New Quinoxalines with Nitrogen Functions in the Side Chain. Potential Inhibitors of 5-HT_3

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Starting with benzofuroxane **1**, 2-ethoxy-carbonyl-3-methylquinoxaline 1,4-dioxide **7** is obtained. From this compound different amides **5a-q** and amino esters **6a-c** are obtained. From 2-amino-3-cyanoquinoxaline 1,4-dioxide **7**, new amidines **9**, [5,4-*b*]pyrimido **10** and [6,5-*b*]diazepinoquinoxalines **11** were prepared.

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We have recently communicated the results found, as inhibitors of 5-HT_3, in new 2-cyano-3-piperazinylquinoxalines [1] and in esters and amides derived from piperazinylquinoxalines [2].

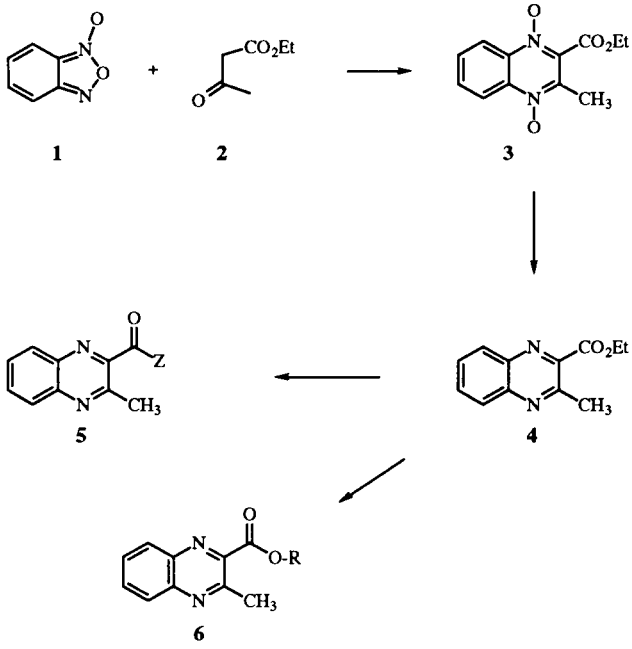
Interest in the biological activity found, has motivated us to prepare new series of quinoxaline without a piperazine residue in position 2, with the aim of investigating the contribution of the quinoxaline ring to the biological activity being studied.

The proposed structures are quinoxalines with substituents in positions 2 and 3. In short, on the one hand, esters and amides with substituents that have shown important activity in the given receptor are suggested and on the other hand, amines in the positions considered, are proposed.

From a merely structural standpoint, the quinoxalines with an amine function in the side chain have been studied very little in spite of the important biological activity found in some of the examples described [3].

An important review on the present interest of the 5-HT_3 antagonists can be found in the works of Zifa [4] and of Aapro [5].

