Dyes and Pigments **20** (1992) 83–96

Substituent Effects on the Spectra of Fluorescent Arylsubstituted *N*-Methylpyrrolo[3,4-c]pyridines

Shuntaro Mataka,* Masashi Tashiro

Institute of Advanced Material Study, Kyushu University 6-1, Kasuga-koh-en, Kasuga-shi, Fukuoka 816, Japan

Osamu Misumi, Wei Hua Lin

Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University 6-1, Kasuga-koh-en, Kasuga-shi, Fukuoka 816, Japan

Kazufumi Takahashi & Akiyoshi Tori-i

Kurume National College of Technology 1232, Komorino, Kurume-shi, Fukuoka 830, Japan

(Received 24 April 1992; accepted 25 May 1992)

ABSTRACT

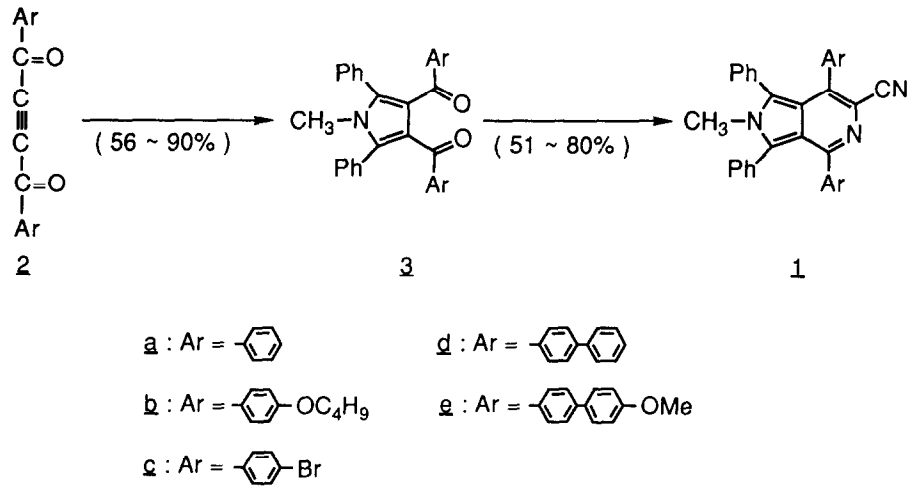
Introduction of an alkoxy group into the phenyl ring at the **4** *and* **7** *positions of the tetra-aryl derivatives* **1**, **6** *and* **7** *has little effect on the absorption and emission spectra of a series of* N-*methylpyrrolo-[3,4-c]pyridines, whilst introduction of a bromo substituent caused a red shift in the spectrum of* **1**. *The nitrile derivative* **1**, *the ester* **8**, *and the* **6**-*unsubstituted derivative* **10** *were strongly fluorescent, whilst the fluorescence of* **6** *was weak; the hydrazide* **9** *and carboxylic acid* **7** *were also weakly fluorescent with a large Stokes shift (*c. *150 nm). The pyridazines* **13** *and* **14** *were non-fluorescent.*

1 INTRODUCTION

Much effort has been made in the search for strongly fluorescent organic compounds suitable for the light source in an electroluminescent (EL) device.[1,2] It was recently reported that a thin film of the strongly

* To whom correspondence should be addressed.

Dyes and Pigments 0143-7208/92/$05.00 © 1992 Elsevier Science Publishers Ltd, England. Printed in Great Britain



Scheme 1

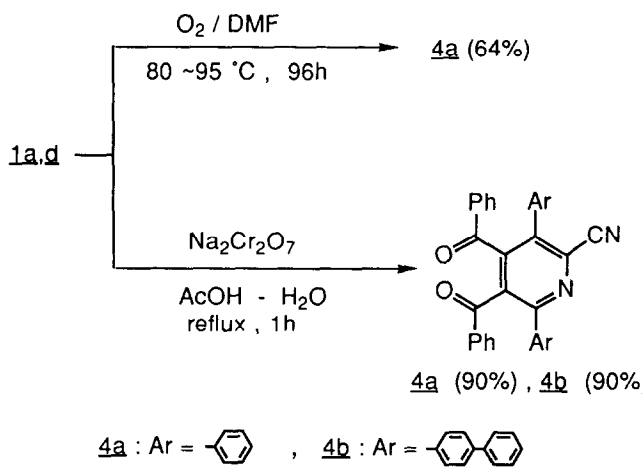
fluorescent cyanotetraphenylpyrrolo[3,4-c]pyridine (**1**) emitted bright green light in the EL device of a double hetero system.[3]

This present paper reports the effect of substituents on the absorption and fluorescent spectra of **1**.

