Pyrrole studies part 47.[1] ^{13}C NMR Spectroscopic characterisation of the products of the reaction of formylpyrroles with aniline and diaminobenzenes

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Dedicated to Professor Gurnos Jones on the occasion of his 70th birthday, and in recognition of our long standing friendship

(received 05 May 00; accepted 13 Feb 00; published on the web 21 Feb 00)

Abstract

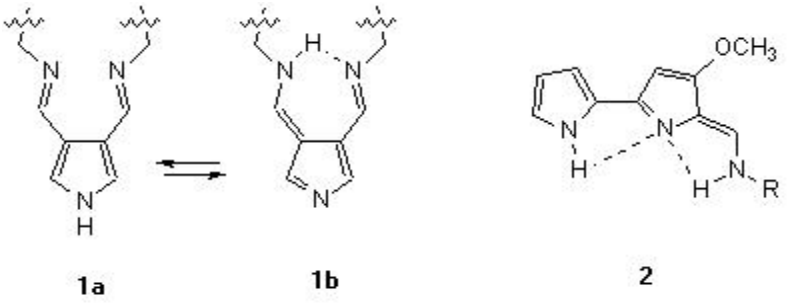
Pyrrole-3,4-dicarboxaldehydes react with aniline to produce "bis-imines" having a 3*H*-pyrrole structure, 3b. In contrast, pyrrole-2-carboxaldehyde and pyrrole-2,5-dicarboxaldehydes produce 1*H*-pyrrolylmethylenimines. Benzimidazolyl derivatives, are formed exclusively from the reaction of β-formylpyrroles with 1,2-diaminobenzene, while α-formylpyrroles form 2:1 bis-imines or benzimidazoles depending upon the reaction conditions. Pyrrole-2,4-dicarboxaldehydes react with aniline preferentially at the 4-CHO group. With an excess of aniline, the bis-imine is produced.

Keywords: Pyrroledicarboxaldehydes, Benzimidazolyl derivatives, ^{13}C NMR

Introduction

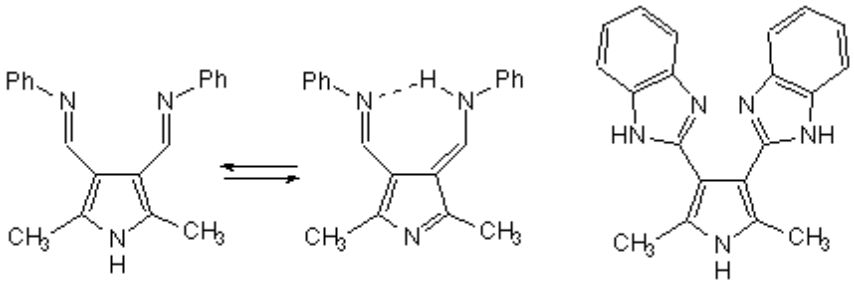
In earlier publications we reported the reaction of α- and β-formylpyrroles with aminoalkanes[2,3] and with α,ω-diaminoalkanes[3,4] and showed that, in the case of the reaction of 3,4-diformylpyrroles with a,w-diaminoalkanes, either 2 + 2 or 1 + 1 cycloadducts were formed depending upon the chain length of the diaminoalkanes. Additionally, we provided ^{13}C NMR evidence that the adducts existed as 3*H*-pyrroles 1b, instead of the expected 1*H*-pyrroles 1a.[3] The unexpected stability of the 3*H*-isomers appears to be derived mainly from a strong intramolecular H-bond, as shown in 1b. In contrast, 2- and 3-formyl- and 2,5-diformylpyrroles react with aliphatic amines to produce 1*H*-pyrrolyl-methylenimines,[2,4] although it has been

reported that the imine derived from 2-formyl-3-methoxy-5-(pyrrol-2-yl)pyrrole exists as the isomeric 2*H*-pyrrole system 2,[5] which is presumably stabilised by intramolecular H-bonding.



1a **1b** **2**

Reactions of 2,5-dimethylpyrrole-3-carboxaldehyde 2,5-dimethylpyrrole-3,4-dicarboxaldehyde



3a **3b** **4**

2,5-Dimethylpyrrole-3-carboxaldehyde reacts with aniline to give the 1*H*-pyrrol-3-ylmethylene-imine, characterised by the ^{13}C NMR signals for the pyrrole ring at δ 104.5, 119.4, 127.9 and 132.8. The ^{1}H and ^{13}C chemical shifts for the CH=N group at δ 8.27 and 154.7, respectively, differ by *ca.* +0.1 and -1.1 ppm, respectively, compared with the corresponding signals for analogous aliphatic imines.[3] In contrast, and analogous to its reaction with aliphatic amines, 2,5-dimethylpyrrole-3,4-dicarboxaldehyde reacts with aniline to produce the "bis-imine", which exists predominantly in the 3*H*-pyrrole form 3b, as evident from the time-averaged ^{13}C NMR chemical shifts for the pyrrole ring carbon atoms at δ 119.5 and 155.8 (*cf.* ref. 3). The time-averaged ^{1}H and ^{13}C signals for the imino group appear at δ 8.36 and 152.9, respectively.