Scheme 1



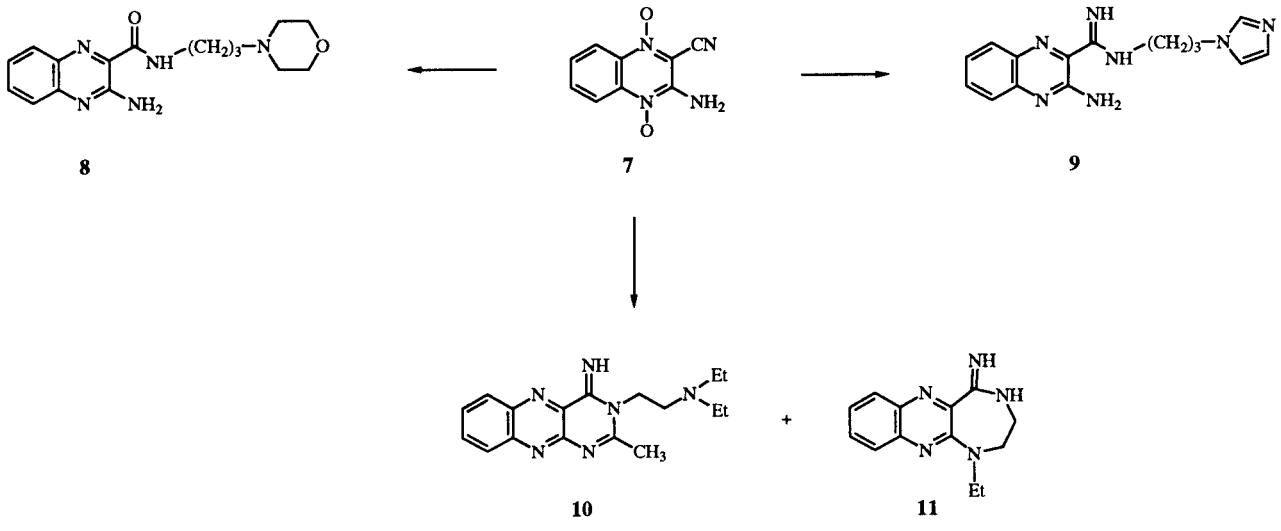
By reacting benzofuroxane with ethyl acetylacetate in basic medium, as described earlier [6], 2-ethoxycarbonyl-3-methylquinoxaline 1,4-dioxide, **3**, is obtained (Scheme 1). This product is reduced with sodium dithionite to 2-ethoxycarbonyl-3-methylquinoxaline, **4** [7]. By reacting this latter compound with different amines, the corresponding amides **5a-g** are obtained. By reaction with different *N,N*-disubstituted aminoalcohols, the corresponding esters **6a, 6b** and **6c** are obtained and unequivocally identified.

The synthesis of amides derived from 2-aminoquinoxaline, **8**, was proposed with the purpose of considering structures that permit the establishment of an intramolecular hydrogen bond which is of interest in the 5-HT_3 activity. Initially, this synthesis was attempted starting from 2-amino-3-cyanoquinoxaline, but without success. Another alternative considered was the utilization of 2-amino-3-cyanoquinoxaline 1,4-dioxide, **7** (Scheme 2), as the starting material, with the purpose of increasing the reactivity of the substituents 2 and 3 of the quinoxaline ring against nucleophilics [8] and in this way 2-amino-3-[*N*-(3-morpholinopropyl)carbamoyl]quinoxaline, **8**, is obtained. Besides the addition reaction of the amine to the nitrile group, the corresponding hydrolysis of the system is produced.

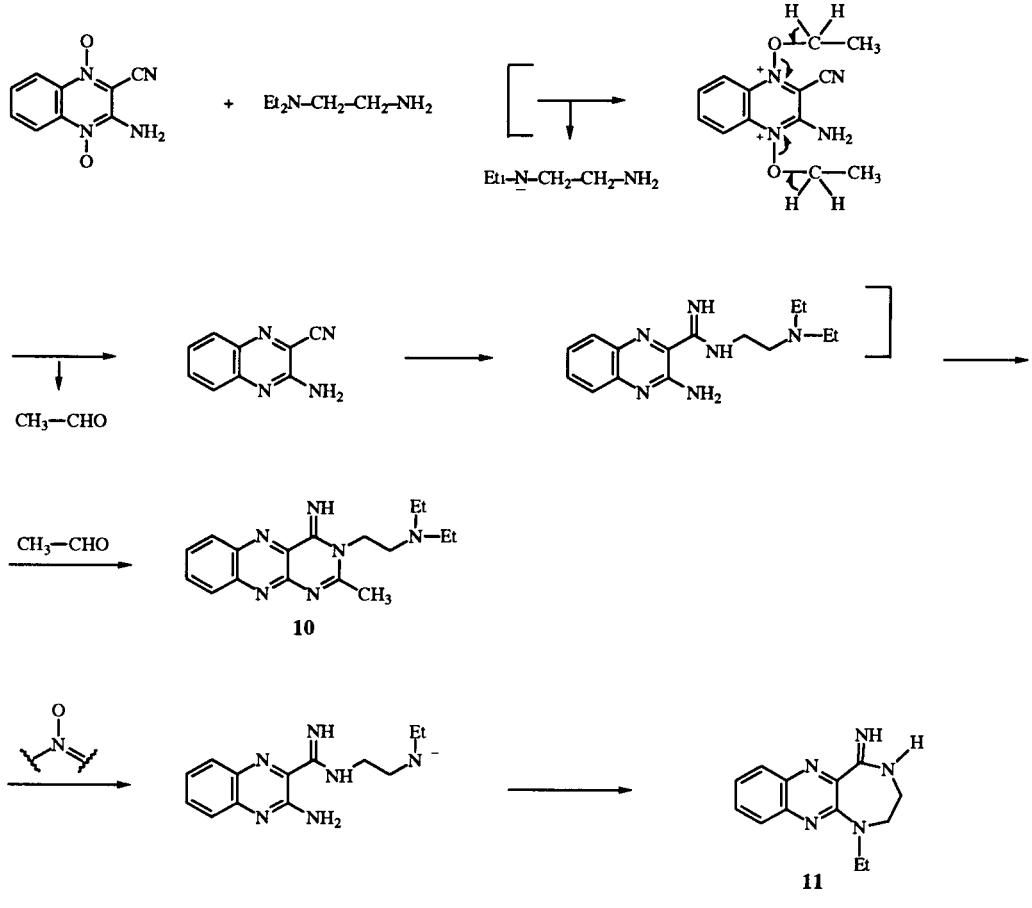
When the reaction is carried out with another amine, 1-(3-aminopropyl)imidazole, the amide analogous to the described, **8**, is not obtained. What is obtained, however, is the corresponding amidine **9**, a product which is expected in the additions of nucleophilics to nitriles [9].

