Regiospecific synthesis of 5,7-disubstituted quinoxalino[2,3-*b*]phenazines

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Dedicated to Prof. Charles W. Rees on the occasion of his 75th birthday

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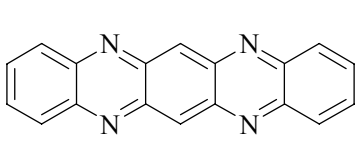
Abstract

Hydrogenation of the readily prepared dinitrobenzenediamines **7** followed by air oxidation affords the green colored 5,7-disubstituted-5*H*,12*H*-quinoxalino[2,3-*b*]phenazines **3** in good yields. Mechanistic rationale, compound characterisation and full experimental details are provided.

Keywords: Heterocycles, zwitterions, fluorindine, quinoxalino[2,3-*b*]phenazines, tetraazapentacenes

Introduction

Interest in the heterocyclic system quinoxalino[2,3-*b*]phenazine (Flourindine) has reemerged. Recently theoretical and experimental studies on the 5,7-diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine **3** established it has a singlet ground state resulting in a zwitterionic structure.[1] A 5,7-bisoctadecyl derivative has shown interesting high temperature liquid crystalline properties.[2,3] These studies were made possible by an improved high yielding and regiospecific synthesis of the 5,7-disubstitued isomers. We now wish to report the full synthetic details.



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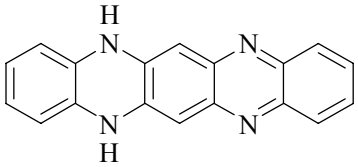

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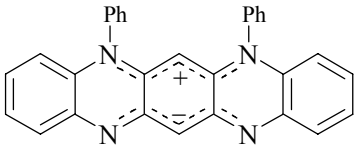

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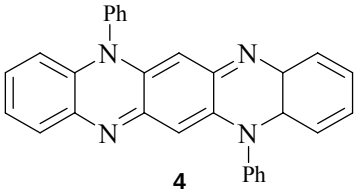

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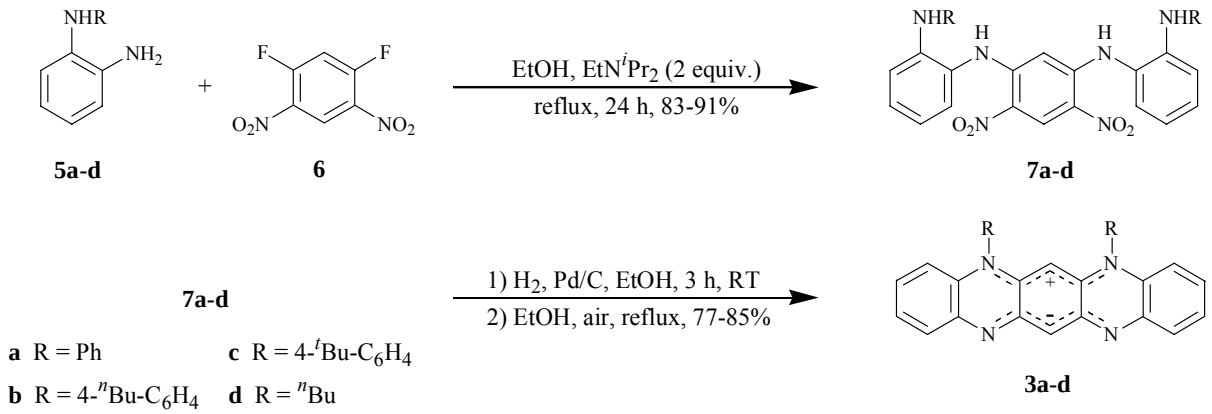
The parent system quinoxalino[2,3-*b*]phenazine **1** is not known. The only dihydro-quinoxalino[2,3-*b*]phenazine is the 5*H*,14*H*-dihydro derivative **2** thought to be in equilibrium with the 5*H*,12*H*-dihydro isomer.[4] However, 5,7-diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]-phenazine (diphenylisofluorindine, 5,7-DPQP, **3a**) exists.[5] The preparation of 5,7-DPQP from the treatment of 3-imino-*N*,5-diphenyl-3*H*,5*H*-2-phenazinamine (3-anilinoaposafranine) with *N*-phenyl-1,2-benzenediamine **5** and two equivalents of mineral acid in refluxing benzoic acid was reported over a 100 years ago, however, at that time its electronic structure was not understood. [5] The product which did not melt (up to 260 ^{o}C) was identified by microanalysis and by comparison of its physical appearance and color in solution with its more commonly known isomer 5,12-diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine (diphenylfluorindine, 5,12-DPQP, **4**). [6] Both isomers dissolve in acid to give a blue solution with a red fluorescence but only the free base of 5,12-DPQP was observed to fluoresce strongly to the naked eye whilst that of the 5,7-DPQP did not. Both compounds crystallize to give blue-green crystals with a metallic luster. Various preparations of 5,12-DPQP are reported. [6] In particular the treatment of 3-anilinoaposafranine with *N*-phenyl-1,2-benzenediamine **5** and one equivalent of mineral acid to give the isomer 5,12-DPQP[6] suggested to us that the formation of a mixture of both isomers was likely *via* this route and would therefore require separation. Furthermore the synthesis of 3-anilinoaposafranine was derived from the oxidative coupling of two equivalents of *N*-phenyl-1,2-benzenediamine **5** which gives a mixture of two isomeric products that again require careful separation.[7]

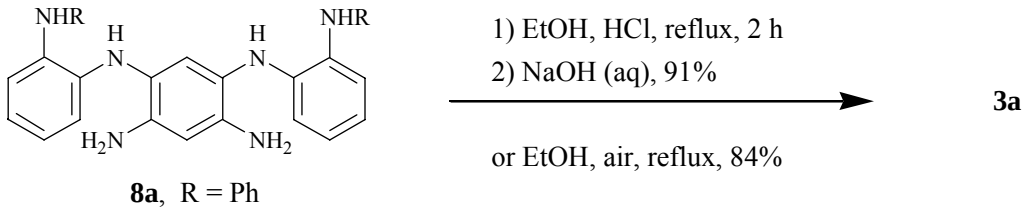
Synthesis

We proposed and successfully carried out a rational synthesis that affords 5,7-DPQP unambiguously and in good yield (Scheme 1).



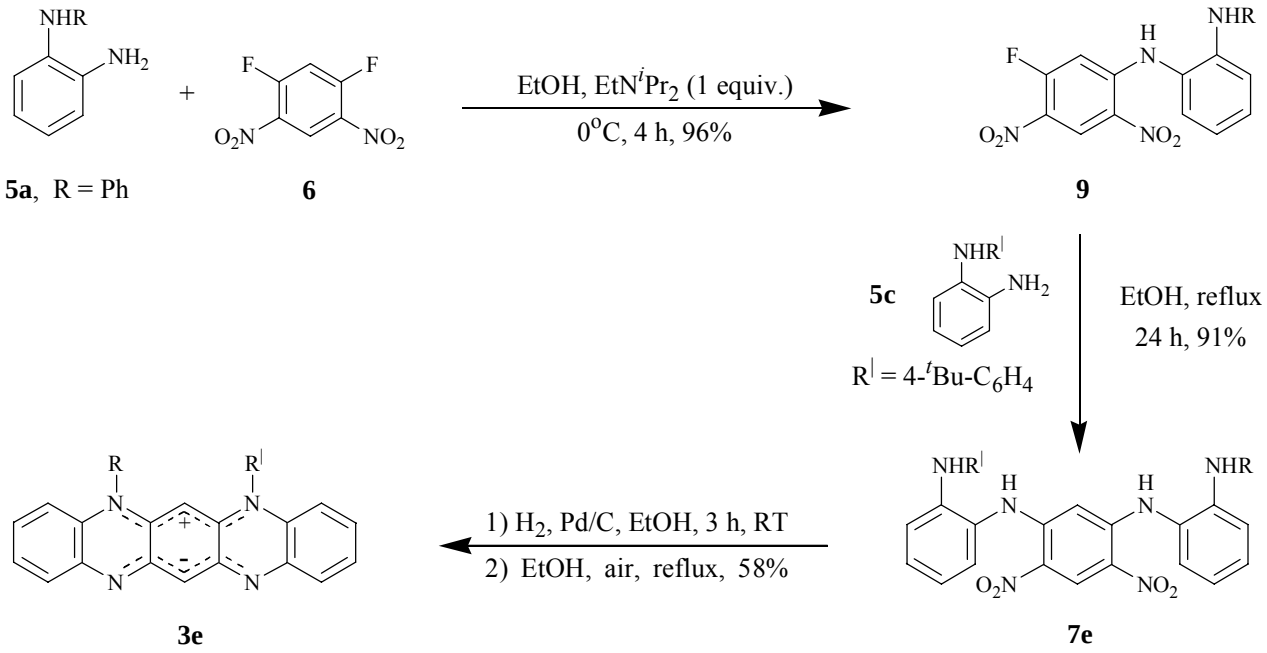
Scheme 1

1,5-Difluoro-2,4-dinitrobenzene **6** reacts with *N*-substituted-1,2-benzenediamines **5** to give dinitrobenzenediamines **7** in good yields. Hydrogenation of compounds **7** gave the benzenetetraamines **8**, which on simple heating in ethanol in the presence of air gave the free base **3**. The benzenetetraamines **8** were very susceptible to oxidation and their isolation and characterization was only carried out with one example (*c.f.* compound **8a**, Experimental section). Treatment of **8a** with ethanol and hydrochloric acid gave the hydrochloride salt of 5,7-DPQP which could be liberated with aqueous hydroxide.



