1.21 (m, 4H), 0.78 (t, 6H, J = 7 Hz) ppm. **pre737** (100 mg, 0.143 mmol) was heated in 70% H_2SO_4 (10 ml) at 130 °C for 8 min with vigorous stirring. The color of the mixture changed from brown to deep red. The hot mixture was poured onto crushed ice and the precipitate was filtered off, washed with 5% aqueous NaOH, dried under reduced pressure, chromatographed through silica in 1 : 1 chloroform : EtOAc and crystallised from butanol. Yield: 50 mg (53%) of brown powder; ^{1}H NMR (400 MHz, $CDCl_3$): ∂ = 9.01 (d, 2H, J = 9 Hz), 8.78 (d, 2H, J = 7 Hz), 8.62 (d, 2H, J = 8 Hz), 8.56 (d, 2H, J = 8 Hz), 8.49 (d, 2H, J = 9 Hz), 8.00 (d, 2H, J = 7 Hz), 7.89 (t, 2H, J = 8 Hz), 7.76 (t, 2H, J = 8 Hz), 3.87 (t, 4H, J = 8 Hz), 2.05 (m, 4H), 1.69 (m, 4H), 1.17 (t, 6H, J = 7 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): ∂ = 182.7, 152.0, 147.2, 145.2, 144.8, 143.6, 134.8, 134.2, 133.9, 132.7, 131.1 (×2), 130.4, 129.9, 129.5, 129.4, 128.9, 126.3, 123.6, 122.9, 33.3, 32.0, 23.2, 14.2 ppm. UV-vis. ($CHCl_3$): λ_{max} (rel. intensity) = 382.0 (1.00); 433.0 (0.47); 456.0 (0.46); 480.0 nm (0.30). MS (m/z (%)): 699.2 (100, $[M + H]^+$).

747: coupling between 1,9-diaminophenazine **4** (250 mg, 1.2 mmol) and **7** (990 mg, 2.4 mmol) leads to **pre747** following the above procedure with $Pd(dba)_2$ (150 mg, 0.26 mmol, 10 mol%), dppf (450 mg, 0.81 mmol), sodium ^{t}butoxide (250 mg, 2.5 mmol) and LiCl (200 mg, 4.75 mmol) in toluene (20 ml). Yield: 460 mg (52%) of deep red powder; ^{1}H NMR (400 MHz, $CDCl_3$): ∂ = 11.16 (broad s, 2H), 8.16 (d, 4H, J = 7 Hz), 8.12 (d, 2H, J = 8 Hz), 7.73 (t, 4H, J = 7 Hz), 7.64 (t, 4H, J = 8 Hz), 7.56 (t, 2H, J = 8 Hz), 6.66 (d, 2H, J = 7 Hz), 2.73 (t, 4H, J = 8 Hz), 1.65 (m, 4H), 1.22 (m, 4H), 0.79 (t, 6H, J = 7 Hz) ppm. **pre747** (440 mg, 0.598 mmol) was heated in 70% H_2SO_4 (15 ml) at 130 °C for 8 min with vigorous stirring. The color changed from dark yellow *via* deep green to deep red. The mixture was worked up as described for **737**. Yield: 170 mg (41%) of brown powder; ^{1}H NMR (400 MHz, $CDCl_3$): ∂ = 8.92 (d, 2H, J = 9 Hz), 8.79 (d, 2H, J = 7 Hz), 8.51 (d, 2H, J = 7 Hz), 8.45 (d, 2H, J = 7 Hz), 8.10 (d, 2H, J = 9 Hz), 8.04 (d, 2H, J = 7 Hz), 7.78 (t, 2H, J = 7 Hz), 7.62 (t, 2H, J = 7 Hz), 4.12 (t, 4H, J = 7 Hz), 2.12 (m, 4H), 1.54 (m, 4H), 1.00 (t, 6H, J = 7 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): ∂ = 182.9; 152.0; 147.7; 145.6; 145.4; 142.7; 134.9; 134.1; 133.9; 132.7; 131.1; 130.8; 130.6; 130.3; 129.6; 128.8; 128.5; 126.3; 123.4; 122.8; 32.9; 31.4; 22.5; 14.5 ppm. UV-vis. ($CHCl_3$): λ_{max} (rel. intensity) = 385.0 nm (0.96), 439.0 nm (0.52), 464.0 nm (0.54); shoulder at 477.0 nm (0.49). MS (m/z (%)): 699.2 (65, $[M + H]^+$); 700.2 (50, $[M + 2H]^+$); 721.2 (100, $[M + Na]^+$); 722.2 (70, $[M + Na + H]^+$).