Yet when the reaction is carried out with 2-diethylaminoethylamine, it is not the amidine, rather the product **10**, 3-(2-diethylaminoethyl)-3,4-dihydro-4-imino-2-methylpyrimido[5,4-*b*]quinoxaline, that which is isolated. This reaction can be related to an oxidative dealkylation, described earlier in the reduction of *N*-oxides with dimethylamine [10,11] and recorded in Scheme 3. In the same reaction,

Scheme 2



Scheme 3



another compound, **11**, identified as 1-ethyl-5-imino-1,4-diazepino[6,5-*b*]quinoxaline, is isolated. This compound could have been formed as a consequence of an oxidative dealkylation of the quinoxaline *N*-oxide on the molecule of the intermediate amidine, Scheme 3.

EXPERIMENTAL

Melting points were determined with a Mettler FP82 + FP80 apparatus and are uncorrected. Elemental analyses were obtained from vaccum-dried samples (over phosphorus pentoxide at 3-4 mm Hg, 24 hours at about 60-70°). Infrared spectra were recorded on a Perkin-Elmer 681 apparatus, using potassium bromide tablets for solid products and sodium chloride plates for liquid products; the frequencies are expressed in cm^{-1}. The ^{1}H-nmr spectra were obtained on a Bruker AC-200E (200 MHz) instrument, with tetramethylsilane as the internal reference, at a concentration of about 0.1 g/ml, and with dimethyl sulfoxide-d_6 as the solvent; the chemical shifts are reported in ppm relative to tetramethylsilane (δ units), and the abbreviations (s, m, t) are the usual. The mass spectra were recorded on a Hewlett-Packard 5988-A instrument at 70 eV.

Thin-layer chromatography (tlc) was carried out on silica gel (MN-Kieselgel G, Macherey Nagel, 0.3 mm thickness) with toluene:dioxane:acetic acid (90:25:4) as the solvent and the plates were scanned under ultraviolet light = 254 and 366 nm. Column chromatography was carried out on silica gel 60 Merck (70-230 mesh ASTM) with indicated solvents.

Solvents were usually removed under vaccum or in a rotavapory evaporator when stated.

2-[*N*-(2-diethylaminoethyl)carbamoyl]-3-methylquinoxaline (**5a**).