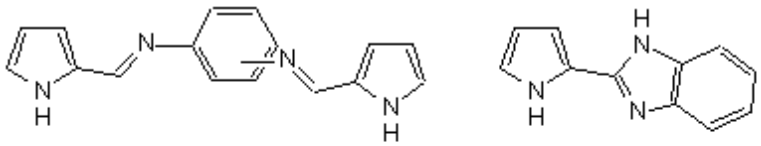
In contrast with its reaction with 1,2-diaminoethane,[3] 2,5-dimethylpyrrole-3,4-dicarboxaldehyde reacted with 1,2-diaminobenzene to yield the 2-(4-formylpyrrol-3-yl)benzimidazole and the bis-benzimidazolyl derivative 4, with no evidence for a macrocyclic 2 + 2 imino adduct analogous to 1. The formation of the benzimidazolyl derivatives, obtained from b-formylpyrroles, is clearly confirmed by their ^{13}C NMR signals at d 144.7 ± 3.9.[6] It is probable

that methylenimines are initially formed in equilibrium with the 1,2-dihydrobenzimidazolyl derivatives but, as the macrocyclic systems analogous to those formed with diaminoalkanes would be anti-aromatic, their formation is energetically unfavourable and a more favourable oxidation of the dihydrobenzimidazoles leads to the isolated aromatic products. Polymeric imine derivatives are formed in trace quantities (δ_H 8.24, δ_C 153.5).

Reactions of pyrrole-2-carboxaldehyde, pyrrole-2,5-dicarboxaldehyde and 3,4-dimethylpyrrole-2,5-dicarboxaldehyde

All NMR spectral data for the imines obtained from aminobenzenes and pyrrole-2-carboxaldehyde indicates that, as with the corresponding reactions with alkylamines,[2,4] the products have the 1*H*-pyrrole structure characterised by the ^{13}C NMR signals for the pyrrole ring at δ 109.8 ± 0.4, 116.7 ± 0.6, 123.7 ± 0.1 and 130.7 ± 0.1. The a-methylenimino group generates ^{1}H and ^{13}C signals at δ 8.26 ± 0.28 and 149.7 ± 1.3, respectively.

The reaction of the 2-carboxaldehyde with 1,2-diaminobenzene has been described previously (e.g. refs. 7 - 11), although there is some confusion with the reaction conditions required specifically to produce the thermally unstable bis-imine 5a or the benzimidazole 6; products having the same melting points have been described (without unequivocal spectral evidence) as having different structures. As with the pyrrol-3-yl isomers, the bis-imine and the benzimidazolyl derivatives are distinguished readily by their ^{1}H and ^{13}C NMR spectra (Table 1). The addition of copper salts to the reaction of the aldehyde with 1,2-diaminobenzene does not act, as might be predicted, as a template for the formation of the bis-imine, but provides a favourable redox system for the conversion of the dihydrobenzimidazole, formed in equilibrium from the bis-imine, into 6. As expected, 1,3- and 1,4-diaminobenzenes produced the bis-imines 5b and 5c.



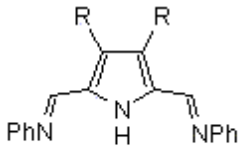
5a 1,2-isomer
5b 1,3-isomer
5c 1,4-isomer

6

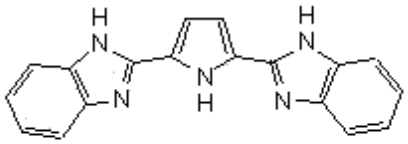
Table 1. Physical data for the products of pyrrole-2-carboxaldehyde with 1,2-, 1,3- and 1,4-diaminobenzene

compound	observed mp (°C)	literature mp (°C)	1H NMR signal[a]	13C NMR signal[a]
5a	197 - 199	148[b]	7.70	150.6
6	260 - 261	278 - 280,[c] 273 - 275,[d] 257 - 258, [e]	-	146.3
5b	145 - 147	137[b]	8.38	150.5
5c	216 - 218	150,[b] 210 - 212[f]	8.37	149.3

[a] N-phenyl (pyrrol-2-yl)methylenimine δ 8.28 and 150.3. [b] ref. 7. [c] *ref. 8.* [d] refs. 9, 10. [e] ref. 11. [f] ref. 12.



