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Synthesis of the Novel Pyrrolo[2,1-d][1,2,5]benzotriazepine, Pyrrolo[2,1-e][1,3,6]benzotriazocine and Pyrrolo[1,2-a]tetrazolo[1,5-d][1,4]benzodiazepine Ring Systems. A New Route to Pyrrolo[1,2-a]quinoxaline via Transamination of in Situ Generated 1-(2-Aminophenyl)-2-iminomethylpyrroles

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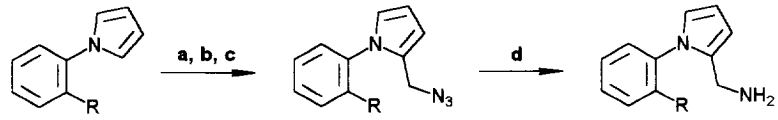
Abstract: Selective reduction of 2-azidomethyl-1-(2-nitrophenyl)pyrrole **5** afforded 2-aminomethyl-1-(2-nitrophenyl)pyrrole **10**. Pyrrolo[1,2-a]quinoxaline **15** is obtained by treating amino-ester **12** with formaldehyde. Diamine **8** reacts with either formaldehyde or benzaldehyde to give pyrrolo[1,2-a]quinoxaline **19**. Compound **10** was reductively cyclised to pyrrolo[2,1-d][1,2,5]-benzotriazepine **22**. Intramolecular coupling of diamine **8** with triphosgene or carbon disulfide yields pyrrolo[2,1-e][1,3,6]benzotriazocine **23** and **24**, respectively. Intramolecular 1,3-dipolar cycloaddition of cyanoazide **6** gives pyrrolo[1,2-a]tetrazolo[1,5-d][1,4]benzodiazepine **25**.

The anthramycins are an important group of naturally-occurring DNA-interactive antitumour antibiotics. They possess the pyrrolo[2,1-c][1,4]benzodiazepine ring system that can recognise and bind to specific sequences of DNA. However, the pronounced antitumour activity of these drugs is accompanied by dose-limiting cardiotoxicity and acute tissue necrosis at the site of injection.[1] Recently, we began a program aimed at synthesising structurally related analogues of these compounds for biological study. So far we have synthesized several examples of the pyrrolo[1,2-a][1,4]benzodiazepine, pyrrolo[2,1-c][1,4]benzodiazocine and pyrrolo[2,1-b][1,3]benzodiazepine ring systems. These compounds have been prepared by intramolecular cyclisation of appropriately substituted 2-aminomethyl-1-arylpyrroles,[2] 2-aminomethyl-1-benzylpyrroles[3] or 1-(2-ethoxy-carbonylbenzyl)-2-nitropyrrole,[4] respectively. 2-Aminomethyl-1-arylpyrroles **7-9** have been synthesized *via* a three step reaction sequence, by converting 1-arylpyrroles **1-3** to Mannich bases, iodomethylating the Mannich bases to quaternary salts, and displacing trimethylamine from the quaternary salts by azide anion to give azides **4-6**, which are then catalytically reduced as shown in Scheme 1.[2]



1: R = H
2: R = NO_2
3: R = CN

4: R = H
5: R = NO_2
6: R = CN

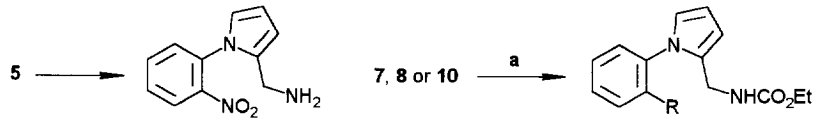
7: R = H
8: R = NH_2
9: R = CN

Reagents: a) CH_2O, $Me_2NH.HCl$, EtOH, reflux **c)** NaN_3, 18-crown-6, dioxan, reflux
b) MeI, Et_2O, room temperature **d)** H_2, Pd-C, MeOH, 3 atmospheres