2-Ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and *N,N*-diethylethylenediamine (5.81 g, 0.05 mole) are refluxed for 1 hour, following the reaction by tlc (methylene chloride:methanol, 9:1). Once the reaction has finalized, methylene chloride (200 ml) is added and the mixture is washed repeatedly with water. The organic layer is dried, concentrated and chromatographed over silica gel, eluting with a mixture of methylene chloride:methanol, 95:5. A yellow oil is obtained, yield 2.16 g (76%); ir (sodium chloride plates): 3410-3080 (m, NH), 2980-2850 (w, C-H aliphat), 1680 (s, C=O), 1510 (m, aromat), 1380 (m, C-N) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.67 (bs, 1H, NH), 8.07 (bs, 2H, H5 and H6 quinoxaline), 7.89 (bs, 2H, H7 and H8 quinoxaline), 3.39-3.29 (m, 2H, NH-CH_2), 2.80 (s, 3H, CH_3), 2.57-2.38 (m, 6H, N-CH_2), 0.90 (t, 6H, CH_3).

Anal. Calcd. for $C_{16}H_{22}N_4O$: C, 67.10; H, 7.74; N, 19.57. Found: C, 66.85; H, 7.48; N, 19.51.

2-Methyl-3-[*N*-(3-morpholinopropyl)carbamoyl]quinoxaline (**5b**).

Starting with 2-ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and *N*-(3-aminopropyl)morpholine (7.21 g, 0.05 mole) and following the general procedure described for obtaining product **5a**, a yellow oil is obtained. This oil crystallized itself rapidly, giving a yellow solid, mp 71-72°, yield 2.4 g (76%); ir (potassium bromide): 3280 (m, N-H), 2860-2820 (w, C-H, aliphat), 1670 (s, C=O), 1500 (m, aromat), 1300 (m, C-N), 1270 (m, C-O), 1120 (s, C-O) cm^{-1}; ^{1}H-nmr (DMSO-d_6) δ: 8.96 (bs, 1H, NH), 8.06 (bs, 2H, H5 and H6 quinoxaline), 7.85 (bs, 2H, H7 and H8 quinoxaline), 3.56 (bs, 4H, -O-CH_2), 3.40 (m, 2H, N-CH_2), 2.84 (s, 3H, CH_3), 2.38 (bs, 6H, N-CH_2), 1.72 (m, 2H, -CH_2-).

Anal. Calcd. for $C_{17}H_{22}N_4O_2$: C, 64.94; H, 7.05; N, 17.82. Found: C, 64.99; H, 7.20; N, 17.80.

2-[*N*-(3-(1-Imidazolyl)propyl)carbamoyl]-3-methylquinoxaline (**5c**).

Starting with 2-ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and 1-(3-aminopropyl)imidazole (6.26 g, 0.05 mole) and following the aforementioned general procedure, a light brown solid is obtained, mp 131-132° (water), yield 2.20 g (75%); ir (potassium bromide): 3410-3240 (m, NH), 2940-2920 (w, C-H aliphat), 1670 (s, C=O), 1510 (m, aromat), 1240 (m, C-N) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.03 (t, 1H, NH), 8.10-7.99 (m, 2H, H5 and H6 quinoxaline), 7.84-7.80 (m, 2H, H7 and H8 quinoxaline), 7.71 (s, 1H, imidazole), 7.23 (s, 1H, imidazole), 6.92 (s, 1H, imidazole), 4.07 (t, 2H, CH_2-imidazole), 3.34 (m, 2H, N-CH_2), 2.83 (s, 3H, CH_3), 2.04 (m, 2H, -CH_2-).

Anal. Calcd. for $C_{16}H_{17}N_5O$: C, 65.06; H, 5.80; N, 23.72. Found: C, 64.90; H, 6.00; N, 23.93.

2-[*N*-(1-(4-Benzylpiperidyl)carbamoyl)]-3-methylquinoxaline (**5d**).

