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-5H,12H-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-5H,12H-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-disubstituted isomers. We now wish to report the full synthetic details.
The parent system quinoxalino[2,3-\textit{b}]phenazine 1 is not known. The only dihydro-quinoxalino[2,3-\textit{b}]phenazine is the 5\textit{H},14\textit{H}-dihydro derivative 2 thought to be in equilibrium with the 5\textit{H},12\textit{H}-dihydro isomer.\textsuperscript{4} However, 5,7-diphenyl-5\textit{H},12\textit{H}-quinoxalino[2,3-\textit{b}]-phenazine (diphenylisofluorindine, 5,7-DPQP, 3a) exists.\textsuperscript{5} The preparation of 5,7-DPQP from the treatment of 3-imino-N,5-diphenyl-3\textit{H},5\textit{H}-2-phenazinamine (3-anilinoaposafranine) with \textit{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.\textsuperscript{5} The product which did not melt (up to 260 °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\textit{H},12\textit{H}-quinoxalino[2,3-\textit{b}]-phenazine (diphenylfluorindine, 5,12-DPQP, 4).\textsuperscript{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.\textsuperscript{6} In particular the treatment of 3-anilinoaposafranine with \textit{N}-phenyl-1,2-benzenediamine 5 and one equivalent of mineral acid to give the isomer 5,12-DPQP\textsuperscript{6} suggested to us that the formation of a mixture of both isomers was likely \textit{via} this route and would therefore require separation. Furthermore the synthesis of 3-anilinoaposafranine was derived from the oxidative coupling of two equivalents of \textit{N}-phenyl-1,2-benzenediamine 5 which gives a mixture of two isomeric products that again require careful separation.\textsuperscript{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 \( \textbf{6} \) reacts with \( N \)-substituted-1,2-benzenediamines \( \textbf{5} \) to give dinitrobenzenediamines \( \textbf{7} \) in good yields. Hydrogenation of compounds \( \textbf{7} \) gave the benzenetetraamines \( \textbf{8} \), which on simple heating in ethanol in the presence of air gave the free base \( \textbf{3} \). The benzenetetraamines \( \textbf{8} \) were very susceptible to oxidation and their isolation and characterization was only carried out with one example (c.f. compound \( \textbf{8a} \), Experimental section). Treatment of \( \textbf{8a} \) 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 \( \textbf{5} \) were prepared from 1-fluoro-2-nitrobenzene and anilines in the presence of potassium fluoride, \( \textbf{8} \) 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 \( \textbf{3e} \) was prepared from the selective displacement of one fluoride from 1,5-difluoro-2,4-dinitrobenzene \( \textbf{6} \) which was achieved under mild conditions to give 5-fluoro-2,4-dinitrobenzamine \( \textbf{9} \) 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 5H,14H-quinoxalino[2,3-b]phenazine from 1,5-dichloro-2,4-dinitrobenzene and excess 1,2-benzenediamine, 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

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>R</th>
<th>R^I</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; nm, (log ε)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>mp (°C)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield (%)</th>
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<tr>
<td>3a</td>
<td>Ph</td>
<td>Ph</td>
<td>763 (4.41)</td>
<td>360-370 dec.</td>
<td>85-91</td>
</tr>
<tr>
<td>3b</td>
<td>4′-BuC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>4′-BuC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>760 (4.50)</td>
<td>310-320 dec.</td>
<td>77</td>
</tr>
<tr>
<td>3c</td>
<td>4′-BuC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>4′-BuC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>763 (4.35)</td>
<td>350-360 dec.</td>
<td>84</td>
</tr>
<tr>
<td>3d</td>
<td>nBu</td>
<td>nBu</td>
<td>768 (4.38)</td>
<td>245-250 dec.</td>
<td>83</td>
</tr>
<tr>
<td>3e</td>
<td>4′-BuC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Ph</td>
<td>760 (4.40)</td>
<td>345-350 dec.</td>
<td>58</td>
</tr>
</tbody>
</table>

<sup>a</sup> UV/VIS recorded in dichloromethane, concentrations approximately 10-5 M. <sup>b</sup> 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 [$\lambda_{\text{max}}$ 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 $\lambda_{\text{max}}$ at 637 (5.01).