868: 3-butyl-5-aminoquinoline **8** (500 mg, 2.5 mmol), $Pd(dba)_2$ (260 mg, 0.45 mmol, 20 mol%), dppf (810 mg, 1.46 mmol), sodium ^{t}butoxide (260 mg, 2.7 mmol) and LiCl (260 mg, 6.1 mmol) were stirred in toluene (10 ml) at 100 °C for 10 min under argon. Then a suspension of **6** (480 mg, 0.96 mmol) in toluene (10 ml) was added dropwise. The deep violet mixture was refluxed overnight and then separated by column chromatography through silica. Chloroform elutes traces of unreacted **6**, and 1 : 1 chloroform : EtOAc elutes first a red trace impurity (presumably a monocyclised intermediate) and then **pre868**, which is recrystallised from butanol. Yield: 232 mg (40%) of deep red powder; ^{1}H NMR (400 MHz, $CDCl_3$): ∂ = 11.64 (broad s, 2H), 8.83 (s, 2H), 8.17 (s, 2H), 8.04 (d, 2H, J = 8 Hz), 7.80 (d, 2H, J = 8 Hz), 7.70 (t, 2H, J = 8 Hz), 7.60 (d, 2H, J = 8 Hz), 7.47 (t, 2H, J = 8 Hz), 7.13 (d, 2H, J = 8 Hz), 2.79 (t, 4H, J = 8 Hz), 1.66 (m, 4H), 1.38 (m, 4H), 0.93 (t, 6H, J = 7 Hz) ppm. **pre868** (150 mg, 0.248 mmol) was heated in 70% sulfuric acid at 170 °C for 30 min with vigorous stirring. The hot mixture was poured onto ice and the precipitate was filtered off and washed with 5% aqueous NaOH, dried in air, purified by column chromatography through silica in chloroform and recrystallised from methanol. Yield: 90 mg (64%) of red powder. Single crystals for X-ray crystallography were made by slow evaporation of solvent of a chloroform solution. ^{1}H NMR (400 MHz, $CDCl_3$): ∂ = 9.55 (s, 2H), 8.92 (s, 2H), 8.72 (d, 2H, J = 9 Hz), 8.42 (m, 4H), 8.05 (d, 2H, J = 8 Hz), 7.99 (t, 2H, J = 8 Hz), 2.96 (t, 4H, J = 8 Hz), 1.84 (m, 4H), 1.51 (m, 4H), 1.02 (t, 6H, J = 7 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): ∂ = 152.8, 148.6, 148.2, 147.0, 137.1, 135.5, 132.6, 131.2, 130.1, 130.1, 129.5, 128.7, 127.2, 126.8, 123.5, 121.0, 33.8, 33.4, 22.6, 14.1 ppm. UV-vis. ($CHCl_3$): λ_{max} (rel. intensity) = 338.0 nm (0.92); 469.0 nm (0.21); 499.0 nm (0.48); 535.0 nm (0.66). MS (m/z (%)): 568.2 (40, $[M]^+$); 569.2 (100, $[M + H]^+$); 570.2 (80, $[M + 2H]^+$).

Acknowledgements

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Notes and references

1 A. H. Cook and W. Waddington, *J. Chem. Soc.*, 1945, 402–405.
2 D. W. Rangnekar and S. V. Sunthankar, *Indian J. Technol.*, 1974, **12**, 548.
3 H. Otomasu, *Chem. Pharm. Bull.*, 1958, **6**, 77.
4 P. Huszthy, E. Samu, B. Vermes, G. Mezey-Vandor, M. Nogradi, J. S. Bradshaw and R. M. Lzatt, *Tetrahedron*, 1999, **55**, 1491–1504.
5 M. S. Taylor and T. M. Swager, *Angew. Chem., Int. Ed.*, 2007, **46**, 8480.
6 X. Lu, F. Tian, N. Wang and Q. Zhang, *Org. Lett.*, 2002, **4**, 4313.
7 R. Gletier, B. Esser and S. C. Kornmayer, *Acc. Chem. Res.*, 2009, **42**, 1108.
8 M. Matsuoka, T. Takei, I. Nakamura, K. Yoshida and T. Kitao, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2225.
9 J. D. Crowley, I. M. Steele and B. Bosnich, *Chem.–Eur. J.*, 2006, **12**, 8935.
10 M. Viaud, P. Jamoneau, L. Savelon and G. Guillaumet, *Heterocycles*, 1995, **41**, 2799.
11 R. Sanz, V. Guilarte and A. Pérez, *Tetrahedron Lett.*, 2009, **50**, 4423.
12 J. Muzart, *Tetrahedron*, 2009, **65**, 8313–8323.
13 S. Doherty, E. G. Robbins, I. Pal, C. R. Newman, C. Hardacre, D. Rooney and D. A. Mooney, *Tetrahedron: Asymmetry*, 2003, **14**, 1517.
14 J. Louie, M. S. Driver, B. C. Hamann and J. F. Hartwig, *J. Org. Chem.*, 1997, **62**, 1268.
15 We are puzzled by this difference in outcome. The expected double dehydration product from **13** may be formally considered as consisting of a benzene and a 5,8-diaza-pentaphene fragment linked by two single bonds, and 5,8-diaza-pentaphene has been reported to be exceedingly resistant to further oxidation even with CrO_3 in sulfuric acid (see G. M. Badger and R. Pettit, *J. Chem. Soc.*, 1952, 1874–1877). Fragility of the double cyclisation product from **13** under the harsh reaction conditions therefore does not seem to be an evident explanation for our failure to isolate it.
16 E. Clar, *Polycyclic Hydrocarbons*, Academic Press & Springer Verlag, 1964.
17 P.-M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Am. Chem. Soc.*, 1991, **113**, 1050.