7a R = H
7b R = CH_3



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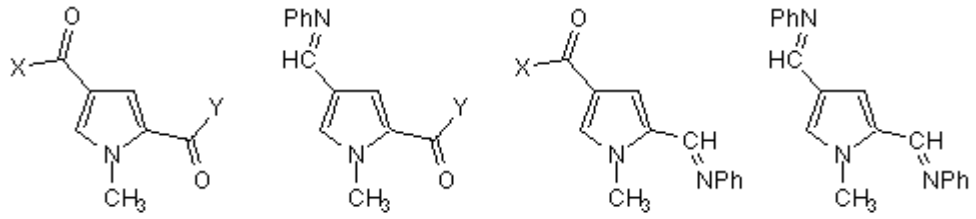
Pyrrole-2,5-dicarboxaldehydes are converted into the bis-imines 7a and 7b upon reaction with aniline but, as with the 3,4-dicarboxaldehydes, reaction with 1,2-diaminobenzene produced a complex mixture comprised mainly of 8 (δ_C 142.0), together with a polymeric imine and the macrocyclic 2 + 2 imino adduct (δ_H 8.22, δ_C 150.0), analogous to that formed from the reaction of pyrrole-2,5-dicarboxaldehyde with a,w-diaminoalkanes.[4,13] None of the products could be obtained in sufficiently pure condition for full characterisation.

Reactions of 1-methylpyrrole-2,4-dicarboxaldehyde

Predictably, reaction of the dialdehyde with an excess of aniline produces the bis-imine 12 but, when reacted with one equivalent of aniline, two mono-imines are produced in a *ca*. 2:1 ratio, as indicated by ^{1}H NMR spectral integration of the CHO and *N*-methyl signals. Comparison of the NMR spectral data (in particular, the ^{13}C NMR chemical shifts of the CH=N group) for the two mono-imines with those for analogous mono-imines 10b, 11b and 11c (Table 2) indicate that the major product is the imine 10a, while 11a is the minor product.



9a X = H; Y = H
9b X = H; Y = OEt
9c X = Me; Y = H
9d X = OMe; Y = H

10a Y = H
10b Y = OEt

11a X = H
11b X = Me
11c X = OMe

12

Table 2. ^{1}H and ^{13}C NMR signals for imines derived from 2- and 4-pyrrolecarboxaldehydes

	2-CH=N group[a]		4-CH=N group[b]	
compound	^{1}H NMR signal	^{13}C NMR signal	^{1}H NMR signal	^{13}C NMR signal
10a	-	-	8.28	153.8
10b	-	-	8.30	153.9
11a	8.28	150.4	-	-
11b	8.23	150.4	-	-
11c	8.17	150.4	-	-
12	8.22	150.7	8.22	152.8

[a] N-phenyl (pyrrol-2-yl)methylenimine δ 8.28 and 150.3 [b] N-phenyl (2,5-dimethylpyrrol-3-yl)-methylenimine δ 8.22 and 154.7.

Experimental Section

General Procedures. Unless indicated otherwise, ^{1}H spectra were measured for $CDCl_3$ solutions at 60, 100 or 270 MHz using JEOL PMX60SI, JEOL FX-100 JEOL JNM-EX-270 spectrometers and ^{13}C NMR spectra were obtained at 67.5 or 100 MHz using JEOL JNM-EX-270 or JEOL JNM-GX-400 spectrometers. All chemical shifts are recorded relative to Me4Si. Infrared spectral measurements were obtained for Nujol mulls using a Perkin-Elmer 577 spectrometer. High resolution mass spectral data were obtained under EI conditions at 70 eV with a AEI MS902 spectrometer.

***N*-[(2,5-Dimethylpyrrol-3-yl)methylene]-*N*-phenylamine.** Aniline (0.37 g, 4 mmol) and 2,5-dimethylpyrrole-3-carboxaldehyde (0.49 g, 4 mmol)in benzene (20 mL) were heated under reflux for 6 h in the presence of A4 molecular sieves and then kept at 15°C for 12 h.. The precipitated product was recrystallised from benzene to give the imine (0.55 g, 69%) as colourless needles, mp 185 - 187°C. Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.75; H. 7.1; N, 14.1. Found:

C, 78.6; H, 7.0; N, 13.8. δ H 2.21 (s, 5-Me), 2.39 (s, 2-Me), 6.33 (d, 1.5 Hz, pyrrolyl 4-CH), 7.00 - 7.45 (m, 5 x phenyl CH), 8.27 (s, CH=N). dC 11.3 (q, 2-Me) 12.7 (q, 5-Me), 104.5 (d, pyrrolyl 4-C), 119.4 (s, pyrrolyl 3-C), 120.9 (d, phenyl 2-C/6-C), 124.5 (d, phenyl 4-C), 127.9 (s, pyrrolyl 5-C), 128.9 (d, phenyl 3-C/5-C), 132.8 (s, pyrrolyl 2-C), 153.8 (s, phenyl 1-C), 154.7 (d, CH=N).