The *N*-aryl-1,2-benzenediamines **5** were prepared from 1-fluoro-2-nitrobenzene and anilines in the presence of potassium fluoride, [8] followed by hydrogenation. The *N*-alkyl derivatives were prepared from the action of the more nucleophilic alkylamines on 1-fluoro-2-nitrobenzene in refluxing ethanol, followed by hydrogenation.

Unsymmetrical quinoxalino[2,3-*b*]phenazine **3e** was prepared from the selective displacement of one fluoride from 1,5-difluoro-2,4-dinitrobenzene **6** which was achieved under mild conditions to give 5-fluoro-2,4-dinitrobenzamine **9** in good yield (Scheme 2).



Scheme 2

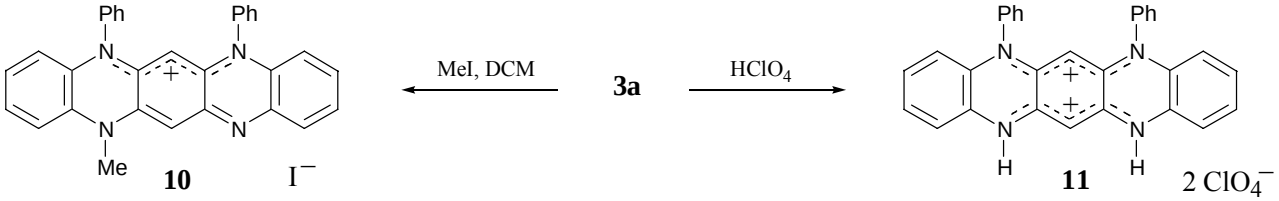
Nearly quantitative yields (*c.f.* Method 1, compound **7a**, Experimental section) were obtained for the preparation of compounds **7** with the use of 4 equivalents of benzenediamine **5**. The cost, however, of preparing more complex diamines **5** prevented the repeated use of 4 fold excesses and despite lower yields the use of 2 equivalents of diamine **5** followed by 2 equivalents of Hünig's base was preferred (*c.f.* Method 2, compound **7a**, Experimental section). The overall synthesis, analogous to that used for the preparation of 5*H*,14*H*-quinoxalino[2,3-*b*]phenazine from 1,5-dichloro-2,4-dinitrobenzene and excess 1,2-benzenediamine, [9] allows the preparation of a variety of 5,7-disubstituted quinoxalinophenazines (Table 1).

Table 1. 5,7-Disubstituted quinoxalino[2,3-b]phenazines 3 and selected properties

Comp. No.	R	R|	λ_{max} nm, (log ε)[a]	mp (°C)[b]	Yield (%)
3a	Ph	Ph	763 (4.41)	360-370 dec.	85-91
3b	4-^{n}BuC$_6$H$_4$	4-^{n}BuC$_6$H$_4$	760 (4.50)	310-320 dec.	77
3c	4-^{t}BuC$_6$H$_4$	4-^{t}BuC$_6$H$_4$	763 (4.35)	350-360 dec.	84
3d	^{n}Bu	^{n}Bu	768 (4.38)	245-250 dec.	83
3e	4-^{t}BuC$_6$H$_4$	Ph	760 (4.40)	345-350 dec.	58

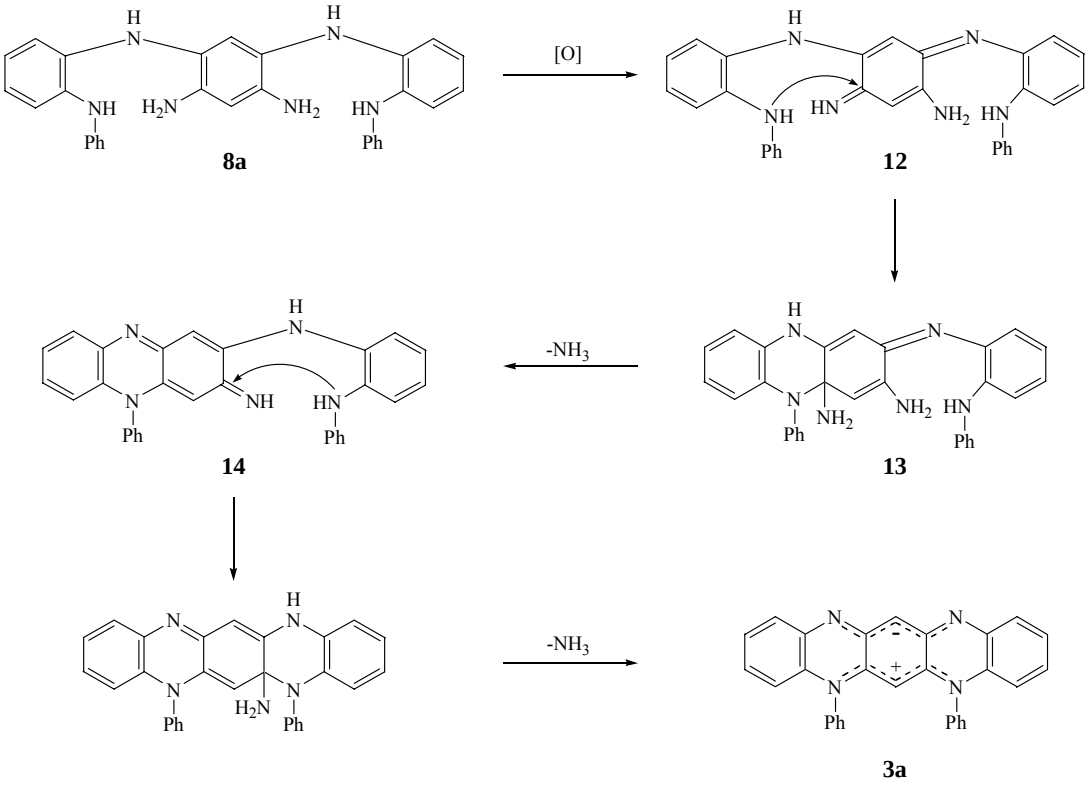
[a] UV/VIS recorded in dichloromethane, concentrations approximately 10-5 M. [b] Recrystallised from ethanol and dried overnight under vacuum (30mmHg) at 60 oC.

Quinoxalinophenazine **3a** is readily monomethylated in MeI to give the trisubstituted quinoxalinophenazine cation **10** that is dark blue in color and has a UV/vis spectrum [λ_{max} 652 nm (log ε 4.56)] that closely resembles that of the monoprotonated 5,7- or 5,12-diphenyl quinoxalino[2,3-*b*]phenazines. A bis protonated material **11** was crystallized from perchloric acid which exhibits a λ_{max} at 637 (5.01).



10 I^- **11** $2\ ClO_4^-$

Mechanistic rationale. The mechanism for the cyclization closely follows that proposed for the synthesis of dihydroquinoxalino[2,3-*b*]phenazine.[9] A dilute solution of tetraamine **8** in DCM (λ_{max} 241 nm), at *ca.* 20 C, becomes brown in color (over 24 h) and absorption spectroscopy shows the formation of two new strong absorptions at 283 and 472 nm; the absorption at 241 nm is no longer visible. Over a period of 7 days the intensity of the absorption at 472 nm decreases until the spectrum resembles that of 5,7-DPQP; the solution's color changing from brown to green. This suggests that the first cyclization to give presumably phenazine **14** is more rapid than the second cyclization to give 5,7-DPQP **3a**. A probable mechanism is described in Scheme 3. Air oxidation of benzenetetraamine **8a** gives species **12** which can cyclize *via* nucleophilic attack of the diphenylamine on the NH imine to give **13** and ultimately quinoxalinophenazine **3a**.



Scheme 3

Conclusions

We have developed a regiospecific and high yielding synthesis for 5,7-disubstituted quinoxalino[2,3-*b*]phenazines. The synthetic route makes these unusual zwitterions readily available for further study.

Experimental Section

General Procedures. Reactions and column eluents were monitored by TLC using plastic-backed thin layer chromatography plates (Kodak) viewed under UV light at 254 and 350 nm. Dry flash chromatography on Bodman flash silica 32-63 was used for separations. UV/vis spectra were measured on HP 8453 UV-visible spectrometer. IR spectra were measured on a Mattson Infinity Series FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were measured on Brucker AMX500, AMX400 and AC200 machines. Mass spectra were recorded on VG ZAB-SE or Autospec "Q" machines. Microanalyses were carried out by Desert Analytics, Inc.

