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QUINOXALINES AND RELATED COMPOUNDS—X[1]

THE FORMATION OF INDOLO[2,3-*b*]QUINOXALINES AND 2-*p*-AMINOPHENYL-3-ANILINOQUINOXALINES FROM 2-ANILINOQUINOXALINES

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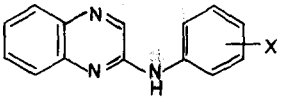
Abstract—The reactions which occur when 2-chloroquinoxaline is heated with an excess of aromatic amine are unexpectedly complex. For example, when 2-chloroquinoxaline is heated with excess aniline a mixture of the expected anilino derivative (**1**), 6H-indolo[2,3-*b*]quinoxaline (**7**), 2,3-dianilinoquinoxaline (**11**), and 2-*p*-aminophenyl-3-anilinoquinoxaline (**16**) is obtained.

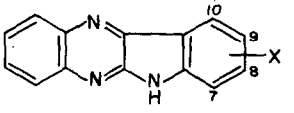
Attempts to prepare 2-anilinoquinoxaline (**1**) by heating 2-chloroquinoxaline in aniline, on a scale larger than that quoted in the literature,[2] gave variable results. In addition to the desired material (**1**), 6H-indolo[2,3-*b*]quinoxaline (**7**), traces of 2,3-dianilinoquinoxaline (**11**), and 2 - *p* - aminophenyl - 3 - anilinoquinoxaline (**16**) were formed. Heating 2-chloroquinoxaline in *m*-toluidine gave a similar range of products (**2**, **8**, **12** and **17**). It is probable that the exorthermic nature of these reactions is such that they are not easily controlled except on a small scale. No analogous products have been reported as being formed from other chlorodiazines with anilines and in order to investigate this reaction further a number of 2-anilinoquinoxalines (**1–5**; Table 1) were prepared by the alternative procedure of acid-catalysed condensation of anilines with 2-chloroquinoxaline in aqueous medium.[3] This method did not work with the weakly nucleophilic *o*-nitroaniline. Also synthesised, for comparison purposes, were some 2,3-dianilinoquinoxalines (**11–15**; Table 2) by the standard procedure of heating 2,3-dichloroquinoxaline in the appropriate aniline;[4] these latter reactions were free of complication.

Clearly the formation of indoles (e.g. **7**) and *para* aminophenyl compounds (e.g. **16**) from 2-chloroquinoxaline could entail C–C bond formation between the quinoxaline nucleus and the aniline either prior or subsequent to halide displacement (see Ref. 1). That the formation of these materials could occur in the latter fashion was simply demonstrated. Heating 2-anilinoquinoxalines (**1**, **2** and **4**) in their respective anilines under acid-catalysis gave both indoloquinoxalines and *para* aminophenyl compounds, the ease of reaction increasing with the nucleophilicity of the aniline (Table 3).

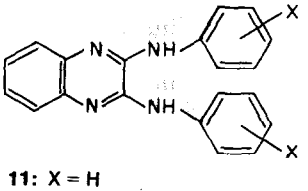
Product identification, in the case of the dianilino compounds and 6H-indolo[2,3-*b*]quinoxaline (**7**) was accomplished by comparison with authentic specimens. The three new indoloquinoxalines (**8–10**) (Table 4) all had similar spectral characteristics to be parent material (**7**) with the position of cyclisation being evident from their PMR spectra. The aminophenyl compounds (**16** and **17**) were shown to be *para* linked by the use of a shift reagent [Eu(dpm)$_3$]; this complexes preferentially with the primary amino function and the resonances due to



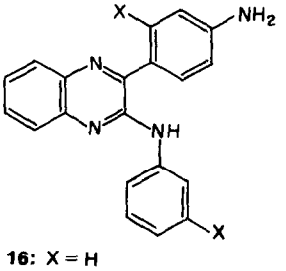
1: X = H
2: X = *m*-Me
3: X = *p*-Me
4: X = *m*-OMe
5: X = 3,5-Me$_2$
6: X = *o*-NO$_2$



7: X = H
8: X = 8-Me
9: X = 8-OMe
10: X = 10-OMe

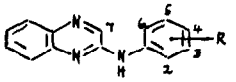


11: X = H
12: X = *m*-Me
13: X = *p*-Me
14: X = *m*-OMe
15: X = 3,5-Me$_2$



16: X = H
17: X = Me

Table 1. 2-Anilinoquinoxalines.