3-Benzimidazol-2-yl-2,5-dimethylpyrrole. 2,5-Dimethylpyrrole-3-carboxaldehyde (1.23 g, 10 mmol) was stirred with 1,2-diaminobenzene (1.1 g, 10 mmol) in methanol (20 mL) at 25°C for 18 h. The solvent was removed under reduced pressure an the red residue was purified by centrifugally accelerated chromatography on Kiesegel using a Chromatatron® Model 7924T with dichloro-methane: ethyl acetate (3:1) as the eluent to give 3-benzimidazol-2-yl-2,5-dimethylpyrrole (0.18 g, 8.5%), mp 200 - 204°C. Anal. Calcd for $C_{13}H_{13}N_3$ C, 73.9; H. 6.2; N, 19.9. Found: C, 73.7; H, 6.0; N, 19.5. δ_H 2.18 (s, 2-Me), 2.45 (s, 5-Me), 6.18 (d, 1.5 Hz, pyrrolyl 4-CH), 6.65 - 6.73 (m, aryl CH), 7.47 (m, aryl CH). δ_C 12.7 (q, 2-Me), 13.1 (q, 5-Me), 105.6 (d, pyrrolyl 4-C), 111.1 (d, benzimidazolyl 4-C/7-C), 114.7 (s, pyrrolyl 3-C), 121.6 (s, pyrrolyl 5-C), 121.9 (d, benzimidazolyl 5-C/6-C), 126.8 (s, pyrrolyl 2-C), 129.1 (s, benzimidazolyl 3a-C/7a-C), 144.2 (s, benzimidazolyl 2-C).

1,3-Dimethyl-4-(phenyliminomethyl)-6-(phenylamino)-2-azafulvene (3b). Aniline (0.74 g, 8 mol) and 2,5-dimethylpyrrole-3,4-dicarboxaldehyde (0.6 g, 4 mmol) and in benzene (25 mL) were heated under reflux for 2 h in the presence of A4 molecular sieves. The reaction mixture was cooled to room temperature, filtered, and evaporated under reduced pressure. The crude product was recrystallised from CCl4:petroleum ether (3:1) to yield 3b (0.86 g, 71%) as red crystals, mp 125°C. Anal. Calcd. for $C_{20}H_{19}N_3$: C, 79.7; H, 6.35; N, 13.9. Found: C, 79.5; H, 6.5; N, 13.8. δ_H 2.52 (s, 3-Me/4-Me), 6.97 - 7.50 (m, 10 x phenyl CH), 8.36 (br s, CH=N/=CH-NH). δ_C 11.1 (q, 3-Me/4-Me), 119.5 (d, pyrrolyl 2-C/5-C), 120.8 (d, phenyl 2-C/6-C), 125.5 (d, phenyl 3-C/5-C), 129.7 (d, phenyl 4-C), 148.7 (s, phenyl 1-C), 152.9 (d, CH=N/CH-NH), 155.8 (s, pyrrolyl 3-C/4-C).

3-Benzimidazol-2-yl-2,5-dimethylpyrrole-4-carboxaldehyde and 3,4-bis-(benzimidazol-2-yl)-2,5-dimethylpyrrole (4). 2,5-Dimethylpyrrole-3,4-dicarboxaldehyde(1.51 g, 10 mmol) was stirred with 1,2-diaminobenzene (1.08 g, 10 mmol) in MeOH (20 mL) at 25°C for 24 h. The solvent was removed under reduced pressure an the red residue was purified by centrifugally accelerated chromatography on Kiesegel using a Chromatatron® Model 7924T with methanol as the eluent to give 3-benzimidazol-2-yl-2,5-dimethylpyrrole-4-carboxaldehyde (0.08 g, 3%), mp 244 - 247°C. Anal. Calcd. for $C_{14}H_{13}N_3O$: C, 70.3 H, 5.5; N, 17.6. Found: C, 70.1; H, 5.4; N, 17.5. δ_H 2.54 (s, 2-Me), 2.67 (s, 5-Me), 7.40 (m, aryl CH), 7.56 (m, aryl CH), 9.86 (s, CHO). δ_C 11.0 (q, 2-Me), 12.9 (q, 5-Me), 108.5 (s, pyrrolyl 3-C), 117.8 (d, benzimidazolyl 4-C/7-C), 121.2 (d, benzimidazolyl 5-C/6-C), 130.0 (s, benzimidazolyl 3a-C/7a-C), 131.9 (s, pyrrolyl 2-C), 142.7 (s pyrrolyl 5-C), 148.8 (s, benzimidazolyl 2-C), 185.7 (d, CHO) and 4 (0.98 g, 30%) mp 270°C (decomp). Anal. Calcd. for $C_{20}H_{17}N_5$: C, 73.4; H, 5.2; N, 21.4, *m*/*z* 327.1484. Found: C, 70.1; H, 5.4; N, 17.5, 327.1489. δ_H 2.75 (s, 2-Me/5-Me), 7.67 (dd, 3.3 Hz, 6.4 Hz), 7.99 (dd, 3.3 Hz, 6.4

Hz). δ_C 12.0 (q, 2-Me,/5-Me), 110.0 (d, benzimidazolyl 4-C/7-C), 128.2 (s 2 x pyrrolyl 2-C/5-C), 128.3 (d, 2 x benzimidazolyl 5-C/6-C), 128.8 (s, 2 x benzimidazolyl 3a-C/7a-C), 128.8 (d, 2 x pyrrolyl 3-C/4-C), 141.1 (s, 2 x benzimidazolyl 2-C).