Preparation of *N*-aryl substituted 2-nitrobenzamines

***N*-(4-*n*-Butylphenyl)-2-nitrobenzamine.** To a stirred mixture of 1-fluoro-2-nitrobenzene (3.33mL, 31.60mmol) and 4-*n*-butylaniline (10mL, 63.32mmol) at *ca.* 20 C, under argon, potassium fluoride (1.9g, 32.76mmol) was added in one portion. The reaction mixture was heated at *ca.* 180 C for 48 h and then allowed to cool to *ca.* 20 C. The mixture was dissolved in dichloromethane and extracted with dilute aqueous hydrochloric acid (5-10%) to remove unreacted amine. The organic layer was separated, dried ($MgSO_4$), and filtered through fluted filter paper. Dry flash chromatography gave the title compound (7g, 82%) as a red oil (Found: C, 71.38; H, 6.51; N, 10.35. $C_{16}H_{18}N_2O_2$ requires C, 71.11; H, 6.67; N, 10.37%); λ_{max}(DCM)/nm 230 (log ε 4.10), 260 (4.15), 285 inf (4.08), 437 (3.83); ν_{max}(Drift)/cm^{-1} 3369m and 3359m (Ar NH), 3078m, 3039m and 3028m (Ar CH), 2964s, 2943s, 2887s and 2863s (CH_2 and CH_3), 1626s, 1579s, 1522s, 1502m, 1446m, 1408m, 1356s, 1331m, 1279s, 1234m, 1165m, 1153m, 1119m, 1080m, 1043m, 1020m, 953w, 930w, 893m, 849s, 781s, 748s, 696m, 628m; δ_H(200MHz; CD_2Cl_4) 9.45 (1H, br s, N**H**), 8.18 (1H, d, *J* 8.6 Hz, Ar **H**), 7.36 (1H, dd, *J* 7.7, 7.6 Hz, Ar **H**), 7.28-7.16 (5H, m, Ar **H**), 6.75 (1H, dd, *J* 7.9, 7.8 Hz, Ar **H**), 2.66 (2H, t, *J* 7.4 Hz, ArC**H**$_2$), 1.72-1.57 (2H, m, C**H**$_2$), 1.49-1.30 (2H, m, C**H**$_2$), 0.97 (3H, t, *J* 7.2 Hz, C**H**$_3$); δ_C(50MHz; CD_2Cl_2) 143.97, 141.17, 136.59, 135.99 (Ar **C**H), 133.34, 129.98 (Ar **C**H), 126.81 (Ar **C**H), 124.97 (Ar **C**H), 117.45 (Ar **C**H), 116.39 (Ar **C**H), 35.69 (Ar**C**H$_2$), 34.26 (**C**H$_2$), 22.95 (**C**H$_2$), 14.33 (**C**H$_3$); *m/z* (FAB) 270 (M$^+$, 100%) (Found: M$^+$, 270.1366. $C_{16}H_{18}N_2O_2$ requires *M*, 270.1368).

***N*-(4-*t*-Butylphenyl)-2-nitrobenzamine.** Similarly the treatment of 1-fluoro-2-nitrobenzene with 4-*t*-butylaniline gave the title compound (95%) as a red oil (Found: C, 71.34; H, 6.59; N, 10.29. $C_{16}H_{18}N_2O_2$ requires C, 71.11; H, 6.67; N, 10.37%); λ_{max}(DCM)/nm 232 (log ε 4.09), 259 (4.16), 285 inf (4.03), 439 (3.82); ν_{max}(Drift)/cm^{-1} 3367m, 3357m and 3342m (Ar NH), 3078m and 3041m (Ar CH), 2978s, 2943s, 2902s and 2873s (CH_3), 1624s, 1583m, 1523s, 1504w, 1446m, 1431m, 1367m, 1356m, 1331m, 1281s, 1236w, 1167m, 1153m, 1117m, 1080m, 1045m, 950w, 895m, 858m, 810m, 781m, 748s, 690m, 617m; δ_H(200MHz; CD_2Cl_2) 9.45 (1H, br s, N**H**), 8.18 (1H, d, *J* 8.7 Hz, Ar **H**), 7.46 (2H, d, *J* 6.6 Hz, Ar **H**), 7.37 (1H, dd, *J* 7.8, 7.8 Hz, Ar **H**), 7.25-7.19 (3H, m, Ar **H**), 6.76 (1H, dd, *J* 7.7, 7.7 Hz, Ar **H**), 1.36 (9H, s, C**H**$_3$); δ_C(50MHz; CD_2Cl_2) 149.28, 143.88, 136.40, 136.00 (Ar **C**H), 133.61, 126.94 (Ar **C**H), 126.81 (Ar **C**H), 124.53 (Ar **C**H), 117.51 (Ar **C**H), 116.44 (Ar **C**H), 34.82 (**C**me$_3$), 31.50 (**C**H$_3$); *m/z* (FAB) 270 (M$^+$, 100%) (Found: M$^+$, 270.1362. $C_{16}H_{18}N_2O_2$ requires *M*, 270.1368).

Preparation of *N*-alkyl substituted 2-nitrobenzamines

***N*-(*n*-Butyl)-2-nitrobenzamine.** To a stirred mixture of 1-fluoro-2-nitrobenzene (2.68g, 18.98mmol) and *n*-butylamine (11.8mL, 12mmol) in EtOH (30mL) at *ca.* 20 C, under argon, Hünig's base (2.1mL, 12mmol) was added in one portion. The reaction mixture was heated to reflux (*ca.* 80 C) for 24 h and then allowed to cool to *ca.* 20 C. The mixture was diluted with DCM and extracted with dilute aqueous HCl (5-10%) to remove unreacted amines. The organic layer was separated, dried ($MgSO_4$) and filtered. Dry flash chromatography gave the title

compound (2.68g, 87%) as an orange oil (Found: C, 62.07; H, 7.27; N, 14.16. $C_{10}H_{14}N_2O_2$ requires C, 61.86; H, 7.22; N, 14.43%); λ_{max}(DCM)/nm 242 (log ε 4.02), 280 (3.60), 435 (3.60); ν_{max}(Drift)/cm^{-1} 3392m (Ar NH), 3086w and 3057w (Ar CH), 2970m, 2939m and 2877m (CH_2 and CH_3), 1627s, 1581s, 1539s, 1522m, 1479m, 1446m, 1425m, 1363s, 1282s, 1245w, 1203w, 1171m, 1117w, 1076w, 1043w, 953w, 866s, 810m, 783s, 752s, 730w, 696m, 659m; δ_H(200MHz; CD_2Cl_2) 8.10 (1H, d, *J* 8.6 Hz, Ar **H**), 8.04 (1H, br s, N**H**), 7.43 (1H, dd, *J* 7.7, 7.5 Hz, Ar **H**), 6.86 (1H, d, *J* 6.7 Hz, Ar **H**), 6.61 (1H, dd, *J* 7.7, 7.6 Hz, Ar **H**), 3.29 (2H, quartet, NC**H**$_2$), 1.70 (2H, quintet, C**H**$_2$), 1.47 (2H, hextet, C**H**$_2$), 0.98 (3H, t, *J* 7.2 Hz, C**H**$_3$); δ_C(50MHz; CD_2Cl_2) 146.05 (Ar **C**NHR), 136.48 (Ar **C**H), 132.07 (Ar **C**NO$_2$), 126.94 (Ar **C**H), 115.26 (Ar **C**H), 114.27 (Ar **C**H), 43.10 (N**C**H$_2$), 31.41 (**C**H$_2$), 20.61 (**C**H$_2$), 13.91 (**C**H$_3$); *m/z* (EI) 194 (M$^+$, 69%) (Found: M$^+$, 194.1055. $C_{10}H_{14}N_2O_2$ requires *M*, 194.1055).

Preparation of *N*-substituted 1,2-benzenediamines

***N*-(4-*n*-Butylphenyl)-1,2-benzenediamine (5b).** To a stirred solution of *N*-(4-*n*-butylphenyl)-2-nitrobenzamine (1.96g, 7.26mmol) in EtOH (50ml) at *ca.* 20 C, under argon, (10%) palladium on carbon (500mg) was added in one portion. The reaction mixture was evacuated (to 25mmHg) and flushed with argon 3 times then the mixture was evacuated (to 25mmHg) and flushed with hydrogen 3 times. The reaction mixture was then left to stir under an atmosphere of hydrogen. The color of the mixture became dark red and after 1 h this red color disappeared and consumption of hydrogen had ceased. The mixture was filtered through a celite pad to remove palladium residues and the filtrate was diluted with water until a flocculant cream colored percipitate was obtained. Filtration gave the title compound **5b** (1.69g, 97%) as cream colored solid, mp 72-73.5 C (from EtOH/water) (Found: C, 80.14; H, 8.51; N, 11.74. $C_{16}H_{20}N_2$ requires C, 80.00; H, 8.33; N, 11.67%); λ_{max}(DCM)/nm 237 (log ε 4.20), 272 (3.91), 296 (3.87); ν_{max}(Drift)/cm^{-1} 3425m, 3340s and 3313s (Ar NH), 3033w (Ar CH), 2953s, 2924s, 2868m, 2852s (CH_2 and CH_3), 1616s, 1558w, 1520s, 1466m, 1456m, 1444m, 1402m, 1375w, 1317s, 1300m, 1259m, 1246w, 1246w, 1221w, 1203w, 1178w, 1134w, 1120m, 1059w, 928w, 887w, 863w, 825m, 750m, 649w; δ_H(200MHz; CD_2Cl_2) 7.13-6.96 (4H, m, Ar **H**), 6.83-6.67 (4H, m, Ar **H**), 5.22 (1H, br s, N**H**), 3.80 (2H, br s, N**H**$_2$), 2.56 (2H, t, *J* 7.6 Hz, NC**H**$_2$), 1.59 (2H, quintet, C**H**$_2$), 1.39 (2H, heptet, C**H**$_2$), 0.97 (3H, t, *J* 7.1 Hz, C**H**$_3$); δ_C(50MHz; CD_2Cl_2) 143.51, 142.07, 134.43, 129.84, 129.48 (Ar **C**H), 125.41 (Ar **C**H), 124.23 (Ar **C**H), 119.29 (Ar **C**H), 116.38 (Ar **C**H), 116.01 (Ar **C**H), 35.14 (N**C**H$_2$), 34.41 (**C**H$_3$), 22.76 (**C**H$_2$), 14.15 (**C**H$_3$); *m/z* (EI) 240 (M$^+$, 100%) (Found: M$^+$, 240.1628. $C_{16}H_{20}N_2$ requires *M*, 240.1626).