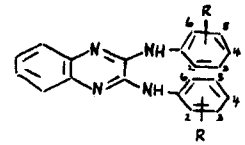
R	Yield (%)	Crystallisation Solvent	M.p.(°C)	Found(%)			Required(%)			Chemical Shifts(δ) in $CDCl_3$ [a]							
				C	H	N	C	H	N	Me	2H	3H	4H	5H	6H	7H	Others
H	71	Benzene - Petrol 60-80°	135-137[b]													8.55	7.2-8.2
3-Me	63	Benzene - Petrol 60-80°	105-107	76.5	5.7	17.5	76.6	5.6	17.9	2.35	7.5	-	6.95		7.25	8.45	7.4-8.1
4-Me	43	Benzene-Petrol 60-80°	155-157	76.2	5.8	17.7	76.6	5.6	17.9	2.33	7.6	7.2	-	7.2	7.6	8.45	7.3-8.1
3-MeO	69	Toluene-Petrol 60-80°	129-131	71.6	5.5	17.0	71.7	5.2	16.7	3.8		-	6.7			8.45	7.25-8.25
3,5-Me_2	62	Benzene-Petrol 60-80°	133-135	77.2	6.6	16.9	77.1	6.1	16.9	2.3	7.3	-	6.8	-	7.3	8.5	7.4-8.1
2-NO_2	53	Petrol 100-120°	183-185	63.2	4.3	21.1	63.1	3.8	21.0	-	-	8.55[c]	7.3		9.7	8.8	7.7-8.3

[a] Assignments made by consideration of couplings and double resonance techniques; particularly useful were the benzylic couplings exhibited by three of the compounds. All assigned protons showed the expected couplings and multiplicity.

[b] Lit. 137°.[2]

[c] Assignments based on assumption that the multiplet at 7.3δ is attributable to H-4; H-6 resonates at remarkably low field.

Table 2. 2,3-Dianilinoquinoxalines



R	Yield (%)	Crystallisation Solvent	M.p.(°C)	Found(%)			Required(%)			Chemical Shifts (δ) in $DMSO_4$ [a,b]							
				C	H	N	C	H	N	Me	2H	3H	4H	5H	6H	NH	Others
H	81	Petrol 100-120°	143-144[c] 98-104[d]							-	7.95				7.95	9.1	7.1-7.75
3-Me	47	Methanol	125-127[e]	77.7	6.0	16.8	77.6	5.9	16.5	2.35	7.75	-	6.9			9.1	7.1-7.95
4-Me	73	Petrol 100-120°	147-149[f]	77.8	6.0	16.4	77.6	5.9	16.5	2.3	7.85	7.2	-	7.2	7.85	9.2	7.3-7.8
3-MeO	69	Nitromethane	190-192[g]	70.9	5.6	15.2	71.0	5.4	15.0	3.8	7.8	-	6.9			9.4	7.2-7.7
3,5-Me_2	62	Petrol 60-80°	148-150 88[d]	78.1	6.8	15.1	78.2	6.6	15.2	3.2	7.7	-	6.8	-	7.7	9.8	7.3-7.8

[a] see note a Table I.

[b] Whilst freely soluble in $CDCl_3$ these compounds exhibited totally unresolved spectra in this solvent.

[c] Lit. 137°.[17]

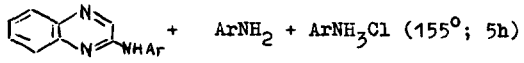
[d] From methanol.

[e] M.p. unchanged upon recrystallisation from petrol 100-120°; the m.p. of 225 quoted by Lockhart and Turner[4] is for material recrystallised from acetic aci which is presumably[17] the acetate.

[f] Recrystallisation from methanol gave a material of the same m.p. which contained (PMR,IR) solvent of crystallisation (1 mol.);the higher melting point quotedby Lockhart and Turner[4] is again,presumably, for the monoacetate

[g] Recrystallisation from methanol gave a material of the same m.p.

Table 3.

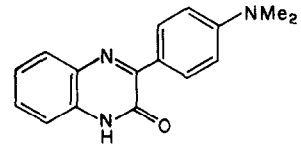


Ar	C_6H_5	3Me-C_6H_4	3MeO-C_6H_4
Starting Material	72%	59%	-
Dianilino cpd.	-	Traces	-
Indolo cpd.	6%	25%	53% (8-OMe) 5% (10-OMe)
p-Amino cpd.	14%	13%	-

the aminophenyl moiety move to low field of the other aromatic signals giving a simply interpreted spectrum (Experimental).