***N*-Pyrrol-2-ylmethylene-*N*-phenylamine.** Pyrrole-2-carboxaldehyde (1.90 g, 20 mmol) was converted into the methylenimine (2.6 g, 77%), mp 93 - 94.5°C (lit.,[2] mp 93 - 94°C), using the procedure described in the literature.[2] δ_H (DMSO-*d*6) 6.22 (t, 3.5 Hz, pyrrolyl 4-CH), 6.68 (dd, 3.5, 2.0 Hz, pyrrolyl 3-CH), 6.95 - 7.10 (m, pyrrolyl 5-CH), 7.11 - 7.41 (m, 5 x phenyl CH), 8.27 (s, CH=N). δ_C (DMSO-*d*6) 109.5 (d, pyrrolyl 4-C), 116.1 (d, pyrrolyl 3-C), 120.6 (d, phenyl 2-C/6-C), 123.6 (d, pyrrolyl 5-C), 124.8 (d phenyl 4-C), 129.0 (d, phenyl 3-C/5-C), 130.6 (s, pyrrolyl 2-C), 150.3 (d, CH=N), 152.1 (s, phenyl 1-C).

Reaction of pyrrole-2-carboxaldehyde with 1,2-diaminobenzene

(a) 1,2-Diaminobenzene (1.08 g, 10 mmol) and pyrrole-2-carboxaldehyde (1.90 g, 20 mmol) in MeOH (45 mL) were stirred at 15°C for 96 h. The precipitated brown solid was collected, recrystallised from EtOH, and further purified by preparative TLC from silica (R*f* 0.54) to give 2-(pyrrol-2-yl)benzimidazole 6 (0.07 g, 3.8%), mp 260 - 261°C (lit.[8-11], mp 257 - 258°C; 274 - 275°C; 278 - 280.5°C). Anal. Calcd. for $C_{11}H_9N_3$: C, 72.1; H, 4.95; N, 22.9. Found: C, 71.9; H, 5.1; N, 22.7. δ_H 6.35 - 6.45 (m, pyrrolyl 4-H), 7.07 - 7.20 (m, pyrrolyl 3-H), 7.40 - 7.52 (m, pyrrolyl 5-H), 7.60 - 7.72 (m, benzimidazolyl 4-H/5-H/6-H/7H). δ_C 110.1 (d, pyrrolyl 4-C), 110.4 (d, pyrrolyl 3-C), 114.3 (d, benzimidazolyl 4-C/7-C), 121.4 (s, pyrrolyl 2-C), 122.5 (d, benzimidazolyl 5-C/6-C), 123.1 (d, pyrrolyl 5-C), 137.6 (s, benzimidazolyl 3a-C/7a-C), 146.3 (s, benzimidazolyl 2-C).

(b) 1,2-Diaminobenzene (2.16 g, 20 mmol) and pyrrole-2-carboxaldehyde (1.90 g, 20 mmol) in *iso*-PrOH (40 mL) were added to $(MeCO_2)_2Cu.H_2O$ (8.0 g, 40 mmol) in H_2O (100 mL). The reaction mixture was heated at 80 - 90°C for 2 h and then cooled to 0°C. The precipitated Cu(II) complex was collected and suspended in *iso*-PrOH through which H_2S was passed for 1 h. The precipitated CuS was removed and H_2O added to the filtrate to produce a yellow solid, which was recrystallised from EtOH to give 6 (1.88 g, 51%), mp 260 - 262°C.

(c) 1,2-Diaminobenzene (1.4 g, 13 mmol) and pyrrole-2-carboxaldehyde (2.47 g, 26 mmol) in MeOH (60 mL) were stirred heated under reflux for 10 h. The reaction mixture was cooled to 15°C and the precipitated solid was purified by preparative TLC from silica (R*f* 0.71) to give *N*,*N'*-bis(pyrrol-2-ylmethylene)-1,2-diaminobenzene 5a (3.1 g, 91%), mp 197 - 199°C (decomp.) (lit.[7], mp 148°C). Anal. Calcd. for $C_{16}H_{14}N_4$: C, 73.3; H, 5.4; N, 21.4. Found: C, 72.9; H, 5.3; N, 21.4. δ_H 6.01 (dd, 3.5, 2.2 Hz, 2 x pyrrolyl 4-H), 6.28 - 6.40 (m, 2 x pyrrolyl 3-H), 6.41 (dd, 3.5, 1.5 Hz, 2 x pyrrolyl 5-H), 7.32 - 7.40 (m, 4 x aryl CH), 7.70 (s, CH=N). δ_C 109.6 (d, pyrrolyl 4-C), 117.2 (d, pyrrolyl 3-C), 118.9 (d, aryl 3-C/6-C), 123.8 (d, pyrrolyl 5-C), 126.6 (d, aryl 4-C/5-C), 130.9 (s, pyrrolyl 2-C), 145.7 (s, aryl 1-C/2-C), 150.6 (d, CH=N).