***N*-(4-*t*-Butylphenyl)-1,2-benzenediamine (5c).** Similarly hydrogenation of *N*-(4-*t*-butylphenyl)-2-nitrobenzamine gave the title compound **5c** (95%) as cream colored solid, mp 82-85 C (from EtOH/water) (Found: C, 79.95; H, 8.19; N, 11.79. $C_{16}H_{20}N_2$ requires C, 80.00; H, 8.33; N, 11.67%); λ_{max}(DCM)/nm 237 (log ε 4.15), 273 (3.83), 296 (3.80); ν_{max}(Drift)/cm^{-1} 3425m and 3342s (Ar NH), 3043w and 3022m (Ar CH), 2962s, 2904m and 2866m (CH_2 and CH_3), 1612s, 1591m, 1515s, 1500s, 1464m, 1442m, 1394w, 1363w, 1304s, 1257m, 1221w, 1192w, 1136w, 1124w, 1059w, 1010w, 929w, 887w, 865w, 825m, 750m, 692w, 644w; δ_H(200MHz; CD_2Cl_2)

7.28 (2H, d, *J* 6.8 Hz, Ar **H**), 7.13 (1H, d, *J* 7.8 Hz, Ar **H**), 7.02 (1H, dd, *J* 7.7, 7.6 Hz, Ar **H**), 6.82 (1H, d, *J* 6.7 Hz, Ar **H**), 6.73 (3H, m, Ar **H**), 5.25 (1H, br s, N**H**), 3.80 (2H, br s, N**H**$_2$), 1.34 (9H, s, C**H**$_3$); δ_C(50MHz; CD_2Cl_2) 143.33, 142.65, 142.21, 129.72, 126.43 (Ar **C**H), 125.55 (Ar **C**H), 124.44 (Ar **C**H), 119.30 (Ar **C**H), 116.40 (Ar **C**H), 115.62 (Ar **C**H), 34.31 (**C**me$_3$), 31.72 (**C**H$_3$); *m/z* (EI) 240 (M^+, 100%) (Found: M^+, 240.1622. $C_{16}H_{20}N_2$ requires *M*, 240.1626).

***N*-(*n*-Butyl)-1,2-benzenediamine (5d).** Similarly hydrogenation of *N*-(*n*-butyl)-2-nitrobenzamine gave the title compound **5d** (97%) as a dark colored oil that solidifies on standing, mp 33-35 C (crude) (Found: C, 73.24; H, 9.52; N, 17.14. $C_{10}H_{16}N_2$ requires C, 73.17; H, 9.76; N, 17.07%); λ_{max}(DCM)/nm 229 (log ε 3.92), 249 (3.91), 298 (3.57); ν_{max}(Drift)/cm^{-1} 3388s, 3356s, 3317s, 3265m and 3234m (Ar NH), 3066m, 3045m and 3032m (Ar CH), 2966s, 2941s, and 2873s (CH_2 and CH_3), 1635m, 1606m, 1575m, 1558m, 1522m, 1472m, 1458m, 1377m, 1363m, 1340m, 1315m, 1279m, 1230m, 1207m, 1151m, 1115m, 1043m, 908m, 848m, 754s, 687m, 642m; δ_H(200MHz; CD_2Cl_2) 6.87-6.63 (4H, m, Ar **H**), 3.36 (3H, br s, N**H** and N**H**$_2$), 3.14 (2H, t, *J* 7.0 Hz, NC**H**$_2$), 1.69 (2H, quintet, C**H**$_2$), 1.52 (2H, hextet, C**H**$_2$), 1.03 (3H, t, *J* 7.2 Hz, C**H**$_3$); δ_C(50MHz; CD_2Cl_2) 138.73, 134.90, 121.02 (Ar **C**H), 118.70 (Ar **C**H), 116.71 (Ar **C**H), 112.00 (Ar **C**H), 44.58 (N**C**H$_2$), 32.45 (**C**H$_2$), 21.08 (**C**H$_2$), 14.40 (**C**H$_3$); *m/z* (EI) 164 (M^+, 100%) (Found: M^+, 164.1312. $C_{10}H_{16}N_2$ requires *M*, 164.1313).

Preparation of 5-fluoro-2,4-dinitrobenzamines

1-[*N*-(*N'*-phenyl-1,2-benzenediamino)]-5-fluoro-2,4-dinitrobenzene (9). To a stirred solution of 1,5-difluoro-2,4-dinitrobenzene **6** (6.63g, 32.5mmol) in EtOH (200mL) at *ca.* 0 C, under argon, *N*-phenyl-1,2-benzenediamine **5a** (5.98g, 32.5mmol) was added in several portions. The color of the reaction mixture became orange and within 2 h an orange crystalline precipitate was observed. To the cooled reaction mixture (*ca.* 0 C) Hünig's base (5.65mL, 32.44mmol) was added in three portions over a period of 2 h and on complete addition the mixture was left to warm to *ca.* 20 C. The orange precipitate was removed by filtration, washed (H_2O) and dried to afford the title compound **9** (11.42g, 95%) as orange red needles, mp 164-166 C (from EtOH) (Found: C, 58.52; H, 3.56; N, 14.63. $C_{18}H_{13}FN_4O_4.1/2C_2H_6O$ requires C, 58.31; H, 4.09; N, 14.32%); λ_{max}(DCM)/nm 230 (log ε 4.28), 276 (4.39), 327 (4.18), 360 inf (4.03); ν_{max}(Drift)/cm^{-1} 3379s and 3300s (Ar NH), 3101w and 3039w (Ar CH), 1643m, 1620s, 1597s, 1545s, 1518s, 1500s, 1477s, 1464s, 1421s, 1367s, 1336s, 1327s, 1271s, 1236m, 1221m, 1132m, 1051m, 928w, 897w, 885w, 860w, 831w, 752m, 719w, 700m, 677w, 642w, 604m; δ_H(200MHz; DMSO-d_6) 10.02 (1H, br s, N**H**), 8.94 (1H, d, J_{HF} 8.0 Hz, Ar **H**-3), 7.83 (1H, br s, N**H**), 7.38-7.19 (5H, m, Ar **H**), 7.08-6.97 (3H, m, Ar **H**), 6.88 (1H, dd, *J* 7.2, 7.1 Hz, Ar **H**), 6.55 (1H, d, J_{HF} 14.2 Hz, Ar **H**-6); observable peaks δ_C(50MHz; DMSO-d_6) 158.60 (d, J_{CF} 264.9 Hz, Ar **C**F), 148.39 (d, J_{CF} 13.3 Hz, Ar **C**NH), 142.52 (Ar **C**NH), 139.87 (Ar **C**NH), 129.01 (Ar **C**H), 128.76 (Ar **C**H), 128.45 (Ar **C**H), 128.26, 126.85 (Ar **C**H), 125.80, 125.67, 125.61, 120.90 (d, J_{CF} 12.3 Hz, Ar **C**H-6), 118.72 (Ar **C**H), 117.92 (Ar **C**H), 103.06 (d, J_{CF} 27.1 Hz, Ar **C**H-3); *m/z* (FAB) 368 (M^+, 100%) (Found: M^+, 368.0922. $C_{18}H_{13}FN_4O_4$ requires *M*, 368.0921).