The mode of formation of the aminophenyl compounds seems clear (Scheme 1); the final oxidation step would be expected to occur readily[5] and close analogy exists in the nucleophilic attack of N,N-dimethylaniline upon certain azines giving *para* linked species.[6,7] Of particular relevance is the formation of the quinoxaline (**18**) from 2-hydroxyquinoxaline and N,N-dimethylaniline in acetic acid containing ammonium nitrate.[8]

When one considers the mechanistic route leading to the indoloquinoxalines two possibilities present themselves; the first (Scheme 2) is but an extension of the



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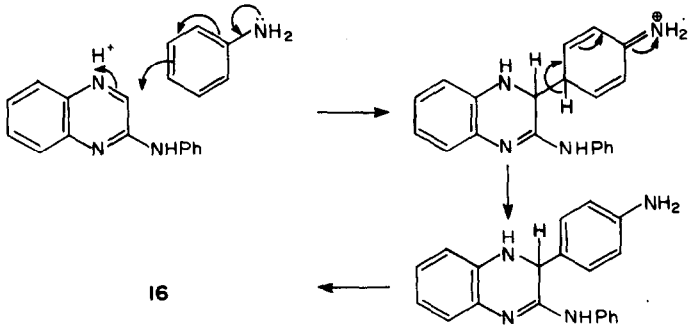
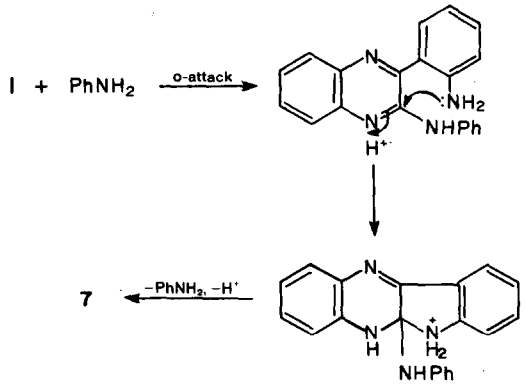
mechanism presented in Scheme 1 with initial *ortho* attack upon the aniline. The second possibility is a simple dehydrogenative ring closure of the 2-arylaminoquinoxaline (Scheme 3); formation via the dianilinoquinoxalines can be eliminated as they survive the reaction conditions.

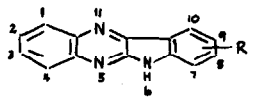


Scheme 1.



Scheme 2.

Table 4. 6H-Indolo[2,3-*b*]quinoxalines



R	M.p.(°C)	Crystallisation Solvent	Found(%)			Required(%)			Chemical Shifts (δ)[a]						
			C	H	N	C	H	N	NH[b]	7H	8H	9H	10H	Me	Others
H	295-297[c]	Nitromethane							12.1						7.35-8.6[b]
8-Me	320-324	"	77.2	5.0	18.0	77.2	4.8	18.0	12.1	7.9[d]	-	7.7[d]		2.7[d]	8.3-8.8[d]
8-MeO	295-297	"	72.6	4.7	17.0	72.3	4.5	16.9	12.0	7.65[d]	-	7.43[d]		4.21[d]	8.2-8.8[d]
10-MeO	318-320	e	72.0	4.5	16.8	72.3	4.5	16.9	12.2	7.03[b,f]		7.27[b,f]	-	4.1[b]	7.6-8.5[b]

[a] See note a to Table I.

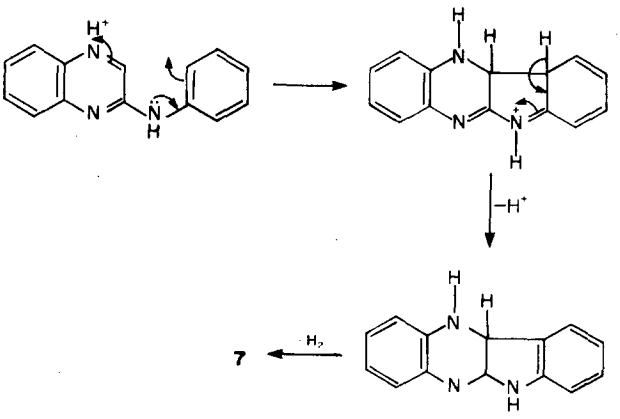
[b] In DMSO d_6

[c] Lit. 295-296[18]

[d] In TFA

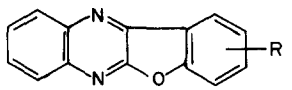
[e] Purified by vacuum sublimation only.