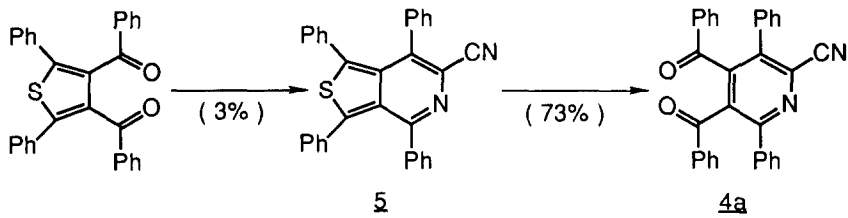
2 RESULTS AND DISCUSSION

2.1 Preparation

Five tetraarylpyrrolopridines **1a–e** were prepared according to the reported method[4] in yields of 30–56% from the diaroylacetylenes **2** via the



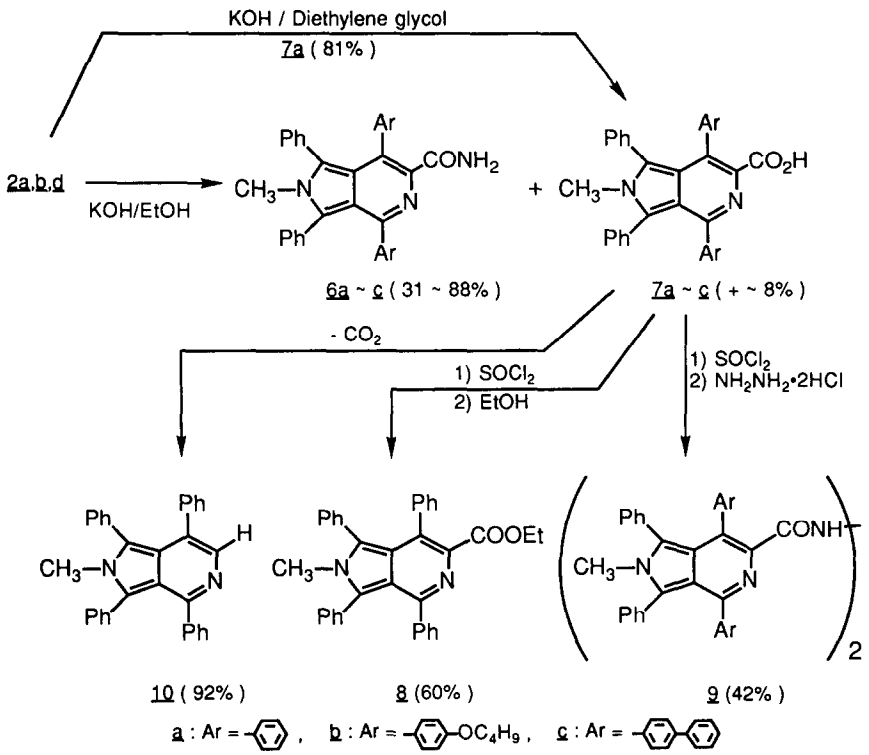
Scheme 2



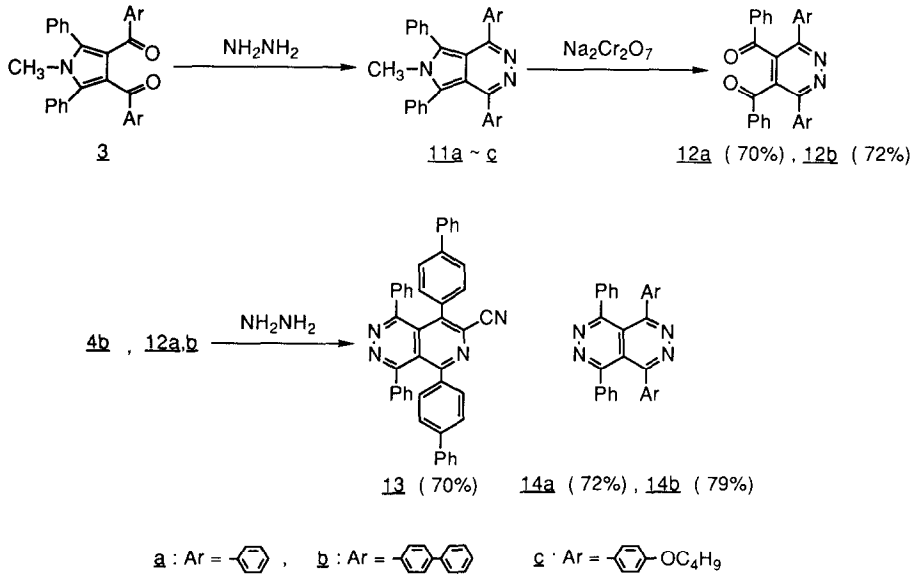
Scheme 3

diaroylpyrroles **3** (Scheme 1). During the work, the disappearance of the fluorescence of **1** on TLC plates in air at room temperature for several days was observed. This indicates the oxidative degradation of the pyrrole ring, since **1** possesses an isoindole-like skeleton. On both air oxidation at 80–95°C and on treatment with aqueous sodium dichromate, **1** produced **4** in 64% and 90% yields, respectively; compound **4** had been previously prepared via **5** in poor yields[5] (Schemes 2 and 3).

The amide **6**, carboxylic acid **7**, ester **8**, hydrazide **9**, and unsubstituted derivative **10** were prepared according to Scheme 4.



Scheme 4



Scheme 5

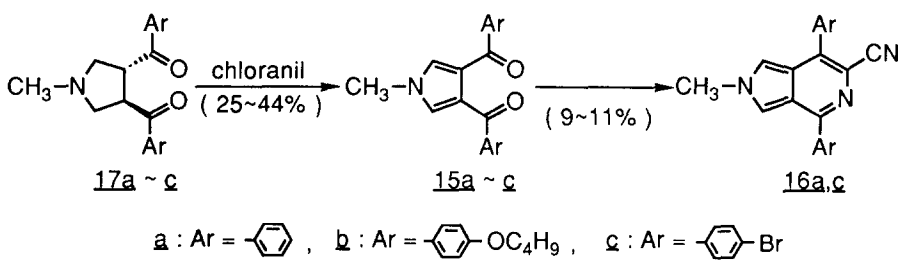
The diaroylpyridine **4** and the diaroylpyridazine **12** (which was obtained from **11**), when condensed with hydrazine, gave the triazanaphthalene **13** and tetraaza derivative **14**, respectively (Scheme 5).