Preparation of 1,5-bisamino-2,4-dinitrobenzenes

1,5-Bis[*N*-(*N'*-phenyl-1,2-benzenediamino)]-2,4-dinitrobenzene (7a). Method 1. To a stirred solution of *N*-phenyl-1,2-benzenediamine **5a** (14.75g, 80mmol) in EtOH (120mL) at *ca.* 20 C, under argon, 1,5-difluoro-2,4-dinitrobenzene **6** (4.08g, 20mmol) was added in one portion. The color of the reaction mixture became red and within 15 min a red crystalline precipitate was observed. The reaction mixture was heated under reflux for 12 h, then allowed to cool to *ca.* 20 C. The red precipitate was filtered, washed with hot water and then with cold EtOH and dried to afford compound **7a** (10.48g, 98.5%) as brick red prisms, mp 219-220 C (from EtOH) (Found: C, 67.88; H, 4.47; N, 15.94. $C_{30}H_{24}N_6O_4$ requires C, 67.67; H, 4.51; N, 15.79%); λ_{max}(DCM)/nm 231 (log ε 4.46), 283 (4.59), 331 (4.45), 369 inf (4.29); ν_{max}(Drift)/cm^{-1} 3402s, 3379s, 3336s and 3321s (Ar NH), 3186w, 3089m, 3077m and 3046m (Ar CH), 1605m, 1592m, 1585m, 1564m, 1555m, 1530m, 1513m, 1493m, 1484m, 1463m, 1424m, 1335m, 1318m, 1279m, 1254m, 1161m, 1104m, 1069m, 1028w, 971w, 897w, 744m, 690m; δ_H(400MHz; DMSO-d_6) 9.42 (2H, s, N**H**), 8.98 (1H, s, **H**-3), 7.61 (2H, s, PhN**H**), 7.17-7.10 (10H, m, Ar **H**), 6.89-6.78 (8H, m, Ar **H**), 5.97 (1H, s, **H**-6); one carbon signal missing δ_C(100MHz; DMSO-d_6) 146.60 (Ar **C**NH), 142.80 (Ar **C**NH), 139.28 (Ar **C**NH), 128.92, 127.57, 127.52, 127.38, 126.65, 125.03, 120.56, 118.28, 117.69, 95.01 (**C**H-3); *m/z* (FAB) 532 (M^+, 100%) (Found: M^+, 532.1876. $C_{30}H_{24}N_6O_4$ requires *M*, 532.1859).

Method 2. To a stirred solution of *N*-phenyl-1,2-benzenediamine **5a** (7.38g, 40mmol) in EtOH (120mL) at *ca.* 20 C, under argon, 1,5-difluoro-2,4-dinitrobenzene **6** (4.08g, 20mmol) was added in one portion. The color of the reaction mixture became orange-red and Hünig's base (7mL, 40mmol) was then added in one portion. Within 30 min. a red crystalline precipitate was observed. The reaction mixture was heated under reflux for 24 h, then allowed to cool to *ca.* 20 C. The red precipitate was filtered, washed with hot water and then with cold EtOH and dried to afford compound **7a** (9.68g, 91%) as brick red prisms, mp 219-220 C (from EtOH), identical to an authentic sample.

1,5-Bis[*N*-(*N'*-4-*n*-butylphenyl-1,2-benzenediamino)]-2,4-dinitrobenzene (7b). Similarly (Method 2) the treatment of 1,5-difluoro-2,4-dinitrobenzene **6** with *N*-(4-*n*-butylphenyl)-1,2-benzenediamine **5b** and Hünig's base gave the title compound **7b** (85%) as a brick red precipitate, mp 166.5-169 C (from EtOH) (Found: C, 71.11; H, 6.17; N, 13.34. $C_{38}H_{40}N_6O_4$ requires C, 70.81; H, 6.21; N, 13.04%); λ_{max}(DCM)/nm 230 (log ε 4.44), 283 (4.54), 331 (4.39), 375 (4.21); ν_{max}(Drift)/cm^{-1} 3398s, 3373s, and 3325s (Ar NH), 3092w, and 3025w (Ar CH), 2956m, 2928s, 2870m and 2856m (CH_2 and CH_3), 1618m, 1597s, 1569s, 1520s, 1508s, 1486s, 1459s, 1436m, 1408s, 1340s, 1322s, 1284s, 1247s, 1202m, 1160m, 1121w, 1104m, 1067m, 1043w, 926w, 897m, 829m, 820m, 810m, 753m, 742m, 627w; δ_H(500MHz; DMSO-d_6) 9.39 (2H, s, N**H**), 8.98 (1H, s, **H**-3), 7.48 (2H, s, PhN**H**), 7.12-7.07 (6H, m, Ar **H**), 6.95 (4H, d, *J* 8.1 Hz, Ar **H**), 6.82-6.79 (2H, m, Ar **H**), 6.71 (4H, d, *J* 8.2 Hz, Ar **H**), 5.97 (1H, s, **H**-6), 2.45 (4H, t, *J* 7.7 Hz, Ar C**H**$_2$), 1.50-1.44 (4H, quintet, C**H**$_2$), 1.30-1.23 (4H, sextet, C**H**$_2$), 0.87 (6H, t, *J* 7.6 Hz, C**H**$_3$); one carbon signal missing δ_C(125MHz; DMSO-d_6) 146.69 (Ar **C**NH), 140.21 (Ar **C**NH), 139.94 (Ar **C**NH), 134.79 (Ar **C**NH), 128.64, 127.53, 127.38, 125.93, 125.01, 119.84,

119.02, 116.88, 94.97 (**C**H-3), 34.17 (Ar **C**H_2), 33.32 (**C**H_2), 21.68 (**C**H_2), 13.77 (**C**H_3); *m/z* (FAB) 644 (M^+, 100%) (Found: M^+, 644.3121. $C_{38}H_{40}N_6O_2$ requires *M*, 644.3111).

1,5-Bis[*N*-(*N'*-4-*t*-butylphenyl-1,2-benzenediamino)]-2,4-dinitrobenzene (7c). Similarly (Method 2) the treatment of 1,5-difluoro-2,4-dinitrobenzene **6** with *N*-(4-*t*-butylphenyl)-1,2-benzenediamine **5c** and Hünig's base gave the title compound **7c** (87%) as a brick red precipitate, mp 194.5-198 C (from EtOH) (Found: C, 71.04; H, 6.33; N, 13.16. $C_{38}H_{40}N_6O_4$ requires C, 70.81; H, 6.21; N, 13.04%); λ_{max}(DCM)/nm 231 (log ε 4.43), 285 (4.61), 331 (4.48), 365 inf (4.28); ν_{max}(Drift)/cm^{-1} 3355s and 3311s (Ar NH), 3095w, 3071w and 3055w (Ar CH), 2963s, 2904s and 2869s (CH_3), 1636s, 1605s, 1540s, 1508s, 1488s, 1439s, 1424s, 1363s, 1349s, 1307s, 1243s, 1206m, 1126m, 1111m, 1069m, 1020m, 950w, 931m, 877w, 843m, 829m, 745w; δ_H(400MHz; CD_2Cl_2) 9.33 (2H, s, N**H**), 9.26 (1H, s, **H**-3), 7.23 (4H, d, *J* 8.6 Hz, Ar **H**), 7.15-7.14 (4H, m, Ar **H**), 7.09 (2H, d, *J* 7.7 Hz, Ar **H**), 6.86-6.81 (2H, m, Ar **H**), 6.78 (4H, d, *J* 8.6 Hz, Ar **H**), 5.98 (1H, s, **H**-6), 5.63 (2H, s, PhN**H**), 1.27 (18H, s, C**H**$_3$); δ_C(50MHz; CD_2Cl_2) 148.02 (Ar **C**NH), 146.05 (Ar **C**NH), 141.01 (Ar **C**NH), 139.51 (Ar **C**NH), 129.19, 128.88, 128.02, 126.65, 126.18, 125.62, 120.94, 120.26, 116.93, 96.87 (**C**H-3), 34.67 (**C**Me3), 31.72 (**C**H_3); *m/z* (EI) 644 (M^+, 5%) (Found: M^+, 644.3117. $C_{38}H_{40}N_6O_4$ requires *M*, 644.3111).

1,5-Bis[*N*-(*N'*-*n*-butyl-1,2-benzenediamino)]-2,4-dinitrobenzene (7d). Similarly the treatment of 1,5-difluoro-2,4-dinitrobenzene **6** with *N*-(*n*-butyl)-1,2-benzenediamine **5d** and Hünig's base gave the title compound **7d** (83%) as bright red prisms, mp 144-147 C (from EtOH) (Found: C, 63.35; H, 6.44; N, 17.33. $C_{26}H_{32}N_6O_4$ requires C, 63.41; H, 6.50; N, 17.07%); λ_{max}(DCM)/nm 230 (log ε 4.46), 244 (4.46), 331 (4.42), 365 inf (4.25); ν_{max}(Drift)/cm^{-1} 3413m and 3379s (Ar NH), 3103w, 3074w and 3043w (Ar CH), 2956s, 2931s and 2870m (CH_2 and CH_3), 1602s, 1583s, 1523s, 1460m, 1431m, 1412m, 1379w, 1342m, 1327m, 1302m, 1265m, 1223m, 1190m, 1159w, 1103w, 1072w, 1043w, 989w, 924w, 831w, 744w, 690w, 634w; δ_H(200MHz; CD_2Cl_2) 9.24 (1H, s, **H**-3), 9.21 (2H, br s, N**H**), 7.13 (2H, dd, *J* 7.7, 7.6 Hz, Ar **H**), 6.99 (2H, d, *J* 7.4 Hz, Ar **H**), 6.63-6.56 (4H, m, Ar **H**), 5.73 (1H, s, **H**-6), 3.82 (2H, br s, N**H**), 3.03-2.97 (4H, m, NC**H**$_2$), 1.59-1.14 (8H, m, C**H**$_2$), 0.93 (6H, t, *J* 7.1 Hz, C**H**$_3$); δ_C(50MHz; CD_2Cl_2) 148.14, 144.76, 129.28 (Ar **C**H), 129.22 (Ar **C**H), 127.44 (Ar **C**H), 126.06, 122.57, 117.04 (Ar **C**H), 111.85 (Ar **C**H), 96.94 (Ar **C**H), 43.80 (N**C**H_2), 32.05 (**C**H_2), 20.86 (**C**H_2), 14.23 (**C**H_3); *m/z* (FAB) 492 (M^+, 100%) (Found: M^+, 492.2491. $C_{26}H_{32}N_6O_4$ requires *M*, 492.2485).