2-Ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and 4-amino-1-benzylpiperidine (9.51 g, 0.05 mole) are refluxed for 3 hours and following the aforementioned general procedure of purification, a red solid is obtained, mp 127-128°, yield 1.60 g (44%); ir (potassium bromide): 3.380 (m, NH), 2920-2760 (w, C-H aliphat), 1670 (s, C=O), 1510 (m, C-C, aromat quartet), 1370 (m, C-N), 700 (m, monosubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.73 (d, 1H, NH), 8.12-7.01 (m, 2H, H5 and H6 quinoxaline), 7.84 (bs, 2H, H7 and H8 quinoxaline), 7.29 (bs, 5H, phenyl), 3.87 (bs, 1H, NH-CH-), 3.45 (s, 2H, N-CH_2Ph), 2.83 (m, 2H, H_{eq} piperidine), 2.77 (s, 3H, CH_3), 2.2 (m, 2H, H_{ax} piperidine), 1.90 (m, 2H, H_{ax} piperidine), 1.60 (m, 2H, H_{eq} piperidine).

Anal. Calcd. for $C_{22}H_{24}N_4O$: C, 73.30; H, 6.71; N, 15.54. Found: C, 73.80; H, 6.98; N, 15.48.

2-Methyl-3-[*N*-(1-piperazinyl)carbonyl]quinoxaline (**5e**).

2-Ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) is melted with piperazine (17.2 g, 0.2 mole). The mixture is refluxed for 4 hours and following the aforementioned general procedure of purification, a beige solid is obtained, mp 142-143°, yield 0.40 g (16%); ir (potassium bromide): 3450 (m, N-H), 2930 (w, C-H aliphat), 1640 (s, C=O), 1560 (m, aromat), 1480 (m, aromat), 1260 (m, C-N) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.02 (bs, 2H, H5 and H6 quinoxaline), 7.83 (bs, 2H, H7 and H8 quinoxaline), 3.85 (bs, 2H, H_{eq} piperazine), 3.13 (bs, 2H, H_{ax} piperazine), 2.97 (bs, 1H, NH), 2.80 (bs, 2H, H_{eq} piperazine), 2.64 (bs, 2H, H_{ax}, piperazine), 2.64 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{16}N_4O$: C, 65.60; H, 6.29; N, 21.86. Found: C, 65.50; H, 6.46; N, 21.67.

2-Methyl-3-[*N*-(1-(4-methylpiperazinyl))carbonyl]quinoxaline (**5f**).

2-Ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and *N*-methylpiperazine (5.01 g, 0.05 mole) are refluxed for 4 hours and purified by chromatography in the aforementioned general conditions. A brown solid is obtained, mp 106-107°, yield 0.30 g (11%); ir (potassium bromide): 2950-2790 (w, C-H aliphat), 1640 (s, C=O), 1560 (m, aromat), 1440 (m, aromat), 1290 (m, C-N), 1270 (m, C-N) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.03 (bs, 2H, H5 and H6 quinoxaline), 7.83 (bs, 2H, H7 and H8 quinoxaline), 3.74 (bs, 2H, H_{eq} piperazine), 3.23 (bs, 2H, H_{ax} piperazine), 2.66 (s, 3H, CH_3), 2.41 (bs, 2H, H_{eq} piperazine), 2.24 (bs, 2H, H_{ax}, piperazine), 2.18 (s, 3H, N-CH_3).

Anal. Calcd. for $C_{15}H_{18}N_4O$: C, 66.69; H, 6.71; N, 20.73. Found: C, 66.58; H, 6.99; N, 20.89.

2-Methyl-3-[*N*-(1-(4-methylpiperazinyl))carbamoyl]quinoxaline (**5g**).

2-Ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and

1-amino-4-methylpiperazine (5.76 g, 0.05 mole) are refluxed for 6 hours. The aforementioned general procedure is followed and a beige solid is obtained, mp 173-174° (2-propanol), yield 1.00 g (35%); ir (potassium bromide): 3210 (m, N-H), 1660 (s, C=O), 1550 (m, aromat), 1280 (m, C-N) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.77 and 9.70 (2 singlets, 1H, NH), 8.11-7.99 (m, 2H, H5 and H6 quinoxaline), 7.84 (bs, 2H, H7 and H8 quinoxaline), 2.91 (bs, piperazine), 2.76 (s, 3H, CH_3), 2.65 (s, piperazine), 2.46 (bs, piperazine), 2.20 (s, 3H, N-CH_3), 1.94 (s, piperazine).