Scheme 1

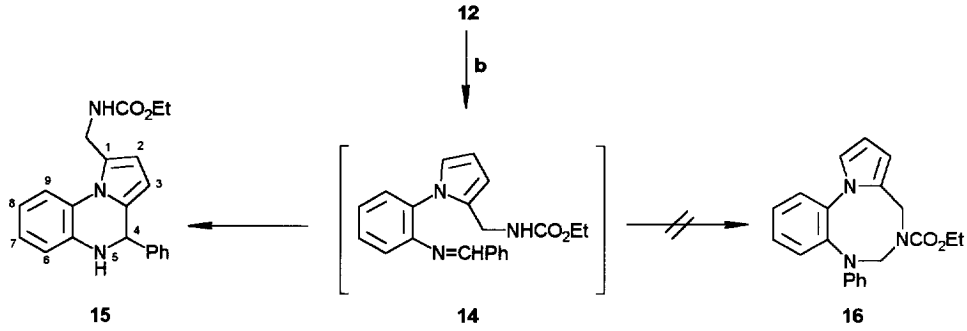
We report here further studies on the chemistry of 2-azidomethyl-1-(2-nitrophenyl)pyrrole **5**, 2-azidomethyl-1-(2-cyanophenyl)pyrrole **6** and 1-(2-aminophenyl)-2-aminomethylpyrrole **8**, which have been used as precursors for the preparation of tricycles **18**, **22**, **25-27** and tetracycle **28**.

Pyrrole **10** was chosen as a useful precursor for the synthesis of novel tricycles since it possesses both electrophilic and nucleophilic groups. It was synthesised by selectively reducing the azido group of pyrrole **5**. This was accomplished *via* the Staudinger reaction followed by subsequent hydrolysis of the intermediate iminophosphorane. Thus, although reaction with triphenylphosphine[5] failed, with tributylphosphine a 72% yield of 2-azidomethylpyrrole **5** was obtained. 2-Aminomethylpyrroles **7**, **8** and **10** were treated with ethyl chloroformate in tetrahydrofuran containing triethylamine to yield the corresponding 2-ethoxycarbonyl-aminomethyl derivatives **11**, **12** and **13** in 88, 70 and 81% yields, respectively. Attempted cyclisation of aminoester **12** in refluxing pyridine, or toluene containing p-toluenesulfonic acid, or with trimethylaluminium in dichloromethane at room temperature,[6] failed. Reduction of nitroester **13** with sodium borohydride in the presence of 10% palladium on carbon and 2% aqueous sodium hydroxide, reaction conditions that are known to reduce aromatic nitro compounds to hydroxylamines,[7] gave aminoester **12**. Treatment of the latter with an equivalent of benzaldehyde in pyridine afforded 4,5-dihydropyrroloquinoxaline **15** and not pyrrolo-benzotriazocine **16** as predicted. The postulated intermediate for this reaction is imine **14** (Scheme 2). This type of intramolecular cyclisation of 1-arylpyrroles has been reported in 1971 by Cheeseman and Rafiq.[8]



10

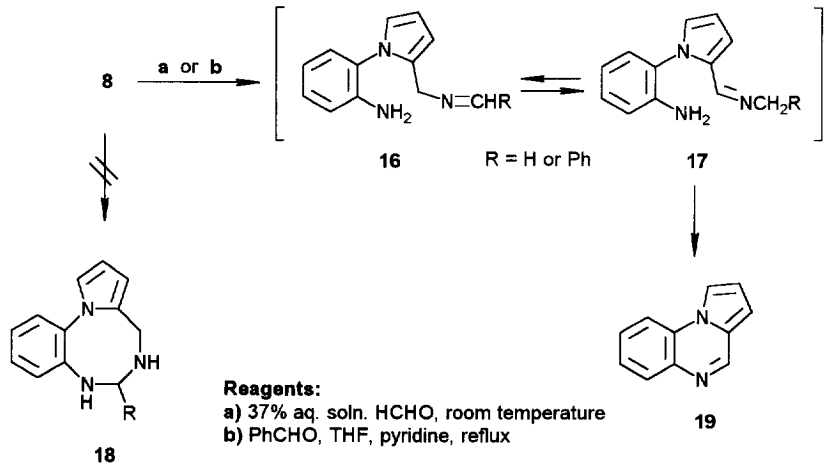
11: R = H
12: R = NH_2
13: R = NO_2



Reagents: a) $ClCO_2Et$, Et_3N, THF, 0 °C- room temperature, **b)** PhCHO, pyridine, reflux