The diaroylpyrrole **15** afforded **16** on condensation with cyanomethylamine (Scheme 6); the diarylpyrrolopyridine **16** is unstable in solution and its decomposition during chromatography lowered the yield.

2.2 Spectra

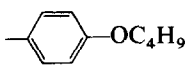
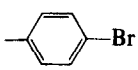
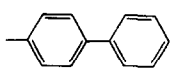
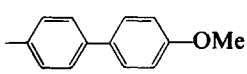
Absorption and emission spectra of compounds prepared above are given in Tables 1–3.

The introduction of the electron-donating butoxy group into the phenyl group of the cyanopyridine ring has little effect on the absorption



Scheme 6

TABLE 1
Spectral Data of **1**, **6** and **7** $CHCl_3$

Ar		*Compound*		
		1 λ_{max} (*nm*)	**6** λ_{max} (*nm*)	**7** λ_{max} (*nm*)
	Abs. (log ε) Fl. (Rel. Int.)	388 (3·98) 484 (3·1)	384 (3·97) 485 (1·0)	391 (4·04) 540 (1·1)
	Abs. (log ε) Fl. (Rel. Int.)	390 (4·06) 477 (3·4)	382 (4·09) 479 (1·1)	392 (3·99) 539 (1·4)
	Abs. (log ε) Fl. (Rel. Int.)	396 (3·93) 502 (3·0)	— 	— —
	Abs. (log ε) Fl. (Rel. Int.)	397 (4·06) 503 (3·1)	389 (4·03) 506 (1·0)	395 (4·01) 548 (1·4)
	Abs. (log ε) Fl. (Rel. Int.)	395 (4·09) 500 (4·0)	—	—