[f] Assignment may be interchangeable.



Scheme 3.

We therefore made attempts to convert 2-anilinoquinoxaline (1) into the indole (7) based upon known procedures for dehydrogenative ring closure (e.g. treatment with aluminium chloride,[9,10] polyphosphoric acid,[1] or copper(II) chloride).[11] In no case was any cyclic material isolated although traces may have been formed (UV spectroscopy) after heating (170–180°; 6 hr) with sulphur and iodine. This makes it clear that dehydrogenative ring closure is not a facile reaction for 1 and that an intramolecular displacement mechanism (Scheme 2) is a more likely pathway to the indoloquinoxalines. Similar ambident behaviour may also be responsible for the formation of the related benzofuro[2,3-*b*]quinoxalines (19) from 2-chloroquinoxaline and phenols;[1] in this context the phenoxide ion has recently been reported as forming both *para* and *ortho* C–C adducts with 1,3,5-trinitrobenzene.[12]



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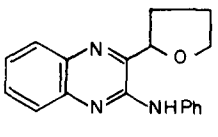
A further attempt to distinguish between the two possibilities, by carrying out a crossed experiment, was vitiated by rapid aniline exchange. Heating 2-*m*-toluidinoquinoxaline (2) in aniline gave only 2-anilinoquinoxaline (1) and its related indole (7) and *para*-aminophenyl (16) derivatives.

Irradiation of 2-anilinoquinoxaline (1) in tetrahydrofuran, conditions which convert anilinopyridines into pyrido[*b*]indoles,[13] gave the tetrahydrofuranyl derivative (20) as the only product. Such irradiative substitution of (*inter alia*) the quinoxaline nucleus is well established.[14]



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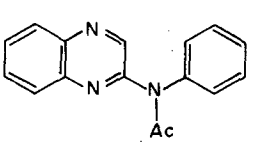

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EXPERIMENTAL

M.ps are uncorrected and were determined using a Gallenkamp m.p. apparatus or (where stated) a Koffler hotstage. IR spectra were taken on a Unicam SP-200 spectrometer in Nujol mulls. UV spectra were taken on a Unicam SP-800A machine in 96% EtOH. NMR spectra were recorded using a Perkin–Elmer R12B spectrometer with TMS as an internal standard. Mass spectra were obtained using an AEI MS9 or MS30 spectrometer at 70 eV and peak abundances are quoted as a percentage of the base peak. Column chromatography was carried out using Merck 7734 silica or Laporte alumina type H.

2-*m-Toluidinoquinoxaline* (2). 2-Chloroquinoxaline[15] (4.2 g, 25.5 mmol) and *m*-toluidine (5 g, 46.7 mmol) were heated in refluxing water in the presence of conc. HCl (0.25 ml) for 4 hr 40 min. After cooling and strong acidification the product was filtered off as a red hydro-chloride. The free base was obtained by partition between dichloromethane and 2N NaOH, separation of the organic phase, drying over $MgSO_4$ and evaporation to dryness, giving the crude product (6.6 g, 89%); ν_{max} 3300 cm^{-1} (NH); λ_{max} 277 sh (ϵ 25,300), 284 (ϵ 25,800) and 383 nm (ϵ 9900). Similarly prepared were the following compounds:-

2-*Anilinoquinoxaline* (1). ν_{max} 3300 cm^{-1} (NH); λ_{max} 282 and 382 nm. Acetylation of 1 gave N - *quinoxalin* - 2 - *ylacetanilide* (21) as white needles; m.p. 161–163° (EtOH–water); ν_{max} 1666 cm^{-1}; λ_{max} 237,251 (sh) and 333 nm; $\delta(CDCl_3)$ 2.2 (3H, s, Me), 7.4–8.3 (8H, m, carbocyclic Ar–H) and 9.23 (1H, s, pyrazinyl-H). (Found: C, 73.1; H, 4.9; N, 15.9. $C_{16}H_{13}N_3O$ requires: C, 73.0; H, 5.0; N, 16.0%).

2-*p-Toluidinoquinoxaline* (3). ν_{max} 3300 cm^{-1} (NH); λ_{max} 274 (ϵ 25,300), 286 (ϵ 26,000) and 385 nm (ϵ 9800).