Scheme 2

Attempted synthesis of the pyrrolobenzotriazocine **18** (R = H or Ph) by reacting diamine **8** with either aqueous formaldehyde at room temperature and then refluxing in pyridine or benzaldehyde in a refluxing mixture of tetrahydrofuran and pyridine, gave instead the known pyrrolo[1,2-a]quinoxaline **19**[9] as the sole product. The reaction with formaldehyde was spontaneous and did not require further heating with pyridine. We propose that the above reactions proceed by initial formation of the imine **16** (R = H or Ph) transamination involving prototropic rearrangement to the corresponding imine **17** (R = H or Ph) and then intramolecular cyclisation to pyrroloquinoxaline **19** with loss of methylamine and aniline, respectively (Scheme 3). This tautomerism for imines containing hydrogen as a substituent on both carbon and nitrogen was first introduced by Ingold and Piggot[10] and since then has been studied in depth.[11] Several applications of the reaction in synthesis have been reported including the conversion of primary amines into carbonyl compounds.[12]

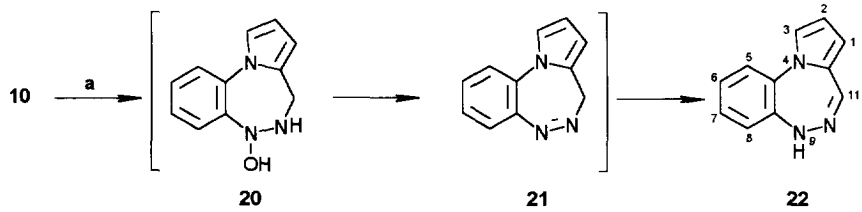


Scheme 3

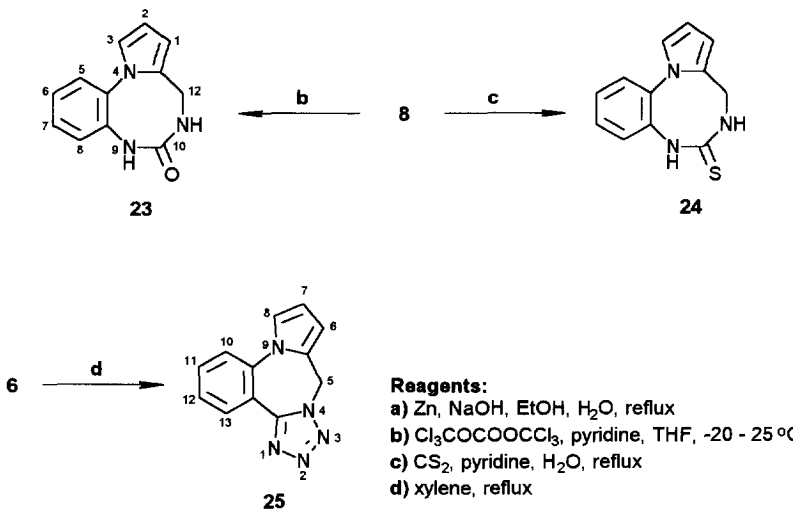
Although the reaction of aromatic nitroso compounds with primary arylamines is well established for the preparation of symmetrical or unsymmetrical azo compounds,[13] intramolecular reactions between alkyl or arylamines and the nitroso group are unknown. Reductive cyclisation of compound **10** with zinc in boiling aqueous sodium hydroxide afforded pyrrolo[2,1-d][1,2,5]benzotriazepine **22**, in 30% yield. Similar reaction conditions have been used for the reductive cyclisation of o-nitrobenzamides to indazolinones.[14] The proposed mechanism (Scheme 4) involves intramolecular coupling between amino and in *situ* generated nitroso group to give intermediate **20**. Under the strongly basic conditions the latter loses water to give azo intermediate **21**, which undergoes prototropic interconversion to hydrazone **22**. We have isolated compound **20** by reductively cyclising compound **10** with zinc and aqueous ammonium chloride. These reaction conditions have been used by Bird and Latif[15] to cyclise 3-hydroxy-2′-hydroxynitrodiphenyl ethers to 3H-phenoxazin-3-ones.

Recently, 1,3-benzodiazocines were prepared by reacting an appropriate diamine with phosgene or carbon disulphide.[16] Phosgene however being a highly toxic gas is difficult and dangerous to handle. In 1987 Eckert and Foster[17] introduced bis(trichloromethyl)carbonate (triphosgene) as a safe alternative. Since then the reagent has been used for several heterocyclic ring closures.[18-20] When diamine **8** was treated with triphosgene in tetrahydrofuran containing pyridine intramolecular coupling occurred to give pyrrolo[2,1-e][1,3,6]benzotriazocine **23** in 45% yield. The corresponding thioxo derivative **24** was prepared in 57% yield by heating diamine **8** in a mixture of carbon disulphide, water and pyridine (Scheme 4). The IR spectra of compounds **23** and **24** show absorption bands due to the NH groups at 3210 and 3195 cm^{-1} and to the C=O and C=S groups at 1690 and 1610 cm^{-1}, respectively. In the ^1H NMR spectra the methylene groups appear as broad doublets at δ= 3.75 ppm for compound **23** and at δ= 3.82 ppm (J=16.8Hz) and δ= 3.97 ppm (J=16.8Hz) for compound **24**.