Preparation of unsymmetrical derivative

1-[*N*-(*N'*-*t*-Butylphenyl-1,2-benzenediamino)]-5-[*N*-(*N'*-phenyl-1,2-benzene-diamino)]-2,4-dinitrobenzene (7e). To a stirred suspension of 1-[*N*-(*N'*-phenyl-1,2-benzenediamino)]-5-fluoro-2,4-dinitrobenzene **9** (1.37g, 3.72mmol) in EtOH (50mL) at *ca.* 20 C, under argon, *N*-(4-*t*-butylphenyl)-1,2-benzenediamine **5c** (2g, 8.33mmol) was added in one portion. The color of the reaction mixture became deep orange and the reaction mixture was heated under reflux for 24 h, then allowed to cool to *ca.* 20 C. The red precipitate was filtered, washed with hot water, dried and recrystallised to afford the title compound **7e** (1.99g, 91%) as an orange powder, mp 179-185 C (from EtOH) (Found: C, 69.70; H, 5.55; N, 14.15. $C_{34}H_{32}N_6O_4$ requires C, 69.39; H,

5.44; N, 14.29%); λ_{max}(DCM)/nm 229 (log ε 4.42), 284 (4.54), 331 (4.40), 374 (4.21); ν_{max}(Drift)/cm^{-1} 3411m, 3382m, 3337s and 3327s, (Ar NH), 3064w and 3040w (Ar CH), 2962m, 2901w, 2866w, 1619s, 1598s, 1571s, 1518s, 1482s, 1465s, 1459s, 1409s, 1361m, 1339s, 1324s, 1313s, 1287s, 1247s, 1204s, 1191s, 1158m, 1123w, 1102w, 1068m, 932w, 897w, 835w, 781w, 740m, 694m; δ_H(200MHz; CD_2Cl_2) 9.39 (1H, s, N**H**), 9.36 (1H, s, N**H**), 9.14 (1H, s, **H**-3), 7.29-7.11 (10H, m, Ar **H**), 6.99-6.83 (7H, m, Ar **H**), 6.09 (1H, s, **H**-6), 5.88 (1H, s, N**H**), 5.81 (1H, s, N**H**), 1.32 (9H, s, C**H**$_3$); one peak missing δ_C(50MHz; CD_2Cl_2) 147.84, 147.72, 145.82, 142.35, 140.86, 140.14, 139.39, 129.68 (Ar **C**H), 128.98 (Ar **C**H), 128.70 (Ar **C**H), 128.63 (Ar **C**H), 127.77 (Ar **C**H), 127.69 (Ar **C**H), 126.48 (Ar **C**H), 126.31, 125.93, 125.46, 122.37 (Ar **C**H), 121.48 (Ar **C**H), 120.75 (Ar **C**H), 120.09 (Ar **C**H), 119.57 (Ar **C**H), 117.68 (Ar **C**H), 116.79 (Ar **C**H), 96.62 (Ar **C**H), 34.51 (**C**CH$_3$), 31.58 (C**C**H$_3$); *m/z* (FAB) 588 (M$^+$, 100%) (Found: M$^+$, 588.2486. $C_{34}H_{32}N_6O_4$ requires *M*, 588.2485).

***N′,N′′′′′*-Bis[2-(*N*-phenylbenzamino)]-1,2,4,5-benzenetetraamine (8a).** To a stirred suspension of 1,5-bis[*N*-(*N′*-phenyl-1,2-benzenediamino)]-2,4-dinitrobenzene **7a** (100mg, 0.188mmol) in EtOH (20mL) at *ca.* 20^{O}C, under argon, (10%) palladium on carbon (100mg) was added in one portion. The reaction mixture was evacuated (to 25mmHg) and flushed with argon 3 times then the mixture was evacuated (to 25mmHg) and flushed with hydrogen 3 times. The reaction mixture was then left to stir under an atmosphere of hydrogen. The color of the mixture became dark red and after 1 h the color disappeared and a cream colored precipitate was observed. The suspension was diluted with sufficient dichloromethane to dissolve the precipitate, which was filtered through a celite pad and all volatiles were removed to afford brown oil. This was diluted with cold EtOH and triturated to afford a crude specimen of the title compound **8a** (80mg, 90%) as brown needles. A sample of the crude product was further purified by dry flash chromatography on silica (Et_2O, 100%) to give compound **8a** as colorless needles, mp 127-130 C starts to melt in this range, becoming green in color and further melting stops (from Et_2O) (Found: C, 76.60; H, 6.06; N, 17.90. $C_{30}H_{28}N_4$ requires C, 76.27; H, 5.93; N, 17.79%); λ_{max}(DCM)/nm 241 (log ε 4.61), 300 inf (4.32); ν_{max}(Drift)/cm^{-1} 3450w, 3415w, 3373m, 3337w and 3277m (NH and NH_2), 3084w and 3047w (Ar CH), 1623m, 1603s, 1595s, 1524s, 1499s, 1470m, 1459m, 1443m, 1424m, 1347m, 1319s, 1296m, 1258s, 1203w, 1178w, 1152w, 1104m, 1042m, 994w, 880w, 845m, 798w, 756m, 746m, 693m, 654m; δ_H(500MHz; DMSO-d_6) 7.21 (2H, s, PhN**H**), 7.14 (4H, dd, *J* 7.4, 7.5 Hz, Ph **H**-3), 7.09 (2H, d, *J* 7.7 Hz, $C_6H_4N_2$ **H**-2 or 5), 6.84 (2H, dd, *J* 7.8, 7.7 Hz, Ph **H**-4), 6.80 (4H, d, *J* 8.6 Hz, Ph **H**-2), 6.69 (2H, dd, *J* 7.3, 7.5 Hz, $C_6H_4N_2$ **H**-3 or 4), 6.61 (2H, dd, *J* 7.5, 7.6 Hz, $C_6H_4N_2$ **H**-3 or 4), 6.61 (1H, s, $C_6H_2N_4$ **H**-3 or 6), 6.48 (2H, d, *J* 8.1 Hz, $C_6H_4N_2$ **H**-2 or 5), 6.21 (1H, s, $C_6H_2N_4$ **H**-3 or 6), 5.98 (2H, s, N**H**), 4.48 (4H, s, N**H**$_2$); δ_C(50MHz; DMSO-d_6) 146.14, 142.92, 141.92, 129.15, 128.79, 125.64, 124.27, 123.13, 118.12, 117.25, 116.78, 114.98, 113.07, 101.27; *m/z* (EI) 472 (M$^+$, 100%), 470 (M$^+$-2H, 90), 453 (M$^+$-2H-NH$_3$, 20), 436 (M$^+$-2H-2NH$_2$, 45), 378 (5), 361 (20), 287 (M$^+$-2H-PhNHC$_6$H$_4$NH$_2$, 95) (Found: M$^+$, 472.2383. $C_{30}H_{28}N_6$ requires *M*, 472.2375).

5,7-Diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine (3a). Method 1. To a stirred solution of *N′,N′′′′′*-bis[2-(*N*-phenylbenzamino)]-1,2,4,5-benzenetetraamine **8a** (444mg, 0.94mmol) in EtOH

(20mL) at *ca.* 20 C, under an atmosphere of air, hydrochloric acid (36%, 10mL) was added in one portion. The color of the reaction mixture became lilac, then blue. The reaction mixture was heated under reflux for 2 h then allowed to cool to *ca.* 20 C. A green-blue precipitate was observed and assumed to be the hydrochloride salt of compound **3a**. The mixture was made basic (aq. NaOH) and the precipitate was filtered, washed (hot water then cold ethanol) and dried to afford compound **3a** (375mg, 91%) as dark green needles, mp > 365 C dec. (from EtOH) (Found: C, 82.81; H, 4.76; N, 12.80. $C_{30}H_{20}N_4$ requires C, 82.57; H, 4.59; N, 12.84%); λ_{max}(DCM)/nm 228 (log ε 4.26), 298 (4.98), 361 (3.90), 382 (4.09), 401 (4.50), 423 (4.79), 450 (3.90), 478 (4.02), 512 (3.84), 629 (4.15), 688 (4.41), 763 (4.41); ν_{max}(Drift)/cm^{-1} 3052s, 3026s and 3007s (Ar CH), 1615w, 1590m, 1560s, 1539m, 1505s, 1497s, 1492s, 1456s, 1440s, 1356s, 1333s, 1318m, 1308m, 1250s, 1227w, 1192m, 1169m, 1143m, 1120w, 1071w, 1028w, 1004w, 920w, 818m, 775m, 730s, 702m, 687m; ^{1}H NMR assignments supported by NOE experiment δ_H(500MHz; CD_2Cl_2) 7.42-7.39 (6H, m, Ph **H'**-3,4 and 5), 7.07-7.04 (6H, m, Ph **H'**-2,6 and **H**-1), 6.94 (2H, dd, *J* 7.4, 7.3 Hz, **H**-2), 6.56 (2H, dd, *J* 7.5, 7.6 Hz, **H**-3), 6.16 (1H, s, **H**-6), 6.05 (2H, d, *J* 8.4 Hz, **H**-4), 4.25 (1H, s, **H**-13); the following carbon resonance's could be observed, δ_C(125MHz; CD_2Cl_2) 137.03, 131.35, 130.83, 130.16, 128.11, 127.42, 122.48, 116.46; *m/z* (FAB) 437 (MH^+, 40%), *m/z* (EI) 436 (M^+, 100%), 359 (M^+-Ph, 30) (Found: M^+, 436.1689. $C_{30}H_{20}N_4$ requires *M*, 436.1688).