2-*m-Anisidinoquinoxaline* (4). ν_{max} 3320 cm^{-1} (NH); λ_{max} 274 (ϵ 26,000) and 383 nm (10,000).

2-(3,5-*Dimethylanilino*)*quinoxaline* (5). ν_{max} 3350 cm^{-1} (NH); λ_{max} 275 (ϵ 25,100), 285 (ϵ 25,400) and 384 nm (ϵ 9200).

2-*o-Nitroanilinoquinoxaline* (6). 2-Chloroquinoxaline (3.2 g, 19.5 mmol) and *o*-nitroaniline (excess) were heated at 100–130° for 4.5 hr. Unreacted starting materials were removed by vacuum sublimation and the residue recrystallised twice from petrol 100–120° giving deep orange-red ferns; ν_{max} 3300 cm^{-1} (NH); λ_{max} 264 (25,800) and 399 nm (10,800).

2,3-*Di*-m-*toluidinoquinoxaline* (12). 2,3-Dichloroquinoxaline[16] (2.45 g, 12.4 mmol) and *m*-toluidine (6.65 g, 62 mmol) were heated at 160° for 50 min. The semi-solid mixture was recrystallised from AcOH (50 ml) giving a yellow solid (3.4 g) m.p. 235–240°, thought to be a hydrochloride. The free base was obtained as for 2-*m*-toluidinoquinoxaline (2); ν_{max} 3360 and 3240 cm^{-1} (NH); λ_{max} 246 (ϵ 24,400) 274 (ϵ 29,800), 354 sh (ϵ 14,400), 368 (ϵ 16,300) and 384 nm sh (ϵ 12,800). Similarly prepared were the following compounds:

2,3-*Dianilinoquinoxaline* (11). ν_{max} 3410 and 3250 cm^{-1} (NH); λ_{max} 247 (ϵ 23,300), 274 (ϵ 29,600), 356 sh (ϵ 13,300), 368 (ϵ 15,600) and 382 nm sh (ϵ 12,200).

2,3-*Di*-p-*toluidinoquinoxaline* (13). ν_{max} 3410 and 3250 cm^{-1} (NH); λ_{max} 247 (ϵ 26,000), 274 (ϵ 31,700), 356 sh (ϵ 15,900), 369 (ϵ 17,800) and 386 nm sh (ϵ 13,400).

2,3-*Di*-m-*anisidinoquinoxaline* (14). ν_{max} 3320 cm^{-1} (NH); λ_{max} 246 (ϵ 26,700), 273 (ϵ 29,800), 355 sh (ϵ 14,500), 368 (ϵ 16,800) and 383 nm sh (ϵ 13,300).

2,3-*Bis*-(3,5-*dimethylanilino*)*quinoxaline* (**15**). ν_{max} 3350 cm^{-1} (NH); λ_{max} 248 (ϵ 21,800), 275 (ϵ 25,600), 354 sh (ϵ 12,600), 369 (ϵ 13,800) and 384 nm sh (ϵ 10,700).

Reaction of 2-chloroquinoxaline or anilinoquinoxalines with anilines

General work-up procedure. After heating the substrate with the aniline the mixture is basified with $NaHCO_3$aq and excess aniline removed by steam distillation. The resultant suspension, after cooling, is thoroughly stirred with CCl_4; filtration then sometimes gives some of the relatively insoluble indoloquinoxaline. The organic phase of the filtrate is separated and its *para*-aminophenyl content extracted into dil. HCl; after repeated washing with chloroform the aqueous phase contains, in fairly pure state, the *para*-aminophenyl derivative which is isolated by neutralisation with $NaHCO_3$, extraction into chloroform, and evaporation to dryness. The remaining organic phase (plus washings) contains the remainder of the indoloquinoxaline together with any monoanilino and dianilino quinoxalines; after washing with Na_2CO_3aq these three materials are separated by column chromatography. UV spectroscopy was found to be the most efficient method of monitoring these separations.