Tetrazoles can be synthesised by 1,3-dipolar cycloaddition between aromatic azides and aliphatic or aromatic nitriles.[21] By heating cyanoazide **6** with xylene gave pyrrolotetrazolobenzodiazepine **25** in 88% yield. This is the first example of an intramolecular 1,3-dipolar cycloaddition between an aliphatic azide and an aromatic nitrile.



20 **21** **22**



Scheme 4

EXPERIMENTAL

Mps were recorded on a Büchi 510 apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. Solids were taken as Nujol mulls and liquids as thin films between sodium chloride discs. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. The nmr spectra were measured at 360.1 MHz on a Brüker AM 360 spectrometer or at 400.1 MHz on a Brüker AMX 400 spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained with a JEOL JMS-AX 505W machine.

Analytical TLC was carried out on Fluka silica gel 60 F_{254}. Preparative 'flash' chromatography was carried out using Merck 9385 silica gel. Light petroleum refers to the fraction with bp 40-60 °C. Solvents and reagents were used as received from the manufacturers except for dichloromethane, ethanol, ethyl acetate, methanol and light petroleum which were purified according to methods described by Perrin *et al.*[22]

2-Aminomethyl -1-(2-nitrophenyl)pyrrole (10).

To a stirred solution of the azide **5** (2.4 g, 9.9 mmol) in dry dichloromethane (50 ml) under argon, was added dropwise a solution n-tributylphosphine (2 g, 9.9 mmol) in dry dichloromethane (5 ml). Stirring was continued for 16h at room temperature and then water (50 ml) was added and the mixture stirred vigorously for 36h. The organic phase was separated and the aqueous phase washed with dichloromethane (3 × 15 ml). The combined organic phases were washed with brine, dried, the solvent

evaporated and the residual oil eluted through a flash column with ethyl acetate/methanol (1:1). The second fraction contained **10** (1.56 g, 73%) as a brown oil, bp 130-132 °C/5 mmHg; i.r. (Nujol) 3365 asym (NH), 3285 sym (NH), 1510 asym (NO_2) and 1355 sym (NO_2) cm^{-1}; ^1H n.m.r. δ (400 MHz; $CDCl_3$): 2.01 (s, br, 2H, NH_2), 4.53 (s, 1H, CH_2), 6.25-6.27 (m, 2H, H-3 and H-4), 6.62 (dd, 1H, J=2.6, 1.9Hz, H-5), 7.52 (dd, 1H, J=7.8, 1.2Hz, H-6'), 7.59 (td, 1H, J=7.8, 1.2Hz, H-4'), 7.70 (td, 1H, J=7.8, 1.4Hz, H-5') and 7.96 (dd, 1H, J=7.8, 1.4Hz, H-3'); m/z(%): 217 (M^+, 30), 200 (26), 169 (76), 147 (73), 120 (79) and 105 (36) (Found: m/z 217.0850. $C_{11}H_{11}N_3O_2$ requires: 217.0851)

General Procedure for Preparation of 1-Aryl-2-ethoxycarbonylaminomethylpyrroles (11-13).

To a solution of amines **7**, **8** or **10** (5 mmol) in dry THF (20 ml) containing triethylamine (5 mmol) at 0 °C was added dropwise ethyl chloroformate (5 mmol). The temperature of the mixture was allowed to rise to room temperature for 1h. Triethylamine hydrochloride was filtered off and the solvent evaporated to dryness. The residual oil was purified by flash chromatography (silica, 1:4 ethyl acetate/light petroleum) to afford **11-13**.