Method 2. A stirred solution of *N*′,*N*′′′′′-bis[2-(*N*-phenylbenzamino)]-1,2,4,5-benzenetetraamine **8a** (475mg, 1.01mmol) in EtOH (20mL), under an atmosphere of air, was heated under reflux. The color of the reaction mixture rapidly became brown then green and a green crystalline precipitate was formed within 20 min. TLC monitoring over a period of 7 h showed consumption of the starting material had ceased and so the precipitate was collected by filtration and dried to give 101.8mg of a green crystalline material. The filtrate was heated to reflux and rapidly precipitated a further 99.2mg which was removed by filtration. The process was repeated collecting a further four fractions (64.1, 38.0, 49.1 and 16.8mg) until it became impractical to recover more precipitate. No further purification was required, the total recovery of compound **3a** was 369mg, 84% yield; the sample was identical to that described above.

Method 3. To a stirred suspension of 1,5-bis[*N*-(*N*′-phenyl-1,2-benzenediamino)]-2,4-dinitrobenzene **7a** (100mg, 0.188mmol) in EtOH (20mL) at *ca.* 20 C, under argon, (10%) palladium on carbon (100mg) was added in one portion. The reaction mixture was evacuated (to 25mmHg) and flushed with argon 3 times, then evacuated (to 25mmHg) and flushed with hydrogen 3 times. The reaction mixture was then left to stir under a hydrogen atmosphere. The color of the mixture became dark red and after 3 h this red color disappeared and a cream colored precipitate was observed. The mixture was heated gently to dissolve the precipitated amine and then hot-filtered through a short pad of celite to remove the palladium catalyst. The dark ethanolic solution of the amine was heated exposed to atmospheric oxygen until a green precipitate was formed. This was filtered off and the filtrate was taken to reflux until more precipitate was formed. The precipitate was removed and the process repeated until there was no

further precipitate. Combining the precipitated material gave the title compound **3a** (70mg, 85%) identical to an authentic sample.

5,7-Bis(4-*n*-butylphenyl)-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine (3b). Similarly (Method 3) treatment of 1,5-bis[*N*-(*N*′-4-*n*-butylphenyl-1,2-benzenediamino)]-2,4-dinitrobenzene **7b** gave the title compound **3b** (77%) as dark green needles, mp 310-320 C dec. (from EtOH) (Found: C, 83.38; H, 6.69; N, 9.98. $C_{38}H_{36}N_4$ requires C, 83.21; H, 6.57; N, 10.22%); λ_{max}(DCM)/nm 228 (log ε 4.33), 299 (5.05), 333 (3.94), 359 (3.92), 382 (4.12), 401 (4.58), 423 (4.93), 450 (3.89), 478 (4.01), 512 (3.67), 629 inf (3.96), 693 (4.37), 760 (4.50); ν_{max}(Drift)/cm^{-1} 3052m, 3044m and 3032m (Ar CH), 2999m, 2948m, 2927s, 2870m and 2857m (CH_2 and CH_3), 1615w, 1602w, 1592w, 1559s, 1539m, 1507s, 1457s, 1441s, 1365m, 1352s, 1333s, 1308s, 1249m, 1227w, 1194m, 1178m, 1141m, 1115w, 1081w, 1022w, 972w, 918w, 836w, 823m, 816m, 770w, 731m, 672w, 642w, 608m, 589w; δ_H(500MHz; CD_2Cl_2) 7.24 (4H, d, *J* 8.2 Hz, N-Ar **H**), 7.02 (2H, d, *J* 7.9 Hz, **H**-1), 6.97 (4H, d, *J* 8.2 Hz, N-Ar **H**), 6.91 (2H, dd, *J* 7.6, 7.5 Hz, **H**-2), 6.54 (2H, dd, *J* 7.6, 7.7 Hz, **H**-3), 6.15 (1H, s, **H**-6), 6.04 (2H, d, *J* 7.7 Hz, **H**-4), 4.47 (1H, s, **H**-13), 2.62 (4H, t, *J* 7.8 Hz, Ar C**H**$_2$), 1.60 (4H, m, C**H**$_2$), 1.43 (4H, m, C**H**$_2$), 1.01 (6H, t, *J* 7.3 Hz, C**H**$_3$); δ_C(125MHz; CD_2Cl_2) 150.94, 145.46, 144.90, 144.21, 134.50, 131.08, 131.04, 127.83, 127.25, 125.97, 122.86, 116.54, 103.64 (Ar **C**-13), 93.03 (Ar **C**-6), 35.89 (Ar **C**H$_2$), 34.16 (**C**H$_2$), 23.12 (**C**H$_2$), 14.27 (**C**H$_3$); *m/z* (FAB) 549 (MH$^+$, 100%) (Found: MH$^+$, 549.3027. $C_{38}H_{37}N_4$ requires *MH*, 549.3018).

5,7-Bis(4-*t*-butylphenyl)-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine (3c). Similarly (Method 3) treatment of 1,5-bis[*N*-(*N*′-4-*t*-butylphenyl-1,2-benzenediamino)]-2,4-dinitrobenzene **7c** gave the title compound **3c** (84%) as dark green needles, mp 350-360 C dec. (from EtOH) (Found: C, 83.49; H, 6.72; N, 10.12. $C_{38}H_{36}N_4$ requires C, 83.21; H, 6.57; N, 10.22%); λ_{max}(DCM)/nm 227 (log ε 4.23), 298 (4.97), 363 (3.99), 401 (4.49), 423 (4.82), 450 (3.85), 478 (3.96), 512 (3.73), 580 inf (3.78), 628 (4.12), 688 (4.35), 763 (4.35); ν_{max}(Drift)/cm^{-1} 3068w, 3051w and 3029w (Ar CH), 2965s, 2902m and 2870m (CH_3), 1615w, 1588m, 1559s, 1530m, 1507s, 1473m, 1459s, 1440s, 1406m, 1395m, 1365s, 1354s, 1332s, 1310s, 1267m, 1249m, 1217m, 1201m, 1191m, 1148m, 1140m, 1114w, 1033w, 1017m, 930w, 848w, 832m, 823m, 741s, 727m, 649w, 608m; δ_H(400MHz; CD_2Cl_2) 7.46 (4H, d, *J* 8.4 Hz, N-Ar **H**), 7.04-7.00 (6H, m, N-Ar **H** and **H**-1), 6.92 (2H, dd, *J* 7.6, 7.5 Hz, **H**-2), 6.52 (2H, dd, *J* 7.1, 7.2 Hz, **H**-3), 6.19 (1H, s, **H**-6), 5.87 (2H, d, *J* 7.8 Hz, **H**-4), 4.78 (1H, s, **H**-13), 1.32 (18H, s, C**H**$_3$); δ_C(100MHz; CD_2Cl_2) 153.58, 150.70, 144.72, 143.99, 134.11, 131.21, 127.91, 127.38, 127.10, 125.70, 122.58, 116.46, 103.79 (Ar **C**-13), 92.46 (Ar **C**-6), 35.11 (**C**me$_3$), 31.45 (**C**H$_3$); *m/z* (EI) 548 (M$^+$, 13%) (Found: M$^+$, 548.2937. $C_{38}H_{36}N_4$ requires *M*, 548.2940).

5,7-Bis(*n*-butyl)-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine (3d). Similarly (Method 3) treatment of 1,5-bis[*N*-(*N*′-*n*-butyl-1,2-benzenediamino)]-2,4-dinitrobenzene **7d** gave the title compound **3d** (80%) as dark green needles, mp 245-250 C dec. (from EtOH) (Found: C, 78.95; H, 7.02; N, 14.19. $C_{26}H_{28}N_4$ requires C, 78.79; H, 7.07; N, 14.14%); λ_{max}(DCM)/nm 228 (log ε 4.11), 294 (4.82), 332 (3.75), 360 inf (3.88), 380 inf (4.07), 395 (4.50), 417 (4.77), 445 (3.76), 473 (3.95), 506 (3.69), 570 inf (3.73), 631 inf (4.03), 694 (4.30), 768 (4.38); ν_{max}(Drift)/cm^{-1} 3047m and

3030m (Ar CH), 2958s, 2931s and 2866m (CH_2 and CH_3), 1612w, 1562s, 1541m, 1516s, 1487s, 1460s, 1444s, 1411w, 1356s, 1300m, 1246m, 1226m, 1196w, 1151w, 1134w, 1124m, 1063w, 1032w, 976w, 918w, 885m, 852w, 804m, 781w, 731s, 696w, 600m; δ_H(500MHz; CD_2Cl_2) 6.92 (4H, d, *J* 8.1 Hz, **H**-1), 6.86 (4H, dd, *J* 7.0, 7.1 Hz, **H**-2), 6.71 (4H, d, *J* 8.1 Hz, **H**-4), 6.62 (4H, dd, *J* 6.3, 6.4 Hz, **H**-3), 5.95 (1H, s, **H**-13), 5.60 (1H, s, **H**-6), 3.86 (4H, t, *J* 8.2 Hz, NC**H**$_2$), 1.70-1.65 (4H, quintet, C**H**$_2$), 1.54-1.50 (4H, hextet, C**H**$_2$), 1.04 (6H, t, *J* 7.4 Hz, C**H**$_3$); δ_C(125MHz; CD_2Cl_2) 150.65, 145.03, 142.66, 129.10, 126.97, 126.14, 123.15, 114.62, 103.28 (Ar **C**-13), 88.94 (Ar **C**-6), 46.47 (N**C**H$_2$), 28.43 (**C**H$_2$), 20.82 (**C**H$_2$), 14.16 (**C**H$_3$); *m/z* (FAB) 397 (MH^+, 100%) (Found: MH^+, 397.2390. $C_{26}H_{29}N_4$ requires *MH*, 397.2392).