Reaction of pyrrole-2-carboxaldehyde with 1,3- and 1,4-diaminobenzene. Pyrrole-2-carboxaldehyde (0.95 g, 10 mmol) and the appropriate diaminobenzene (0.54 g, 5 mmol) in

MeOH (15 mL) were stirred at 15°C for 12 h. The precipitated solid was collected and recrystallised from EtOH.

***N,N'*-Bis(pyrrol-2-ylmethylene)-1,3-diaminobenzene (5b)** (82%) had mp 145 - 147°C (lit.[7], mp 137°C). Anal. Calcd for $C_{16}H_{14}N_4$: C, 73.3; H, 5.4; N, 21.4. Found: C, 73.3, H, 5.5, N, 21.4. δ_H 6.20 - 6.28 (m, 2 x pyrrolyl 4-CH), 6.69 - 6.78 (m, 2 x pyrrolyl 3-CH), 6.94 - 7.05 (m, 2 x pyrrolyl 5-CH), 7.10 - 7.66 (m, aryl 4-CH/5-CH/6-CH), 7.33 (s, 1H, aryl 2-CH), 8.38 (s, 2 x CH=N). δ_C 110.4 (d, pyrrolyl 4-C), 113.4 (d, aryl 2-C), 117.2 (d, pyrrolyl 3-C), 118.2 (d, aryl 4-C/6-C), 123.7 (d, pyrrolyl 5-C), 129.9 (d, aryl 5-C), 130.6 (s, pyrrolyl 2- C), 150.4 (d, CH=N), 152.8 (s, aryl 1-C/3-C).

***N,N'*-Bis(pyrrol-2-ylmethylene)-1,4-diaminobenzene (5c)** (85%) had mp 216 - 218°C (lit.,[7,12] mp 150°C, 210 - 212°C). Anal. Calcd for $C_{16}H_{14}N_4$: C, 73.3; H, 5.4; N, 21.4. Found: C, 73.1, H, 5.4, N, 21.3. δ_H (DMSO-*d*6) 6.20 - 6.28 (m, 2 x pyrrolyl 4-CH), 6.69 - 6.79 (m, 2 x pyrrolyl 3-CH), 7.00 - 7.12 (m, 2 x pyrrolyl 5-CH), 7.25 (s, 4 x aryl CH), 8.37 (s, 2 x CH=N). δ_C (DMSO-*d*6) 109.7 (d, pyrrolyl 4-C), 116.2 (d, pyrrolyl 3-C), 121.5 (d, aryl 2-C/3-C/5-C/6-C), 123.6 (d, pyrrolyl 5-C), 130.7 (s, pyrrolyl 2-C), 149.1 (s, aryl 1-C/4-C), 149.3 (d, CH=N).

Reaction of pyrrole-2,5-dicarboxaldehydes with aniline. Aniline (0.5 g, 5.4 mmol) and the appropriate pyrrole-2,5-dicarboxaldehyde (2.7 mmol) were heated under reflux in benzene (10 mL) in the presence of A4 molecular sieves for 2 h and then allowed to stand at 15°C for 24 h. The precipitated bis-imine was collected, separated from the molecular sieves, and recrystallised from EtOH.

Pyrrole-2,5-dicarboxaldehyde gave 7a. (75%) mp 172 - 173°C. Anal. Calcd for $C_{18}H_{15}N_3$: C, 79.1; H, 5.5; N, 15.4. Found: C, 78.9; H, 5.5; N, 15.3. dH (DMSO-*d*6) 6.89 (s, pyrrolyl 3-CH/4-CH), 7.05 - 7.49 (m, 10 x phenyl CH), 8.47 (s, CH=N). dC (DMSO-*d*6) 114.8 (d, pyrrolyl 3-C/4-C), 120.6 (d, phenyl 2-C/6-C), 125.4 (d, phenyl 4-C), 129.1 (d, phenyl 3-C/5-C), 134.2 (s, pyrrolyl 2-C/5-C), 150.5 (d, CH=N), 151.5 (s, phenyl 1-C).

3,4-Dimethylpyrrole-2,5-dicarboxaldehyde gave 7b. (80%), mp 154 -155°C. Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.7; H, 6.35; N, 13.9. Found: C, 79.4; H, 6.5; N, 13.9. δ_H 2.20 (s, 3-Me/4-Me), 6.95 - 7.35 (m, 10 x phenyl CH), 8.36 (s, 2 x CH=N). d_C 8.6 (q, Me), 120.9 (d, phenyl 2-C/6-C), 125.6 (d, phenyl 4-C), 125.9 (s, pyrrolyl 3-C/4-C), 129.1 (d, phenyl 3-C/5-C), 130.3 (s, pyrrolyl 2-C/5-C), 147.2 (d, CH=N), 151.9 (s, phenyl 1-C).