2-Ethoxycarbonylaminomethyl-1-phenylpyrrole 11: Obtained as an oil; (88%), b.p. 77-79 °C/11 mmHg; i.r. (neat) 3330 (NH), 1715 (CO) cm^{-1}; ^1H n.m.r. δ (400 MHz; $CDCl_3$): 1.19 (t, 3H, CH_3), 4.05 (q, 2H, CH_2CH_3), 4.30 (d, 2H, CH_2), 4.69 (br s, 1H, NH), 6.21-6.27 (m, 2H, H-3 and H-4), 6.79 (dd, 1H, J=2.8, 1.9, H-5), 7.26-7.48 (m, 5H, benzenoid); m/z(%): 245 [$(M+1)^+$, 96), 215 (32), 199 (19), 171 (16), 156 (100), 77 (6) (Found: m/z 245.2493. $C_{17}H_{17}N_2O_2$ requires 245.2489).

1-(2-Aminophenyl)-2-ethoxycarbonylaminomethylpyrrole 12: Obtained as an oil; (70%); b.p. 98-100 °C/9 mmHg; i.r. (neat) 3370 (NH and NH_2), 1720 (CO) cm^{-1}; ^1H n.m.r. δ (250 MHz; $CDCl_3$) 1.16 (t, 3H, CH_3), 3.51 (br s, 2H, NH_2), 4.17 (q, 2H, CH_2CH_3), 5.13 (br s, 1H, NH), 6.26 (t, 1H, J=2.6Hz, H-4), 6.66 (t, 1H, J= 2.2Hz, H-3), 6.77-6.84 (m, 2H, H-3' and H-5), 7.09-7.26 (m, 3H, benzenoid); m/z(%): 259 (M^+, 4), 169 (100) and 157 (57) (Found: m/z 259.1317. $C_{14}H_{17}N_3O_2$ requires 259.1321).

2-Ethoxycarbonylaminomethyl-1-(2-nitrophenyl)pyrrole 13: Obtained as an oil; (81%), b.p. 48-50 °C/6 mmHg; i.r. (neat) 3330 (NH), 1715 (CO) cm^{-1}; ^1H n.m.r. δ (400 MHz; $CDCl_3$) 1.14 (t, 3H, CH_3), 4.05 (q, 2H, CH_2CH_3), 4.23 (d, 2H, CH_2), 4.78 (br s, 1H, NH), 6.24-6.28 (m, 2H, H-3 and H-4), 6.63 (dd, 1H, J=2.7, 1.9Hz, H-5), 7.48 (dd, 1H, J=7.8, 1.0Hz, H-6'), 7.61 (td, 1H, J=7.8, 1.0 Hz, H-4'), 7.70 (td, 1H, J=7.8, 1.5Hz, H-5'), 7.97 (dd, 1H, J=7.8, 1.5Hz, H-3'); m/z(%): 289 (M^+, 27), 272 (48) 255 (73), 241 (20), 201 (50),183 (29), 169 (100), 155 (87), 143 (45) (Found: m/z 289.1062. $C_{14}H_{15}N_3O_4$ requires 289.1063).

4,5-Dihydro-1-ethoxycarbonylaminomethyl-4-phenylpyrrolo[1,2-a]quinoxaline (15).

A mixture of compound **12** (143 mg, 0.55 mmol) in pyridine (5 ml) containing benzaldehyde (58 mg, 0.55 mmol) was heated under reflux for 16h. The solvent was evaporated under reduced pressure and to the residue water was added and then extracted with chloroform and dried (sodium sulfate). After removal of chloroform the residue was purified by flash chromatography (silica, 1:4 ethyl acetate/light petroleum) to give compound **15** (95 mg, 50%), m.p. 135-137 °C (off-white plates from 2-propanol); i.r. (nujol) 3400 (NH), 3310 (NH), 1705 (CO) cm^{-1}; ^1H n.m.r. δ (360 MHz; $CDCl_3$) 1.70 (t, 3H, CH_3), 4.02 (q, 2H, CH_2CH_3), 4.44 (d, 2H, CH_2NH), 5.36 (s, 1H, H-4), 5.46 (d, 1H, J=3.3Hz, H-2), 6.07 (d, 1H, J=3.3Hz, H-3), 6.58 (s, br, 1H, NH), 6.71-7.4 (m, 9H, benzenoid), 7.62 (t, 1H, $NHCH_2$); m/z(%): 347 (M^+, 71), 270 (100) 245 (56), 181 (9), 113 (6), 77 (2) (Found: m/z 347.1622. $C_{21}H_{21}N_3O_2$ requires 347.1634).

Pyrrolo[1,2-a]quinoxaline (19).