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 ($\lambda_{\text{max}}$ 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-t-Butylphenyl)-2-nitrobenzamine.** To a stirred mixture of 1-fluoro-2-nitrobenzene (3.33mL, 31.60mmol) and 4-t-butylnilamine (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 (MgSO4), 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. C16H18N2O2 requires C, 71.11; H, 6.67; N, 10.37%); \( \lambda_{\text{max}}\) (DCM)/nm 230 (log \( \varepsilon \) 4.10), 260 (4.15), 285 inf (4.08), 437 (3.83); \( \nu_{\text{max}}\) (Drift)/cm\(^{-1}\) 3369m and 3359m (Ar NH), 3078m, 3039m and 3028m (Ar CH), 2964s, 2943s, 2887s and 2863s (CH2 and CH3), 1626s, 1579s, 1522s, 1502m, 1446m, 1431m, 1356m, 1331m, 1279s, 1234m, 1165m, 1153m, 1119m, 1080m, 1043m, 1020m, 953w, 930w, 893m, 849s, 824s, 810m, 781s, 748s, 696m, 628m; \( \delta_{\text{H}}\) (200MHz; CD2Cl2) 9.45 (1H, br s, NH), 8.18 (1H, d, J 8.6 Hz, Ar H), 7.36 (1H, dd, J 7.7 Hz, Ar H), 7.28-7.16 (5H, Ar H), 7.19 (1H, d, J 7.8 Hz, Ar H), 6.75 (1H, dd, J 7.9 Hz, Ar H), 2.66 (2H, t, J 7.4 Hz, ArCH2), 1.72-1.57 (2H, m, CH2), 1.49-1.30 (2H, m, CH2), 0.97 (3H, t, J 7.2 Hz, CH3); \( \delta_{\text{C}}\) (50MHz; CD2Cl2) 143.97, 141.17, 136.59, 135.99 (Ar C H), 133.34, 129.98 (Ar C H), 126.81 (Ar C H), 126.81 (Ar C H), 124.97 (Ar C H), 117.45 (Ar C H), 116.39 (Ar C H), 34.26 (CH2), 22.95 (CH2), 14.33 (CH3); m/z (FAB) 270 (M+, 100%) (Found: M+, 270.1362. C16H18N2O2 requires M., 270.1368).