Reaction of pyrrole-2,5-dicarboxaldehyde with 1,2-diaminobenzene. 1,2-Diaminobenzene (0.82 g, 7.6 mmol) and pyrrole-2,5-dicarboxaldehyde (0.46 g, 3.8 mmol) in EtOH (30 mL) were heated under reflux for 3 h and then cooled to 0°C. H_2O (50 mL) was added to precipitate an inseparable mixture of products (1.2 g) comprising of 8, as the major product [δ_H 6.60 (s, pyrrolyl 3-CH/4-CH), 6.90 - 7.04 (m, aryl CH), 6.55 - 6.73 (m, aryl CH). δ_C 115.4 (d, pyrrolyl 3-C/4-C), 116.6 (d, benzimidazolyl 4-C/7-C), 120.1 (benzimidazolyl 5-C/6-C), 122.6 (s, pyrrolyl 2-C/5-C), 136.8 (s, benzimidazolyl 3a-C/7a-C), 142.0 (s, benzimidazolyl 2-C)] and imino derivatives [*inter alia* dH 8.22 and dC 150.0 (d, CH=N) and 146.9 (d, aryl 1-C/2-C)].

***N*-[(4-Acetyl-1-methylpyrrol-2-yl)methylene]-*N*-phenylamine (11b).** Aniline (0.47 g, 5 mmol) was added to a stirred solution of 4-acetyl-1-methylpyrrole-2-carboxaldehyde (0.76 g, 5 mmol) in benzene (20 mL) and the mixture was heated under reflux for 2 h in the presence of 4A molecular sieves. The mixture was filtered, dried ($MgSO_4$), and evaporated. The residue was subjected to chromatography on silica, using petroleum ether:ethyl acetate (1:1) as the eluent, and then distilled to give 11b (0.98 g, 87%) as a viscous oil, which did not solidify. Anal: Calcd for $C_{14}H_{14}N_2O$: C, 74.3; H, 6.2; N, 12.4. Found: C, 73.9; H, 6.3; N, 12.5. δ_H 2.40 (s, COMe), 4.06 (s, NMe), 6.98 (d, 3 Hz, pyrrolyl 3-CH), 7.07 - 7.39 (m, 5 x phenyl-CH + pyrrolyl 5-CH), 8.24 (s, CH=N). δ_C 27.0 (q, CO<u>Me</u>), 37.8 (q, NMe), 118.4 (d, pyrrolyl 3-C), 120.7 (d, phenyl 2-C/6-C), 125.5 (s, pyrrolyl 4-C), 125.7 (d, phenyl 4-C), 129.2 (d, phenyl 3-C/5-C), 131.5 (s, pyrrolyl 2-C), 132.2 (d, pyrrolyl 5-C), 150.4 (d, CH=N), 152.1 (s, phenyl 1-C), 192.4 (s, C=O).

***N*-[(4-Methoxycarbonyl-1-methylpyrrol-2-yl)methylene]-*N*-phenylamine (11c).** Using a procedure analogous to that described for the preparation of 11b, methyl 2-formyl-1-methylpyrrole-4-carboxylate gave 11c (78%), mp 44 - 47°C. Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.4; H, 5.8; N, 11.6. Found: C, 69.0 H, 5.8; N, 11.3. δ_H 3.78 (s, NMe), 4.01 (s, OMe), 7.08 (d, 3 Hz, pyrrolyl 3-CH), 7.12 - 7.45 (m, 5 x phenyl CH + pyrrolyl 5-CH), 8.23 (s, CH=N). δ_C 37.7 (q, NMe), 51.1 (q, OMe), 115.6 (s, pyrrolyl 4-C), 119.2 (d, pyrrolyl 3-C), 120.6 (d, phenyl 2-C/6-C), 125.5 (d, phenyl 4-C), 129.0 (d, phenyl 3-C/5-C), 131.0 (s, pyrrolyl 2-C), 132.7 (d, pyrrolyl 5-C), 150.4 (d, CH=N), 152.0 (s, phenyl 1-C), 164.3 (s, C=O).