Method A. A mixture of diamine **8** (0.5g, 2.75 mmol), formaldehyde (0.22 ml, 2.75 mmol, 36.5% aqueous solution), pyridine (10 ml) and ethanol (10 ml) was heated under reflux for 12h. The solvents were evaporated and the residue purified by flash chromatography (silica, 1:4 ethyl acetate/light petroleum) to give compound **19** (0.34 g, 74%).

Method B. Compound **19** was prepared in 58% yield by the same experimental method used for the synthesis of compounds **15**. Compound **19** obtained from Methods A and B was identical in all respects with an authentic sample of pyrrolo[1,2-a]quinoxaline.[9]

8-Hydroxy-11H-pyrrolo[2,1-d][1,2,5]benzotriazepine (20).

To a stirred solution of nitroamine **10** (1.22 g, 1 mmol) in ethanol (15 ml) was added a solution of ammonium chloride (0.16g, 3 mmol) in water (5 ml). The mixture was cooled to -5 - 0 °C, zinc dust (0.4 g, 6 mmol) was added and left stirring for 30 minutes. The reaction mixture was then filtered and concentrated in vacuo to about 5 ml. Water (20 ml) was added, extracted with dichloromethane (3 × 10 ml), the combined extracts dried with anhydrous sodium sulfate and the solvent evaporated. The oily residue was eluted through a flash column (silica, ethyl acetate, 8:1 ethyl acetate/methanol) to give in the second fraction compound **20** (0.12 g, 58%) as a deep orange viscous oil; i.r. (neat) 3400 broad (NH) and (OH) cm^{-1}; ^1H n.m.r. δ (400 MHz; $CDCl_3$) 3.87-3.95 (m, 2H, CH_2), 4.01 (s, br, 1H, NH), 6.24 (t, 1H, $J_{1,2}$=3.2Hz, H-1), 6.44 (dd, 1H, $J_{2,3}$=3.4Hz, H-2), 6.65 (dd, 1H, $J_{3,1}$=2.6Hz, H-3), 6.76 (td, 2H, J=7.6, 1.3Hz, H-6 and s, br, 1H, OH), 6.93 (dd, 1H, J=7.6, 1.3Hz, H-8), 7.06 (dd, 1H, J=7.6, 1.5Hz, H-5), 7.20 (td, 1H, J=7.6, 1.5Hz, H-7).

Pyrrolo[2,1-d][1,2,5]benzotriazepine (22).

A stirred solution of nitroamine **10** (0.15 g, 0.75 mmol), sodium hydroxide (0.06 g, 1.84 mmol) ethanol (6 ml) and water (3 ml) was treated with zinc dust (0.09 g, 2.76 mmol) and the resulting mixture heated under reflux for 3h. The reaction mixture was filtered, concentrated to about one-third of its volume, water (10 ml) added and the pH adjusted to 7.5-8 by the addition of dilute hydrochloric acid. The oily suspension was extracted with dichloromethane (3 × 5 ml) and the combined organic extracts dried over anhydrous sodium sulfate and evaporated to give a solid which was recrystallized from toluene/hexane to afford **22** (0.06 g, 45%), m.p. 117-119°C (pale yellow microcrystals). (Found: C, 72.23; H, 5.01; N, 22.64. $C_{11}H_9N_3$ requires C, 72.11; H, 4.95; N, 22.73); i.r. (Nujol) 3370 (NH), 1620 (C=N) cm^{-1}; ^1H n.m.r. δ (400 MHz; $CDCl_3$): 6.32 (t, 1H, $J_{2,3}$=3.0Hz, H-2), 6.45 (dd, 1H, $J_{1,2}$=3.6Hz, H-1), 6.67 (br, 1H, NH), 6.85 (dd, 1H, J=7.7, 1.4Hz, H-8), 7.06 (td, 1H, J=7.7, 1.5Hz, H-6), 7.10-7.12 (m, 2H, H-3 and H-5), 7.15 (td, 1H, J=7.7, 1.6Hz, H-7), 7.45 (s, 1H, H-11); m/z (%): 184 [$(M+1)^+$,100], 183 (M^+, 63), 169 (18), 155 (200), 131 (6), 77 (13).

9,10-Dihydro-10-oxo-12H-pyrrolo[2,1-e][1,3,6]benzotriazocine (23).