N-(4-t-Butylphenyl)-2-nitrobenzamine. Similarly the treatment of 1-fluoro-2-nitrobenzene with 4-t-butylnilamine gave the title compound (95%) as a red oil (Found: C, 71.34; H, 6.59; N, 10.29. C16H18N2O2 requires C, 71.11; H, 6.67; N, 10.37%); \( \lambda_{\text{max}}\) (DCM)/nm 232 (log \( \varepsilon \) 4.09), 259 (4.16), 285 inf (4.03), 439 (3.82); \( \nu_{\text{max}}\) (Drift)/cm\(^{-1}\) 3367m, 3357m and 3342m (Ar NH), 3078m and 3041m (Ar CH), 143.97, 141.17, 136.59, 135.99 (Ar CH), 133.34, 129.98 (Ar CH), 126.81 (Ar CH), 124.97 (Ar CH), 117.45 (Ar CH), 116.39 (Ar CH), 35.69 (ArCH2), 34.26 (CH2), 22.95 (CH2), 14.33 (CH3); m/z (FAB) 270 (M+, 100%) (Found: M+, 270.1362. C16H18N2O2 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-butylnilamine (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 (MgSO4) 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_{2}O_{2} requires C, 61.86; H, 7.22; N, 14.43%); \(\lambda_{\text{max}}\) (DCM)/nm 242 (log \(\varepsilon\) 4.02), 280 (3.60), 435 (3.60); \(\nu_{\text{max}}\) (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; \(\delta_{\text{H}}\) (200MHz; CD\(_2\)Cl\(_2\)) 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\(_2\)H\(_2\)), 1.70 (2H, quintet, C\(_2\)H\(_2\)), 1.47 (2H, hexet, CH\(_3\)), 1.47 (2H, d, \(J\) 7.2 Hz, CH\(_3\)); \(\delta_{\text{C}}\) (50MHz; CD\(_2\)Cl\(_2\)) 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\(_2\)H\(_2\)), 31.41 (C\(_2\)H\(_2\)), 20.61 (C\(_2\)H\(_2\)), 13.91 (C\(_3\)H\(_3\)); m/z (EI) 194 (M\(^+\), 69%) (Found: M\(^+\), 194.1055. C\(_{10}\)H\(_{14}\)N\(_2\)O\(_2\) 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 precipitate 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%); \(\lambda_{\text{max}}\) (DCM)/nm 237 (log \(\varepsilon\) 4.20), 272 (3.91), 296 (3.87); \(\nu_{\text{max}}\) (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; \(\delta_{\text{H}}\) (200MHz; CD\(_2\)Cl\(_2\)) 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, NCH\(_2\)), 1.59 (2H, quintet, CH\(_2\)), 1.39 (2H, heptet, CH\(_2\)), 0.97 (3H, t, \(J\) 7.1 Hz, CH\(_3\)); \(\delta_{\text{C}}\) (50MHz; CD\(_2\)Cl\(_2\)) 143.51, 142.07, 134.43, 129.84, 129.48 (Ar \(C\)), 125.41 (Ar \(C\)), 124.23 (Ar \(C\)), 119.29 (Ar \(C\)), 116.38 (Ar \(C\)), 116.01 (Ar \(C\)), 35.14 (NCH\(_2\)), 34.41 (CH\(_3\)), 22.76 (CH\(_2\)), 14.15 (CH\(_3\)); 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 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%); \(\lambda_{\text{max}}\) (DCM)/nm 237 (log \(\varepsilon\) 4.20), 272 (3.91), 296 (3.87); \(\nu_{\text{max}}\) (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, 1432w, 1413w, 1342w (Ar NH), 3043w and 3022m (Ar CH), 2962s, 2904m and 2866m (CH\(_2\) and CH\(_3\)), 1612s, 1591m, 1515s, 1500s, 1464m, 1432w, 1413w, 1342w (Ar NH), 3043w and 3022m (Ar CH), 2962s, 2904m and 2866m (CH\(_2\) and CH\(_3\)).
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, NH), 3.80 (2H, br s, NH₂), 1.34 (9H, s, CH₃); δ(50MHz; CD₂Cl₂) 143.33, 142.65, 142.21, 129.72, 126.43 (Ar CH), 125.55 (Ar CH), 124.44 (Ar CH), 119.30 (Ar CH), 116.40 (Ar CH), 115.62 (Ar CH), 34.31 (C(CH₃)₃), 31.72 (CH₃); m/z (EI) 240 (M⁺, 100%) (Found: M⁺, 240.1622. C₁₆H₂₀N₂ 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. C₁₀H₁₆N₂ requires C, 73.17; H, 9.76; N, 17.07%); λ(εDCM)/nm 229 (log ε 3.92), 249 (3.91), 298 (3.57); ν(εDrift/cm⁻¹) 3388s, 3356s, 3317s, 3265m and 3234m (Ar NH), 3066m, 3045m and 3032m (Ar CH), 2966s, 2941s, and 2873s (CH₂ and CH₃), 1635m, 1606m, 1575m, 1558m, 1522m, 1472m, 1377m, 1363m, 1340m, 1315m, 1279m, 1230m, 1207m, 1151m, 1115m, 1043m, 908m, 848m, 754s, 687m, 642m;