***N*-[(5-Ethoxycarbonyl-1-methylpyrrol-3-yl)methylene]-N-phenylamine (10b).** Using a procedure analogous to that described for the preparation of 11b, ethyl 4-formyl-1-methylpyrrole-2-carboxylate gave 10b (77%), mp 55 - 57°C. Anal. Calcd for $C_{15}H_{16}N2O_2$: C, 70.3; H, 6.3; N, 10.9. Found: C, 70.3; H, 6.4; N, 10.9. δ_H 1.36 (t, 7.1 Hz, MeCH2), 3.98 (s, NMe), 4.29 (q, 7.1 Hz, MeCH2), 7.01 - 7.46 (m, 5 x phenyl + 2 x pyrrolyl CH), 8.29 (s, CH=N). δ_C 14.4 (q, MeCH2), 37.3 (q, NMe), 60.1 (t, MeCH2), 117.1 (d, pyrrolyl 4-C), 120.8 (d, phenyl 2-C/6-C), 122.2 (s, pyrrolyl 5-C), 124.3 (s, pyrrolyl 3-C), 125.3 (d, phenyl 4-C), 129.0 (d, phenyl 3-C/5-C), 131.0 (d pyrrolyl 2-C), 152.6 (s, phenyl 1-C), 153.9 (d, CH=N), 161.0 (s, C=O).

Reaction of 1-methylpyrrole-2,4-dicarboxaldehyde with aniline

(a)Aniline (0.56 g, 6 mmol) in dry acetonitrile (15 mL) was added to 1-methylpyrrole-2,4-dicarboxaldehyde (0.82 g, 6 mmol) in dry acetonitrile (10 mL) in the presence of 4A molecular sieves. The mixture was heated under reflux for 10 h, filtered, dried ($MgSO_4$), and evaporated to give a 2:1 mixture of *N*-[(5-formyl-1-methylpyrrol-3-yl)methylene]-*N*-phenylamine 10a and *N*-[(4-formyl-1-methylpyrrol-2-yl)methylene]-*N*-phenyl-amine 11a, which could not be separated effectively by chromatography. Anal: Calcd for $C_{13}H_{12}NO$: C, 73.6, H, 5.7, N, 13.2. Found: C, 73.9; H, 5.6; N, 13.5. 10a δ_H 3.92 (s, NMe), 6.94 - 7.55 (5 x phenyl + 2 x pyrrolyl CH), 8.26 (s, CH=N), 9.57 (d, 1.5 Hz, CHO); δ_C 37.6 (q, NMe), 117.4 (d, pyrrolyl 4-C), 120.7 (d, phenyl 2-C/6-C), 122.7 (s, pyrrolyl 5-C), 125.2 (d, phenyl 4-C), 125.5 (d, pyrrolyl 2-C), 129.1 (d, phenyl 3-C/5-C), 131.5 (s, pyrrolyl 3-C), 152.6 (s, phenyl 1-C), 153.8 (d, CH=N), 180.2 (d, CHO). 11a

δ_H 4.04 (s, NMe), 6.94 - 7.55 (5 x phenyl + 2 x pyrrolyl CH), 8.26 (s, CH=N), 9.70 (s, CHO); δ_C 38.1 (q, NMe), 117.5 (d, pyrrolyl 3-C), 120.7 (d, phenyl 2-C/6-C), 123.6 (s, pyrrolyl 4-C), 125.5 (d, phenyl 4-C), 129.1(d, phenyl 3-C/5-C), 133.0 (s, pyrrolyl 2-C), 134.4 (d, pyrrolyl 5-C), 150.4 (d, CH=N), 152.6 (s, phenyl 1-C), 184.5 (d, CHO).

(b) Aniline (1.12 g, 12 mmol) in dry acetonitrile (15 mL) was added to 1-methylpyrrole-2,4-dicarboxaldehyde (0.82 g, 6 mmol) in dry acetonitrile (10 mL) in the presence of 4A molecular sieves. The mixture was heated under reflux for 24 h, filtered, dried ($MgSO_4$), and evaporated. Recrystallisation of the crude product from petroleum ether gave 1-methyl-2,4-bis(phenyl-iminomethyl)pyrrole 12 (1.4 g, 81%). Mp 68 - 71°C. Anal: Calcd for $C_{19}H_{17}N_3$: C, 79.4; H, 6.0; N, 14.6. Found: C, 79.2; H, 6.1; N, 14.7. δ_H 4.05 (s, NMe), 7.04 (s, pyrrolyl 3-CH), 7.08 - 7.44 (m, 10 x phenyl CH + pyrrolyl 5-CH), 8.24 (s, 2 x CH=N). δ_C 37.7 (q, NMe), 117.6 (d, pyrrolyl 3-C), 120.8 (d, phenyl 2-C/6-C), 123.2 (d, pyrrolyl 5-C), 125.2 (d, phenyl 4-C), 125.3 (s, pyrrolyl 2-C), 129.1 (s, pyrrolyl 4-C), 131.5 (d, pyrrolyl 5-C), 131.7 (s, pyrrolyl 2-C), 150.7 (d, 2-CH=N), 152.8 (d, 4-CH=N).

Acknowledgements

We thank the University of Alcalá de Henares, Madrid, for leave of absence and funding from the British Council and Fondo de Investigaciones Sanitarias for G.Q-L and the EC for an Erasmus grant for H.Z.

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