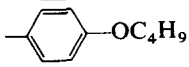
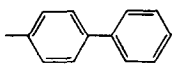
spectra of **1**, **6**, **7** and **11**, whilst the bromo substituent caused a red shift of 8 nm, as seen in **1c**. These observations are in contrast to those in the 1,2,5-thiadiazolopyridine series,[6] in which both types of substituent caused a red shift in the spectra. This difference may be relatable to the electron-donating nature of the pyrrole ring compared to the electron-withdrawing 1,2,5-thiadiazole system. The effect of a substituent in the 6-position of tetraarylpyrrolopyridines on the absorption spectra is small. Removal of the aryl group in the pyrrole ring resulted in a blue shift, as seen in the spectrum of **16**. The pyridazine **11** absorbed at shorter wavelength than the corresponding pyridine **1**.

The tetraarylpyrrolopyridines **1**, **8** and **10** showed strong green to

TABLE 2
Spectral Data of **8**, **9** and **10** $CHCl_3$

	Compound		
	8 λ_{max} (*nm*)	**9** λ_{max} (*nm*)	**10** λ_{max} (*nm*)
Abs. (log ε)	384 (4·03)	383	386 (4 07)
Fl. (Rel. Int.)	504 (3·9)	540	506 (4·4)

TABLE 3
Spectral Data of **11** in $CHCl_3$

Ar	λ_{max} (*nm*)		
	Abs.	(*log ε*)	*Fl.*
	366	(3·91)	541
	366	(4·04)	525
	370	(4·07)	543

yellow-green fluorescence. The amide **6** fluoresced in a similar color, but with weak intensity. The acid **7** and the hydrazide **9** emit weak fluorescence at longer wavelength (540–550 nm). This tendency is in accord with results on 1,2,5-thiadiazolo derivatives.[6]

The diaryl derivative **16** fluoresces bright-blue light. In chloroform solution, this fluorescence disappeared in a short period, probably due to the oxidative decomposition of the pyrrole ring. The Stokes shift (71–75 nm) of **16** are smaller than those (96–106 nm) of the corresponding tetraaryl deriative **1**.

Solutions of **11** showed a weak emission (Table 3) and those of **13** and **14** were not fluorescent.

3 EXPERIMENTAL

3.1 General

Melting points are uncorrected. IR spectra were recorded on a Nippon Bunko (Tokyo, Japan) IR-700 spectrophotometer (KBr). ^{1}H-NMR (internal Me_4Si) spectra were taken on a JEOL (Tokyo, Japan) GSX-270 NMR spectrometer in $CDCl_3$. Mass spectra were recorded on a Nippon Denshi (Tokyo, Japan) JMS-01SG-2 mass spectrometer at 75 eV using a direct-inlet system. Absorption and emission spectra were measured on a Hitachi (Hitachi-shi, Japan) 220A and a Hitachi F-4010 fluorescence spectrophotometer, respectively. Column chromatography was carried out on silica gel (Wako (Osaka, Japan) gel, C-300). IR and ^{1}H-NMR spectral data of **1**, **3**, **4**, **6**, **7**, **12**, **15** and **17** are given in Table 4.

TABLE 4

IR and ^{1}H-NMR Spectral Data of **1**, **3**, **4**, **6**, **7**, **12**, **15** and **17**