Anal. Calcd. for $C_{15}H_{19}N_5O$: C, 63.13; H, 6.71; N, 24.55. Found: C, 62.63; H, 7.02; N, 24.31.

2-(2-Diethylamine)ethoxycarbonyl-3-methylquinoxaline (**6a**).

2-Ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and *N,N*-diethylethanolamine (5.86 g, 0.05 mole) are refluxed for 4 hours. Once the reaction has finalized, methylene chloride (200 ml) is added and the mixture is washed with water (50 ml) three times. The organic layer is dried, concentrated and chromatographed over silica gel, eluting with methylene chloride:methanol (95:5). A reddish oil is obtained, yield 0.60 g (21%); ir (sodium chloride plates): 2990-2820 (w, C-H, aliphat), 1770 (s, C=O), 1570 (m, aromat), 1330 (m, C-O), 1240 (m, C-N), 1080 (m, C-O) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.07-7.77 (m, 4H, quinoxaline), 4.41 (t, 2H, O-CH_2), 2.80 (s, 3H, CH_3), 2.63 (t, 2H, N-CH_2), 2.49 (q, 4H, -CH_2-N-CH_2), 0.92 (t, 6H, CH_3).

Anal. Calcd. for $C_{16}H_{21}N_3O_2$: C, 66.86; H, 7.37; N, 14.62. Found: C, 66.65; H, 7.00; N, 14.13.

2-Methyl-3-(2-morpholino)ethoxycarbonylquinoxaline (**6b**).

Following the procedure described for the product **6a** and starting with 2-ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and *N*-(2-hydroxyethyl)morpholine (6.56 g, 0.05 mole), a reddish oil is obtained, yield 2.00 g (66%); ir (sodium chloride plates): 2960-2830 (w, C-H aliphat), 1730 (s, C=O), 1475 (m, aromat), 1270 (m, C-N), 1230 (m, C-N), 1200 (m, C-O), 1120 (m, C-O) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.00-7.79 (m, 4H, quinoxaline), 4.48 (t, 2H, O-CH_2), 3.52 (bs, 4H, -CH_2-O-CH_2), 2.78 (s, 3H, CH_3), 2.65 (t, 3H, N-CH_3), 2.42 (bs, 4H, N-CH_2).

Anal. Calcd. for $C_{16}H_{19}N_3O_3$: C, 63.77; H, 6.36; N, 13.95. Found: C, 63.99; H, 6.10; N, 14.09.

2-Methyl-3-(*N*-methyl-4-piperidyloxycarbonyl)quinoxaline (**6c**).

Following the general procedure and starting with 2-ethoxycarbonyl-3-methylquinoxaline (2.16 g, 0.01 mole) and 4-hydroxy-1-methylpiperidine (5.76 g, 0.05 mole), a reddish solid is obtained, mp 75-77°, yield 0.35 g (12%); ir (potassium bromide): 2950-2780 (w, C-H aliphat), 1720 (s, C=O), 1600 (m, aromat), 1320 (m, C-O), 1275 (m, C-N), 1080 (m, C-O) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.12-7.79 (m, 4H, quinoxaline), 5.02 (bs, 1H, O-CH-), 2.79 (s, 3H, CH_3), 2.63 (m, 2H, H_{eq} C2 piperidine), 2.30 (m, 2H, H_{ax} C3 piperidine), 2.14 (s, 3H, N-CH_3), 1.96 (m, 2H, H_{ax} C2 piperidine), 1.78 (m, 2H, H_{eq} C3 piperidine).

Anal. Calcd. for $C_{16}H_{19}N_3O_3$: C, 67.35; H, 6.71; N, 14.73. Found: C, 67.20; H, 7.03; N, 14.48.

2-Amino-3-[*N*-(3-morpholinopropyl)carbamoyl]quinoxaline (**8**).