To a solution of diamine **8** (0.2 g, 1.1 mmol) in dry tetrahydrofuran (10 ml) and dry pyridine (0.1 ml) at -20 °C was slowly added triphosgene (0.11 g, 0.36 mmol). The mixture was stirred at -20 °C for 4h and then at room temperature for 16h. The solvents were removed under *vacuo*, water (25 ml) was added to the residue and the mixture extracted with dichloromethane (3 × 10 ml). The combined extracts were dried over anhydrous sodium sulfate, the solvent was evaporated, and the residue was recrystallised from ethyl acetate to give **23** (0.12 g, 54%), m.p. 237-238 °C (colourless needles). (Found: C, 67.52; H, 5.36; N, 19.76. $C_{12}H_{11}N_3O$ requires C, 67.59; H, 5.20; N, 19.71); i.r. (Nujol) 3210 (NH), 1690 (CO) cm^{-1}; ^1H n.m.r. δ (400 MHz; DMSO-d_6): 3.75 (d, br, 2H, CH_2), 6.15 (dd, 1H, $J_{1,2}$=3.8Hz, H-1), 6.21 (t, 1H, $J_{2,3}$=3.6Hz, H-2), 6.86 (t, 1H, NH), 6.98 (dd, 1H, $J_{3,1}$=3.1Hz, H-3), 7.27-7.43 (4 H, m, benzenoid); m/z (%): 213 (M^+, 46), 169 (100), 129 (2), 84 (6).

9,10-Dihydro-10-thioxo-12H-pyrrolo[2,1-e][1,3,6]benzotriazocine (24).

A mixture of diamine **8** (0.3 g, 1.6 mmol), carbon disulphide (3 ml), pyridine (3 ml) and water (3 ml) was heated under reflux for 16h. The solvents were evaporated and to the residue acetone (1 ml) and water (3 ml) were added. The resulting solution was acidified with 4N hydrochloric acid to pH 2. The precipitated solid was filtered off, washed with water, ethanol and dried. Flash chromatography of the solid (silica, 0.5:1:4 chloroform/ethyl acetate/light petroleum) gave **24** (0.21 g, 57%), mp 194-195 °C (off-white needles from 2-propanol). (Found: C, 62.61; H, 4.28; N, 18.25. $C_{12}H_{11}N_3S$ requires C, 62.86;

H, 4.84; N, 18.33); i.r. (Nujol) 3195 (NH) and 1610 (CS) cm^{-1}; ^1H n.m.r. δ (400 MHz; DMSO-d_6): 3.82 (d, 1H, J=16.8Hz, H_a-12), 3.97 (d, 1H, J=16.8Hz, H_b-12), 6.19 (dd, 1H, J=3.7, 1.7Hz, H-2), 6.24 (t, 1H, J=3.6, H-3), 7.07 (dd, 1H, J=3.1, 1.8Hz, H-1), 7.30-7.47 (m, 4H, benzenoid) 8.76 (br s, 1H, *NH*CH_2) and 9.61 (s, 1H, NH); *m/z(%):* 229 (M^+, 86), 195 (84), 169 (100), 116 (31) and 70 (83).

5H-Pyrrolo[1,2-a]tetrazolo[1,5-d][1,4]benzodiazepine (25).

A stirred solution of azide **6** (1 g, 4.5 mmol) in xylene (80 ml) was heated under reflux for 48h. After cooling, activated charcoal (0.2 g) was added and the mixture heated with stirring for 5 min. The charcoal was filtered off and the solvent was evaporated under reduced pressure to give a residue which was crystallised from toluene. Recrystallisation from toluene gave compound **25** (0.88 g, 88%), m.p. 150-152 °C (colourless needles). (Found: C, 64.52; H, 4.24; N, 31.25. $C_{12}H_9N_5$ requires C, 64.56; H, 4.06; N, 31.38); ^1H n.m.r. δ (360 MHz; DMSO-d_6): 5.81 (s, 2H, CH_2), 6.33 (t, 1H, J=3.1Hz, H-7), 6.47 (dd, 1H, J=3.4, 1.7Hz, H-6), 7.38 (dd, 1H, J=3.8, 1.8Hz, H-8), 7.59 (td, 1H, J=7.0, 1.6Hz, H-11), 7.78-7.86 (m, 2H, H-10 and H-12), 8.08 (dd, 1H, J=7.3, 0.9Hz, H-13); m/z (%): 223 (M^+, 54), 194 (100), 162 (12), 151 (11), 113 (10).

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