δ(200MHz; CD₂Cl₂) 6.87-6.63 (4H, m, Ar H), 3.36 (3H, br s, NH and NH₂), 3.14 (2H, t, J 7.0 Hz, CH₂), 1.69 (2H, quintet, CH₂), 1.52 (2H, hextet, CH₂), 1.03 (3H, t, J 7.2 Hz, CH₃); δ(50MHz; CD₂Cl₂) 138.73, 134.90, 121.02 (Ar CH), 118.70 (Ar CH), 116.71 (Ar CH), 112.00 (Ar CH), 44.58 (NCH₂), 32.45 (CH₂), 14.40 (CH₃); m/z (EI) 164 (M⁺, 100%) (Found: M⁺, 164.1312. C₁₀H₁₆N₂ 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 (H₂O) 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. C₁₈H₁₃FN₄O₄ requires C, 58.31; H, 4.09; N, 14.32%); λ(εDCM)/nm 230 (log ε 4.28), 276 (4.39), 327 (4.18), 360 inf (4.03); ν(εDrift/cm⁻¹) 3379s and 3300s (Ar NH), 3101w and 3039w (Ar CH), 1643m, 1607s, 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(200MHz; DMSO-d₆) 10.02 (1H, br s, NH), 8.94 (1H, d, J_HF 8.0 Hz, Ar H-3), 7.83 (1H, br s, NH), 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(εDCM)/nm 158.60 (d, J_CF 264.9 Hz, Ar CF), 148.39 (d, J_CF 13.3 Hz, Ar CNH), 142.52 (Ar CNH), 139.87 (Ar CNH), 129.01 (Ar CH), 128.76 (Ar CH), 128.45 (Ar CH), 128.26, 126.85, (Ar CH), 125.80, 125.67, 125.61, 120.90 (d, J_CF 12.3 Hz, Ar CH-6), 118.72 (Ar CH), 117.92 (Ar CH), 103.06 (d, J_CF 27.1 Hz, Ar CH-3); m/z (FAB) 368 (M⁺, 100%) (Found: M⁺, 368.0922. C₁₈H₁₃FN₄O₄ 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 (14.75 g, 80 mmol) in EtOH (120 mL) at ca. 20 °C, under argon, 1,5-difluoro-2,4-dinitrobenzene 6 (4.08 g, 20 mmol) 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 (10.48 g, 98.5%) as brick red prisms, mp 219-220 °C (from EtOH) (Found: C, 67.88; H, 4.47; N, 15.94. C30H24N6O4 requires C, 67.67; H, 4.51; N, 15.79%); \( \lambda_{\text{max}} \) (DCM)/nm 231 (log \( \varepsilon \) 4.46), 283 (4.45), 369 inf (4.29); \( \nu_{\text{max}} \) (Drift)/cm\(^{-1}\) 3402s, 3379s, 3336s and 3321s (Ar NH), 3186w, 3089m, 3077m and 3046m (Ar CH), 1605m, 1592m, 1585m, 1564m, 1555m, 1530m, 1493m, 1484m, 1463m, 1424m, 1335m, 1318m, 1279m, 1254m, 1161m, 1104m, 1028w, 971w, 947w, 897w, 744m, 690m; \( \delta_{\text{H}} \) (400MHz; DMSO-\( d_6 \)) 9.42 (2H, s, NH), 8.98 (1H, s, H-3), 7.17-7.10 (10H, m, Ar H), 6.90-6.78 (8H, m, Ar H), 5.97 (1H, s, H-6); one carbon signal missing

\[ \delta_{\text{C}} \] (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, 118.28, 117.69, 95.01 (CH-3); m/z (FAB) 532 (M +, 100%) (Found: M +, 532.1876. C30H24N6O4 requires M, 532.1859).

Method 2. To a stirred solution of N-phenyl-1,2-benzenediamine 5a (7.38 g, 40 mmol) in EtOH (120 mL) at ca. 20 °C, under argon, 1,5-difluoro-2,4-dinitrobenzene 6 (4.08 g, 20 mmol) was added in one portion. The color of the reaction mixture became orange-red and Hünig’s base (7 mL, 40 mmol) 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 (9.68 g, 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. C38H40N6O4 requires C, 70.81; H, 6.21; N, 13.04%); \( \lambda_{\text{max}} \) (DCM)/nm 230 (log \( \varepsilon \) 4.44), 283 (4.54), 331 (4.39), 375 (4.21); \( \nu_{\text{max}} \) (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, 1248s, 1247s, 1202m, 1160m, 1121w, 1104m, 1076m, 1043w, 926w, 897m, 829m, 820m, 810m, 753m, 742m, 627w; \( \delta_{\text{H}} \) (500MHz; DMSO-\( d_6 \)) 9.39 (2H, s, NH), 8.98 (1H, s, H-3), 7.48 (2H, s, PhNH), 7.12-7.07 (10H, 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 CH\(_2\)), 1.50-1.44 (4H, quintet, CH\(_2\)), 1.30-1.23 (4H, sextet, CH\(_2\)), 0.87 (6H, t, J 7.6 Hz, CH\(_3\)); one carbon signal missing \( \delta_{\text{C}} \) (125MHz; DMSO-\( d_6 \)) 146.69 (Ar CNH), 140.21 (Ar CNH), 139.94 (Ar CNH), 134.79 (Ar CNH), 128.64, 127.53, 127.38, 125.93, 125.01, 119.84,
119.02, 116.88, 94.97 (CH-3), 34.17 (Ar CH2), 33.32 (CH2), 21.68 (CH2), 13.77 (CH3); m/z (FAB) 644 (M+, 100%) (Found: M+, 644.3121. C38H40N6O2 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. C38H40N6O4 requires C, 70.81; H, 6.21; N, 13.04%); λmax(DCM)/nm 231 (log ε 4.43), 285 (4.61), 331 (4.48), 365 inf (4.28); νmax(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, 877w, 843m, 829m, 745w; δH(400MHz; CD2Cl2) 9.33 (2H, s, NH), 9.26 (1H, s, H-3), 7.23 (4H, d, J 8.6 Hz, Ar), 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, PhNH), 1.27 (18H, s, CH3); δC(50MHz; CD2Cl2) 148.02 (Ar C), 146.05 (Ar C), 141.01 (Ar CNH), 112.19, 128.88, 128.02, 126.65, 125.62, 120.94, 120.26, 116.93, 96.87 (CH3), 34.67 (CMe3), 31.72 (CH3); m/z (EI) 644 (M+, 5%) (Found: M+, 644.3117. C38H40N6O4 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. C26H32N6O4 requires C, 63.41; H, 6.50; N, 17.07%); λmax(DCM)/nm 230 (log ε 4.46), 244 (4.46), 331 (4.42), 365 inf (4.25); νmax(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; δH(200MHz; CD2Cl2) 9.24 (1H, s, H-3), 9.21 (2H, br s, NH), 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, NH), 3.03-2.97 (4H, m, NCH2), 1.59-1.14 (8H, m, CH2), 0.93 (6H, t, J 7.1 Hz, CH3); δC(50MHz; CD2Cl2) 148.14, 144.76, 129.28 (Ar CH), 129.22 (Ar CH), 127.44 (Ar CH), 126.06, 122.57, 117.04 (Ar CH), 111.85 (Ar CH), 96.94 (Ar CH), 43.80 (NCH2), 32.05 (CH2), 20.86 (CH2), 14.23 (CH3); m/z (FAB) 492 (M+, 100%) (Found: M+, 492.2491. C26H32N6O4 requires M, 492.2485).