2-Amino-3-cyanoquinoxaline 1,4-dioxide (4.04 g, 0.2 mole) is added to 4-(3-aminopropyl)morpholine (20 ml) and the mixture is refluxed for 18 hours. The reaction is followed by tlc (methylene chloride:methanol, 9:1) and once the reaction has finished, the mixture is distributed between ethyl acetate (200 ml) and water (50 ml). The organic layer is washed with water (2 x 50 ml) and then dried with sodium sulfate, concentrated and chromatographed over silica gel, eluting with a mixture of methylene chloride:methanol in the proportion 95:5. A brown solid is obtained, mp 162-163°, yield 1.33 g (21%); ir (potassium bromide): 3329 (m, NH), 3270 (m, NH), 3150 (m, NH), 2953-2981 (m, C-H, aliphat), 1660 (s, CO), 1595 (s, aromat), 1510 (m, aromat), 1120 (m, C-O) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.24 (bs, 1H, NH), 7.85-7.41 (m, 4H, quinoxaline), 3.61 (s, 2H, NH_2), 3.60 (bs, 4H, O-CH_2), 3.41 (m, 2H, NH-CH_2), 2.35 (bs, 6H, N-CH_2), 1.71 (m, 2H, CH_2); ms: (m/z, % parent) 315 (M^+, 19.57), 202 (6.05), 173 (7.82), 172 (5.66), 159 (5.10), 149 (6.90), 145 (24.16), 144 (25.90), 137 (5.36), 127 (12.42), 126 (46.09), 125 (5.60), 123 (6.19), 118 (9.33), 117 (9.00), 114 (5.79), 111 (8.81), 109 (7.72), 101 (7.93), 100 (100), 98 (5.69), 97 (14.40), 96 (6.13), 95 (11.07), 91 (5.03), 90 (8.28), 85 (14.73), 84 (5.71), 83 (12.48), 82 (12.48), 81 (17.56), 71 (16.01).

Anal. Calcd. for $C_{16}H_{21}N_5O_2$: C, 60.93; H, 6.71; N, 22.20. Found: C, 61.32; H, 6.97; N, 22.52.

2-Amino-3-[*N*-(3-(1-imidazolyl)propyl)amidino]quinoxaline (**9**).

2-Amino-3-cyanoquinoxaline 1,4-dioxide (4.04 g, 0.2 mole) is added to 1-(3-aminopropyl)imidazole (20 ml) and the mixture is refluxed for 6 hours. The reaction is followed by tlc (methylene chloride:methanol, 9:1) and once the reaction has finished, the mixture is distributed between ethyl acetate (200 ml) and water (50 ml). The organic layer is washed with water (2 x 50 ml) and then dried with sodium sulfate, concentrated and chromatographed over silica gel, eluting with a mixture of chloroform:methanol in the proportion 95:5. A yellow solid is obtained, mp 164-165°, yield 2.80 g (47%); ir (potassium bromide): 3456 (m, NH), 3400-3100 (m, bs, associated NH), 1634 (s, C=NH), 1578 (s, aromat), 1434 (m, aromat), 1225 (m, C-N) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.87 (bs, 1H, NH), 7.85 (d, 1H, H5 quinoxaline), 7.63-7.53 (m, 4H, H6 and H8 quinoxaline, 1H amidinic NH and 1H imidazole), 7.40-7.34 (m, 1H, H7 quinoxaline), 7.19 (s, 1H, imidazole), 6.92 (bs, 3H, 2H amine group and 1H imidazole), 4.13 (m, 2H, methylene bonded to amidinic NH), 3.19 (m, 2H, methylene bonded to imidazole), 2.51 (m, 2H, CH_2); ms: (m/z, % parent) ($M+1^+$, 18.04), 295 (M^+, 100), 227 (14.61), 212 (5.16), 202 (5.51), 201 (48.77), 200.15 (86.16), 199 (10.17), 198 (6.20), 197 (15.28), 188 (5.28), 172 (12.08), 171 (22.73), 170 (6.62), 151 (9.52), 145 (12.58), 144 (26.53), 125 (5.15), 124 (12.23), 118 (13.28), 117 (11.39), 109 (17.27), 108 (10.54), 107 (7.81), 102 (6.53), 97 (5.06), 96 (66.20), 95 (18.64), 89 (14.54), 82 (20.29).