Compound	*IR: ν (cm^{-1})*	*^{1}H NMR: δ (ppm)*
1b	2215	0·98 (3H, t, J = 7 Hz), 1·00 (3H, t, J = 7 Hz), 1 29–1·86 (8H, m), 3·56 (3H, s), 3·86 (4H, t, J = 7 Hz), 6·46 (2H, d, J = 9 Hz), 6·50 (2H, d, J = 9 Hz), 6 85–7·19 (14H, m)
1c	2230	3·59 (3H, s), 6·83–7 29 (18H, m)
1d	2215	3·63 (3H, s), 6·98–7·42 (28H, m)
1e	2230	3·61 (3H, s), 3 84 (6H, s), 6 90–7·44 (26H, m)
3b	1650	0 96 (6H, t, J = 7 Hz, 1·26–1 84 (8H, m), 3 40 (3H, s), 3·88 (4H, t, J = 7 Hz), 6·56 (4H, dd, J = 9 and 2 Hz), 7·26–7 46 (14H, m)
3c	1650	3·38 (3H, s), 7·24–7 32 (18H, m)
3d	1650	3·43 (3H, s), 7 23–7·54 (28H, m)
3e	1645	3·44 (3H, s), 3 88 (6H, s), 6·94 (4H, d, J = 8·8 Hz), 7·26–7 52 (22H, m)
4b	2230, 1675	7·10–7·68 (28H, m)
6a	3490, 3350, 1680, 1660	3 44 (3H, s), 5·10 (1H, br, D_2O-exchanged), 6 88–7 24 (20H, m), 7 94 (1H, br, D_2O-exchanged)
6b	3450, 3400, 1680	0·97 (6H, t, J = 7 Hz), 1·16–1·92 (8H, m), 3·47 (3H, s), 3·82 (2H, t, J = 7 Hz), 3·86 (2H, t, J = 7 Hz), 5 17 (1H, br, D_2O-exchanged), 6 40 (2H, d, J = 9 Hz), 6 48 (2H, d, J = 9 Hz), 6·72–7·16 (14H, m), 7·94 (1H, br, D_2O-exchanged)
6c	3430, 3300, 1690	3 52 (3H, s), 5·22 (1H, br, s, D_2O-exchanged), 6·82–7·49 (28H, m, 8·07 (1H, br, s, DO_2-exchanged)
7a	1750	3 50 (3H, s), 6 84–7 24 (20H, m), 12·35 (1H, br s)
7b	1750	0·96 (6H, t, J = 8 Hz), 1 20–1·84 (8H, m), 3·48 (3H, s), 3·80 (2H, t, J = 6 Hz), 3·84 (2H, t, J = 6 Hz), 6·40 (2H, d, J = 9 Hz), 6·48 (2H, d, J = 9 Hz), 6·80–7 14 (14H, m), 12·50 (1H, br)
7c	1750	3 54 (3H, s), 6 92–7 40 (28H, m), 11 96 (1H, br s)
12a	1660	7·05–7·63 (20H, m)
12b	1670	7·12–7·72 (28H, m)
15a	1640, 1620	3 72 (3H, s), 7·04 (2H, s), 7 12–7 44 (6H, m), 7·60 (4H, dd, J = 8 and 2 Hz)
15b	1640, 1600	0 96 (6H, t, J = 6 Hz), 1·28–1 86 (8H, m), 3·72 (3H, s), 3·92 (4H, t, J = 6 Hz), 6·70 (4H, d, J = 9 Hz), 7·02 (2H, s), 7 60 (2H, d, J = 9 Hz)
15c	1660, 1640	3·64 (3H, s), 6·96 (2H, s), 7·36 (4H, d, J = 8 Hz), 7·40 (4H, d, J = 8 Hz)
17a	1680	2 28 (3H, s), 2 74 (2H, dd, J = 8 and 5 Hz), 3 04 (2H, m), 4 60 (2H, m), 7·28–7 50 (6H, m), 7 91 (2H, dd, J = 8 and 2 Hz)
17b	1670	0·96 (6H, t, J = 6 Hz), 1·30–1·88 (8H, m), 2·32 (3H, s), 2·78 (2H, dd, J = 8 and 5 Hz), 2·94–3·10 (2H, m), 4·00 (4H, t, J = 6 Hz), 4 44–4·56 (2H, m), 6·88 (4H, d, J = 9 Hz), 7 93 (2H, d, J = 9 Hz)
17c	1680	2 31 (3H, s), 2·73 (2H, dd, J = 8 and 5 Hz), 2·94–3·10 (2H, m), 4·44–4 56 (2H, m), 7 58 (4H, d, J = 9 Hz), 7 82 (2H, d, J = 9 Hz)

3.2 Preparation of 3

The diaroylpyrroles **3** were prepared according to the reported method,[7] giving:

*3,4-Di(*p*-butoxybenzoyl)-2,5-diphenyl-1-methylpyrrole* ***(3b)***. Yield 77%; colorless plates (methanol); m.p. 130–131°C; M^+ 585. Calcd for $C_{39}H_{39}NO_4$: C, 79·97; H, 6·71: N, 2·39. Found: C, 79·97; H, 6·60: N, 2·50%.