Preparation of unsymmetrical derivative 1-[N-(N'-4-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. C34H32N6O4 requires C, 69.39; H,
5.44; N, 14.29%; \( \lambda_{\text{max}}(\text{DCM})/\text{nm} \) 229 (log \( \varepsilon \) 4.42), 284 (4.54), 331 (4.40), 374 (4.21); 

\( \nu_{\text{max}}(\text{Drift})/\text{cm}^{-1} \) 3411m, 3382m, 3373s and 3327s, (Ar NH), 3064w and 3040w (Ar CH), 2962m, 2901w, 2866w, 1619s, 1585s, 1518s, 1482s, 1465s, 1459s, 1409s, 1361m, 1339s, 1324s, 1313s, 1287s, 1247s, 1204s, 1191s, 1158m, 1123w, 1102w, 1068m, 932w, 897w, 835w, 781w, 740m, 694m; 

\( \delta_{\text{H}}(200\text{MHz}; \text{CD}_2\text{Cl}_2) \) 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, NH), 5.81 (1H, s, N-H), 1.32 (9H, s, C-H); one peak missing

\( \delta_{\text{C}}(50\text{MHz}; \text{CD}_2\text{Cl}_2) \) 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 (CCH_3), 31.58 (CCH_3); 

\( \text{m/z} \) (FAB) 588 (M +, 100%) (Found: M +, 588.2486. C_34H_32N_6O_4 requires M, 588.2485).

5,7-Diphenyl-5H,12H-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 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_30H_28N_4 requires C, 76.27; H, 5.93; N, 17.79%); 

\( \lambda_{\text{max}}(\text{DCM})/\text{nm} \) 241 (log \( \varepsilon \) 4.61), 300 inf (4.32); 

\( \nu_{\text{max}}(\text{Drift})/\text{cm}^{-1} \) 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; 