(a) 2-*Chloroquinoxaline with aniline.* 2-Chloroquinoxaline (3.2 g, 19.5 mmol) and aniline (9.3 g, 100 mmol) were heated at 150° for 2 hr. The organic material was completely soluble in CCl_4; 2 - p - *aminophenyl* - 3 - *anilinoquinoxaline* (**16**) was isolated as indicated above (966 mg, 16%) and gave a positive β-naphthol test; recrystallisation from MeOH gave a pale yellow solid, m.p. 93–96°; ν_{max} 3450, 3400, 3320 and 3200 cm^{-1} (NH and NH_2); λ_{max} 253 (ϵ 28,400), 284 (ϵ 29,700) and 388 nm (ϵ 15,600); δ ($DMSOd_6$) 5.8 br (2H, s, NH_2), 6.9–8.3 (13H, m, ArH) and 8.6 br (1H, s, NH); δ ($CDCl_3$) 3.7 br (3H, s, NH_2 and NH) and 6.9–8.2 (13H, m, ArH); δ ($CDCl_3$ + 0.38 mol. equiv. Eu(dpm)$_3$) 7.0–8.3 (9H, m) 8.7 (2H, d, J 8 Hz) and 10.85 (2H, d, J 8 Hz); *m/e* 313 (13%), 312 (79%, M), 311 (100%), 156 (16%, M^{++}) and 155.5 (6%). (Found: C, 76.8; H, 5.6; N, 18.2. $C_{20}H_{16}N_4$ requires: C, 76.9; H, 5.2; N, 18.2%). Further recrystallisation from petrol 100–120° gave a spectroscopically identical material of m.p. 154–155°. Chromatographic separation of the other three products (**1**, **7** and **11**) was performed on silica with ether–petrol 40–60° (3:2) as the eluent giving **11** first (traces), then **7** (83 mg, 2%), and finally **1** (1002 mg, 23%).

(b) 2-*Chloroquinoxaline with* m-*toluidine.* 2-Chloroquinoxaline (3 g, 18.3 mmol) and *m*-toluidine (10 g, 93.5 mmol) were heated at 155° for 2 hr. Work up as described gave, upon filtration, a sample of 6H - 8 - *methylindolo*[2,3-b]*quinoxaline* (**8**), purified by vacuum sublimation (230°; 0.05 mm) giving a yellow solid (541 mg, 13%) m.p. 320–325°. Recrystallisation from nitromethane gave pale yellow needles (396 mg), m.p. 320–324°; λ_{max} 269 sh (ϵ 53,200), 273 (ϵ 57,300), 348 sh (ϵ 19,700), 359 (ϵ 22,500) and 386 sh nm (ϵ 5600); *m/e* 234 (14%), 233 (100%, M), 232 (40%) and 116.5 (13%, M^{++}). Work up of the acid extract gave a reddish oil (536 mg, 9%) which crystallised upon the addition of methanol. Recrystallisation from MeOH gave fine yellow needles (227 mg) of 2 - (2 - *methyl* - 4 - *aminophenyl*) - 3 - m - *toluidinoquinoxaline* (**17**) m.p. 177–179°; ν_{max} 3380, 3310 and 3210 cm^{-1} (NH and NH_2); λ_{max} 254 (ϵ 28,600), 281 (ϵ 26,500) and 384 nm (ϵ 12,800); δ ($CDCl_3$) 2.16 (3H, s, Me on aminophenyl ring), 2.35 (3H, s, Me on toluidino ring), 3.45 br (2H, s, NH_2), and 6.7–8.25 (12H, m, NH and ArH); δ ($CDCl_3$ + 0.48 mol. equiv. Eu(dpm)$_3$) 2.3 (3H, s, Me on toluidino ring), 3.05 (3H, s, Me on aminophenyl ring), 6.8–8.3 (8H, m), 8.6 (1H, d, J 9 Hz) and 11.7 (2H, brm); irradiation at 3.05 sharpens the signal at 11.7 to an apparent sextet and irradiation at 11.7 collapses the doublet at 8.6 to a singlet; *m/e* 341 (21%), 340 (100%, M), 339 (63%), 325 (31%, M–Me), 249 (15%), 234 (19%), 170 (18%, M^{++}) and 162.5 (6%); m* 310 (340→325). (Found: C, 77.7; H, 6.0; N, 16.8. $C_{22}H_{20}N_4$ requires: C, 77.6; H, 5.9; N, 16.5%). Chromatographic separation of the organic extracts on alumina, eluting with chloroform, gave **12** (168 mg, 3%), first, then a further 206 mg (5%) of **8** and finally **2** (1082 mg, 25%).