5-(4-*t*-Butylphenyl)-7-phenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine (3e). Similarly (Method 3) treatment of 1-[*N*-(*N*′-*t*-butylphenyl-1,2-benzenediamino)]-5-[*N*-(*N*′-phenyl-1,2-benzenediamino)]-2,4-dinitrobenzene **7e** gave the title compound **3e** (58%) as dark green needles, mp 345-350 C dec. (from EtOH) (Found: C, 82.91; H, 5.81; N, 11.35. $C_{34}H_{28}N_4$ requires C, 82.93; H, 5.69; N, 11.38%); λ_{max}(DCM)/nm 228 (log ε 4.33), 298 (4.98), 382 inf (4.11), 401 (4.50), 423 (4.81), 450 (3.90), 478 (4.01), 512 (3.84), 578 inf (3.90), 629 (4.16), 687 (4.41), 760 (4.40); ν_{max}(Drift)/cm^{-1} 3064w and 3024w (Ar CH), 2966m, 2904w and 2872w (CH_3), 1615w, 1590w, 1562s, 1537m, 1508s, 1461m, 1442m, 1399w, 1367m, 1352s, 1334s, 1308s, 1250m, 1196m, 1173m, 1142m, 1123w, 1072w, 1027w, 973w, 924w, 832m, 823m, 815m, 767m, 731s, 702m, 687w, 649w, 605m; δ_H(500MHz; CD_2Cl_2) 7.46-7.42 (4H, m, N-Ar **H**), 7.38 (1H, dd, *J* 9.2, 8.9 Hz, Ph **H**'-4), 7.13 (2H, d, *J* 8.9 Hz, N-Ar **H**), 7.07-7.00 (4H, m, N-Ar **H**, **H**-1 and **H**-11), 6.91-6.86 (2H, m, **H**-2 and **H**-10), 6.56-6.50 (2H, m, **H**-3 and **H**-9), 6.17 (1H, s, **H**-6), 6.10 (1H, d, *J* 9.2 Hz, **H**-11), 6.00 (1H, d, *J* 9.2 Hz, **H**-4), 4.37 (1H, s, **H**-13), 1.34 (9H, s, C**H**$_3$); observable carbon signals, δ_C(125MHz; CD_2Cl_2) 153.78, 150.56, 144.49, 144.21, 144.09, 137.05, 134.14, 131.31, 130.91, 130.85, 130.27, 128.28, 128.21, 127.44, 127.34, 127.29, 125.84, 125.78, 123.13, 123.09, 116.62, 116.40, 103.62 (Ar **C**-13), 93.10 (Ar **C**-6), 35.30 (**C**me$_3$), 31.64 (**C**H$_3$); *m/z* (FAB) 493 (MH^+, 100%) (Found: MH^+, 493.2385. $C_{34}H_{29}N_4$ requires *MH*, 493.2392).

12-Methyl-5,7-diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazinium iodide (10). To a stirred solution of 5,7-diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine **3a** (22.5mg, 0.0516mmol) in DCM (7mL), at *ca.* 20 C, under argon, was added a large excess of iodomethane (0.5mL) in one portion. After 2 h the color of the reaction mixture had changed from green to blue. Dilution with hexane afforded a hygroscopic precipitate which was dried to give compound **10** (25mg, 84%) as blue crystals with a bronze luster, mp 180-190 C dec. (from 1,2-dichloroethane/pentane) (Found: C, 64.28; H, 4.22; N, 9.16. $C_{31}H_{23}IN_4$ requires C, 64.36; H, 3.98; N, 9.69%); λ_{max}(DCM)/nm 229 (log ε 4.41), 290 (4.94), 360 (3.96), 485 (3.56), 517 (3.85), 561 (4.23), 605 (4.60), 659 (4.70); λ_{max}(EtOH)/nm 201 (log ε 4.67), 230 inf (4.48), 289 (4.88), 360 (3.80), 485 (3.50), 515 inf (3.80), 557 (4.15), 600 (4.50), 652 (4.56); ν_{max}(Drift)/cm^{-1} 3068w, 3050w and 3021w (Ar CH), 2963w (CH_3), 1596m, 1587m, 1570s, 1538m, 1516s, 1489s, 1473s, 1461s, 1449m, 1423m, 1380m, 1354w, 1324m, 1244m, 1233m, 1170m, 1153m, 1125w, 1071w, 1027w, 1001w, 966w, 831w, 777w, 756m, 704w, 688m; δ_H(500MHz; CD_2Cl_2) 7.93 (1H, d, *J* 8.2 Hz, Ar **H**), 7.60-7.50

(7H, m, Ar and Ph **H**), 7.45 (1H, dd, *J* 7.6, 7.4 Hz, Ar **H**), 7.19-7.17 (5H, m, Ar and Ph **H**), 7.13 (1H, d, *J* 8.1 Hz, Ar **H**), 6.86-6.83 (3H, m, Ar **H**), 6.29 (1H, d, *J* 8.0 Hz, Ar **H**), 4.72 (1H, s, Ar **H**), 3.58 (3H, s, C**H**$_3$); δ_C(125MHz; CD_2Cl_2) 149.44, 148.70, 142.18, 140.39, 138.86, 136.26, 135.47, 133.11, 132.21 (Ph **C**H), 132.07, 131.80 (Ph **C**H), 131.68, 131.15, 131.07, 131.02, 130.23, 129.28, 128.25 (Ph **C**H), 128.04, 127.24 (Ph **C**H), 124.65, 118.25, 117.75, 115.16, 104.02, 95.07, 35.27 (**C**H$_3$); *m/z* (EI) 451 (M^+-I, 45%), 128 (HI, 100) (Found: M^+-I, 451.1918. $C_{31}H_{23}N_4$ requires *M-I*, 451.1923).

12,14-Dihydro-5,7-diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazinium bisperchlorate (11). To a suspension of 5,7-diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine **3a** (192mg, 0.44mmol) in acetonitrile (50mL), at *ca.* 20 C, was added (60%) aqueous perchloric acid (1mL). The color of the mixture turned deep blue and the suspension dissolved. The mixture was filtered through a celite pad and the filtrate was then diluted with ether until a cloudy suspension had formed. On standing this formed crystals and filtration gave the title compound **11** (236mg, 88%) as a golden precipitate, mp > 375 C (from acetonitrile/ether) (Found: C, 56.58; H, 3.76; N, 8.80. $C_{30}H_{22}Cl_2N_4O_8$ requires C, 56.60; H, 3.46; N, 8.81%); λ_{max}(EtOH)/nm 206 (log ε 4.95), 225 inf (4.33), 289 (5.02), 365 (4.01), 480 inf (3.75), 516 (3.96), 561 (4.21), 606 (4.58), 660 (4.68); λ_{max}[EtOH/(aq.) $HClO_4$]/nm 206 (log ε 4.93), 225 (4.41), 291 (4.90), 370 (3.79), 510 inf (3.80), 538 (4.18), 585 (4.63), 637 (5.01); ν_{max}(Drift)/cm^{-1} 3609w, 3587w and 3567w (NH), 3146w, 3122w, and 3075w (Ar CH), 1616s, 1558s, 1541s, 1519s, 1508s, 1474s, 1457m, 1345m, 1316m, 1249s, 1161s, 1100s (ClO_4), 1004w, 977w, 931w, 836w, 773m, 697m, 686m, 625m; δ_H(500MHz; CD_2Cl_2) 11.97 (2H, br s, N**H**), 7.60-7.52 (10H, m, Ar **H**), 7.34-7.31 (2H, m, Ar **H**), 7.25 (4H, m, Ar **H**), 7.09 (1H, s, **H**-13), 6.72 (2H, d, *J* 8.5 Hz, Ar **H**), 5.03 (1H, s, **H**-6); δ_C(125MHz; CD_3CN) 146.15, 143.48, 136.34, 133.38, 132.99, 132.82, 131.73, 131.18, 131.02, 127.78, 119.86, 119.84, 98.06 (**C**-6), 95.37 (**C**-13); *m/z* (FAB) 437 (M^+-H.2ClO_4, 55%) (Found: M^+-H.2ClO_4, 437.1767. $C_{30}H_{21}N_4$ requires *M-H.2ClO$_4$*, 437.1766).

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