Anal. Calcd. for $C_{15}H_{17}N_7$: C, 61.00; H, 5.80; N, 33.20. Found: C, 60.78; H, 5.90; N, 33.33.

3-(2-Diethylaminoethyl)-3,4-dihydro-4-imino-2-methylpyrimido-[5,4-*b*]quinoxaline (**10**) and 1-Ethyl-5-imino-1,4-diazepino[6,5-*b*]-quinoxaline (**11**).

2-Amino-3-cyanoquinoxaline 1,4-dioxide (4.04 g, 0.2 mole) is added to *N,N*-diethylaminoethylamine (20 ml) and the mixture is refluxed for 10 hours. The reaction is followed by tlc (methylene chloride:methanol, 9:1) and once the reaction has finished, the mixture is dried and distributed between ethyl acetate (200 ml) and water (50 ml). The organic layer is washed with water (2 x 50 ml), dried with sodium sulfate, concentrated and chromatographed over silica gel, eluting with a mixture of chloroform:methanol in the proportion 98:2. Two yellow compounds are obtained and identified as **10** and **11** respectively. For compound **10**, mp 125-126°, yield 2.80 g (45%); ir (potassium bro-

mide): 3365 (m, NH), 2965 (m, C-H, aliphat), 1601 (s, C=NH), 1562 (s, aromat), 1466 (m, aromat), 1263 (m, C-N) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.86 (bs, 1H, NH), 8.17-8.06 (m, 2H, H5 and H6 quinoxaline), 7.94-7.84 (m, 2H, H7 and H8 quinoxaline), 3.63 (bs, 2H, methylene bonded to amidinic NH), 2.71 (t, 2H, methylene bonded to the diethylamine group), 2.59-2.53 (m, 7H, 4H, methylenes and 3H methyl bonded to the heterocycle), 0.99 (t, 6H, methyls); ms: (m/z, % patent) 310 (M^+, 0.74), 225 (5.39), 212 (5.54), 149 (8.87), 111 (5.76), 102 (6.41), 99 (39.45), 97 (9.64), 95 (5.38), 87 (7.05), 86 (100), 85 (8.61), 84 (7.24), 83 (9.97), 81 (6.58), 71 (17.37).

Anal. Calcd. for $C_{17}H_{22}N_6$: C, 65.77; H, 7.14; N, 27.08. Found: C, 65.62; H, 7.32; N, 27.09.

1-Ethyl-5-imino-1,4-diazepino[6,5-*b*]quinoxaline (**11**).

Following the procedure described for obtaining the product, **10**, product **11** is obtained, mp 118-119°, yield 0.50 g (10%); ir (potassium bromide): 3140 (m, NH), 2980 (m, C-H, aliphat), 1628 (s, C=NH, lactam), 1587 (s, aromat), 1489 (m, aromat), 1276 (m, C-N) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 7.78 (d, deformed 2H, H5 quinoxaline and 1H NH), 7.65-7.52 (m, 2H, H6 and H8 quinoxaline), 7.40-7.34 (m, 1H, H7 quinoxaline), 3.85 (t, 2H, J = 10 Hz methylene bonded to amidinic NH), 3.60-3.41 (m, 4H, $-N-CH_2-$), 1.06 (t, 3H, J = 7 Hz, $-CH_3$); ms: (m/z, % parent) 242 ($M+1^+$, 12.24), 241 (M^+, 67.43), 227 (14.46), 226 (100.00), 212 (6.09), 198 (11.90), 197 (7.14), 171 (17.40), 170 (5.55), 144 (11.61), 117 (5.44), 90 (10.28), 71 (13.78), 70 (6.09), 69 (5.24), 56 (11.96), 55 (6.04).

Anal. Calcd. for $C_{13}H_{15}N_5$: C, 64.71; H, 6.27; N, 29.03. Found: C, 64.63; H, 6.47; N, 29.16.

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