(c) 2-*Anilinoquinoxaline* (**1**) *with aniline.* 2-Anilinoquinoxaline (**1**) (5227 mg, 2.36 mmol) and aniline hydrochloride (1 mol equiv) were heated at 155° in aniline (5 g) for 5 hr. The organic material was completely soluble in CCl_4; the *para* compound **16** (102 mg), the starting material (**1**; 382 mg), and **7** (30 mg) were separated as described. No trace of **11** was observed.

(d) 2-m-*Toluidinoquinoxaline* (**2**) *with* m-*toluidine.* 2-*m*-Toluidinoquinoxaline (**2**) (498 mg, 2.12 mmol) and *m*-toluidine hydrochloride (1 mol equiv) were heated in *m*-toluidine (5 g) at 155° for 5 hr. Work up as described gave, after the initial filtration, a dull yellow solid which upon vacuum sublimation (250°; 0.5 mm) afforded pure **8** (61 mg, 12%). The *para* derivative **17** was isolated by acid extraction as described (92 mg, 13%) and the final chromatographic separation on silica gave **12** (traces), a further 51 mg (10%) of **8** and the starting material (292 mg, 59%).

(e) 2-m-*Anisidinoquinoxaline* (**4**) *with* *m*-anisidine. 2-*m*-Anisidinoquinoxaline **4** (499 mg, 1.99 mmol) and *m*-anisidine hydrochloride (1 mol equiv) were heated at 154° in *m*-anisidine (5 g) for 5 hr. Work up as above gave a yellow solid after the initial filtration; vacuum sublimation (290°; 4 mm) of this gave 6H - 8 - *methoxyindolo*[2,3-b]*quinoxaline* **9**, (69 mg, 14%), m.p. (Koffler) 295–297°. Recrystallisation from nitromethane gave yellow crystals m.p. 293–295°, λ_{max} 236 (ϵ 29,400), 277 (ϵ 42,900) and 365 nm (ϵ 26,800); *m/e* 250 (11%), 249 (100%, M), 234 (6%, M–Me), 220 (2%, M–CHO), 206 (35%, M–Me–CHO) and 124.5 (9%, M^{++}); m* 220 (249→234), 195 (249→220) and 182 (234→206). No para aminophenyl compound was obtained and chromatography on silica gave a further 193 mg (39%) of **9** and a small amount of the isomeric derivative **10**; this latter compound was separated from its isomer (**9**) by preparative tlc giving 23 mg (5%) of material. Vacuum sublimation (260°; 2 mm) gave 6H - 10 - *methoxyindolo*[2,3-b]*quinoxaline* (**10**) as a yellow solid, m.p. (Koffler) 318–320°; λ_{max} 263, 360 and 394 sh nm; *m/e* 249 (63%, M), 248 (71%), 221 (10%), 220 (100%, M–CHO), 219 (35%), 207 (7%) and 124.5 (8%, M^{++}); m* 218 br and 194.5 (249→220).

(f) 2-m-*Toluidinoquinoxaline* (**2**) *with aniline.* 2-*m*-toluidinoquinoxaline **2** (1010 mg, 4.3 mmol) and aniline hydrochloride (1 mol equiv) were heated in aniline (10 g) at 150° for 8.75 hr: Routine work up gave **16** (238 mg, 18%), **7** (109 mg, 12%) and **1** (375 mg, 39%) as the only observed products.

Attempted photocyclisation of 2-anilinoquinoxaline (**1**). 2-Anilinoquinoxaline (215 mg) in dry, peroxide free, THF was irradiated (λ_{max} 350 nm) under N_2 in a Pyrex vessel for 142 hr. Examination (tlc) of the crude product showed the absence of **7** and the presence of a mobile product. Isolation of this material by column chromatography on silica (ether-petrol 40–60°; 3:2) and subsequent preparative tlc gave a yellow solid thought to be 2 - *anilino* - 3 - *tetrahydrofuran* - 2' - *ylquinoxaline* (**20**) (83 mg, 29%); λ_{max} 275 and 375 nm; δ($CDCl_3$) 1.9–2.95 (4H, m, 3',3',4',4'-H), 4.17 (2H, t, $J_{5',4'}$ 7 Hz, 5',5'-H), 5.35 (1H, t, $J_{2',3'}$ 8 Hz, 2'-H), 7.15–8.3 (9H), m, ArH) and 9.5 br (1H, s, NH). Irradiation at other wavelengths either afforded the same material (λ_{max} 300 nm) or tar (λ_{max} 253.7 nm), in no case was any **7** observed.

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