\( \delta_{\text{H}}(500\text{MHz}; \text{DMSO-d}_6) \) 7.21 (2H, s, PhNH), 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_4N_2 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_4N_2 H-3 or 6), 5.98 (2H, s, NH), 4.48 (4H, s, NH_2); \( \delta_{\text{C}}(500\text{MHz}; \text{DMSO-d}_6) \) 146.14, 142.92, 141.92, 129.15, 128.79, 125.64, 124.27, 123.13, 118.12, 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-PhNHCH_2PHNH_2, 95) (Found: M^+, 472.2383. C_30H_28N_6 requires M, 472.2375).
(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 2h 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. C₃₀H₂₀N₄ requires C, 82.57; H, 4.59; N, 12.84%); λₘₐₓ(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); νₘₐₓ(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; ¹H NMR assignments supported by NOE experiment δₜₜ(500MHz; CD₂Cl₂) 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; CD₂Cl₂) 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. C₃₀H₂₀N₄ 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 7h 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 3h 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)-5H,12H-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. C₃₈H₃₆N₄ requires C, 83.21; H, 6.57; N, 10.22%); λₒ 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 (CH₂ and CH₃), 1615w, 1602w, 1592w, 1592w, 1588m, 1559s, 1549m, 1539m, 1507s, 1441s, 1365m, 1352s, 1333s, 1308s, 1249m, 1227w, 1194m, 1178m, 1141m, 1101m, 1081w, 1022w, 972w, 918w, 836w, 823m, 816m, 770w, 731m, 672w, 642w, 608m, 589w; δ_H(500MHz; CD₂Cl₂) 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 CH₂), 1.60 (4H, m, CH₂), 1.43 (4H, m, CH₂), 1.01 (6H, t, J 7.3 Hz, CH₃); δ_C(100MHz; CD₂Cl₂) 153.58, 150.70, 145.90, 144.72, 143.99, 134.11, 131.21, 127.91, 127.38, 127.10, 125.70, 122.58, 116.46, 103.79 (Ar CH), 14.19. C₂₆H₂₈N₄ requires C, 78.79; H, 7.07; N, 14.14%; λₒ 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 (CH2 and CH3), 1612w, 1562s, 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; CD2Cl2) 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, NCH2), 1.70-1.65 (4H, quintet, CH2), 1.54-1.50 (4H, heptet, CH2), 1.04 (6H, t, J 7.4 Hz, CH3); δ(C) (125MHz; CD2Cl2) 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 (NCH2), 28.43 (CH2), 20.82 (CH2), 14.16 (CH3); m/z (FAB) 397 (MH+, 100%) (Found: MH+, 397.2390. C29H22N4 requires C, 64.36; H, 3.98; N, 9.69%);

5-(4-t-Butylphenyl)-7-phenyl-5H,12H-quinazino[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. C34H29N4 requires C, 82.93; H, 5.69; N, 11.38%); ω(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); ω(max)(Drift)/cm−1 3064w and 3024w (Ar CH), 2966m, 2904w and 2872w (Ar CH), 1615w, 1590w, 1562s, 1537m, 1508s, 1442m, 1399w, 1367m, 1354w, 1324m, 1244m, 1233m, 1170m, 1153m, 1125w, 1071w, 1027w, 1001w, 966w, 933w, 883w, 812s, 784w, 760m (Ar CH), 2958s, 2931s and 2866m (CH2 and CH3), 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; CD2Cl2) 7.46-7.42 (4H, m, N-Ar H3e), 7.38 (1H, s, H-13), 7.30 (1H, d, J 8.7 Hz, H-9), 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, CH3); observable carbon signals, δ(C) (125MHz; CD2Cl2) 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 (Cme3), 31.64 (CH3); m/z (FAB) 493 (MH+), 100% (Found: MH+, 493.2385. C34H29N4 requires MH+, 493.2392).

12-Methyl-5,7-diphenyl-5H,12H-quinazino[2,3-b]phenazinium iodide (10). To a stirred solution of 5,7-diphenyl-5H,12H-quinazino[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. C31H23IN4 requires C, 64.36; H, 3.98; N, 9.69%); ω(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); ω(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); ω(max)(Drift)/cm−1 3068w, 3050w and 3021w (Ar CH), 2963w (CH3), 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; CD2Cl2) 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, CH3); δC(125MHz; CD2Cl2) 149.44, 148.70, 142.18, 140.39, 138.86, 136.26, 135.47, 133.11, 132.21 (Ph CH), 132.07, 131.80 (Ph CH), 131.68, 131.15, 131.07, 131.02, 130.23, 129.28, 128.25 (Ph CH), 128.04, 127.24 (Ph CH), 124.65, 118.25, 117.75, 115.16, 104.02, 95.07, 35.27 (CH3); m/z (EI) 451 (M+-I, 45%), 128 (HI, 100) (Found: M+-I, 451.1918. C31H23N4 requires M-I, 451.1923).

12,14-Dihydro-5,7-diphenyl-5H,12H-quinoxalino[2,3-b]phenazinium bisperchlorate (11). To a suspension of 5,7-diphenyl-5H,12H-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. C30H22Cl2N4O8 requires C, 56.60; H, 3.46; N, 8.81%); λmax(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); λmax[EtOH/(aq.) HClO4]/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); νmax(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 (ClO4), 1004w, 977w, 931w, 836w, 773m, 697m, 686m, 625m; δH(500MHz; CD3CN) 11.97 (2H, br s, NH), 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); δC(125MHz; CD3CN) 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.2ClO4, 55%) (Found: M+-H.2ClO4, 437.1766). C31H21N4 requires M-H.2ClO4, 437.1766).

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References