*3,4-Di(*p*-bromobenzoyl)-2,5-diphenyl-1-methylpyrrole (**3c**)*. Yield 69%; colorless prisms (methanol); m.p. 195–199°C; M^+ 601, 599, 597. Calcd for $C_{31}H_{21}NO_2Br_2$: C, 62·13: H, 3·53; N, 2·34. Found: C, 62·13; H, 3·71; N, 2·58%.

*3,4-Di(*p*-phenylbenzoyl)-2,5-diphenyl-1-methylpyrrole (**3d**)*. Yield 90%; colorless prisms (ethanol): m.p. 199–201°C; M^+ 593. Calcd for $C_{43}H_{31}NO_2$: C, 86·99; H, 5·26; N, 2·36. Found: C, 86·84; H, 5·49: N, 2·34%.

*3,4-Di[4-(*p*-methoxyphenyl)benzoyl]2,5-diphenyl-1-methylpyrrole (**3e**)*. Yield 59%; colorless prisms (hexane–benzene): m.p. 241–244°C; M^+ 653. Calcd for $C_{45}H_{35}NO_4$: C, 82·67; H, 5·40; N, 2·14. Found: C, 82·79; H, 5·47; N, 1·93%.

3.3 Preparation of 1

The cyanopyrrolopyridines **1** were obtained by condensation of **3** with cyanomethylammonium hydrogen sulfate, as reported previously,[4] giving:

*6-Cyano-2-methyl-1,3,4,7-tetraphenylpyrrolo[3,4-c]pyridine (**1a**)*. Yellow prisms (ethanol); m.p. 272–274°C (lit.[4] 232–234°C). Found: C, 85·55; H, 5·22; N, 8·91%. Calcd for $C_{33}H_{23}N_3$: C, 85·87; H, 5·02; N, 9·11.

*4,7-Di(*p*-butoxyphenyl)-6-cyano-2-methyl-1,3-diphenylpyrrolo[3,4-c]-pyridine (**1b**)*. Yield 55%; pale yellow needles (methanol); m.p. 207–210°C; M^+ 605. Calcd for $C_{41}H_{39}N_3O_2$: C, 81·29; H, 6·49; N, 6·94. Found: C, 81·75; H, 6·48; N, 7·02%.

*4,7-Di(*p*-bromophenyl)-6-cyano-2-methyl-1,3-diphenylpyrrolo[3,4-c]-pyridine (**1c**)*. Yield 80%; green prisms (methanol); m.p. 313–315°C; M^+ 621, 619, 617. Calcd for $C_{33}H_{21}N_3Br_2$: C, 64·00; H, 3·42; N, 6·78. Found: C, 64·06; H, 3·63; N, 6·78%.

*4,7-Di-(*p*-phenylphenyl)-6-cyano-1,3-diphenylpyrrolo[3,4-c]pyridine (**1d**)*. Yellow-green plates (a 1 : 1 mixture of benzene and ethanol); m.p. 340–343°C; M^+ 613. Calcd for $C_{45}H_{31}N_3$: C, 88·06; H, 5·09; N, 6·85. Found: C, 87·81; H, 5·25; N, 6·74%.

*4,7-Di[4-(*p-*butoxyphenyl)phenyl)]-6-cyano-1,3-diphenylpyrrolo[3,4-c]-pyridine (***1e***).* Yield 51%; yellow needles (benzene); m.p. 386–394°C; M^+ 673. Calcd for $C_{47}H_{35}N_3O_2$: C, 83·78: H, 5·24; N, 6·24. Found: C, 83·66; H, 5·30, N, 5·99%.

3.4 Preparation of 4 and 12

Oxidation of **1** and **11** with sodium dichromate was carried out according to the reported method,[5] giving:

*2-Cyano-4,5-di(*p-*phenylbenzoyl)-3,6-diphenylpyridine (**4b**).* Yield 90%; colorless prisms (a 4:1 mixture of benzene and ethanol); m.p. 278–281°C; M^+ 616. Calcd for $C_{44}H_{28}N_2O_2$: C, 85·69; H, 4·58: N, 4·54. Found: C, 85·75; H, 5·03; N, 4·48%.

*4,5-Dibenzoyl-3,6-tertraphenylpyridazine (**12a**).* Yield 70%; colorless prisms (methanol); m.p. 191–193°C; M^+ 440. Calcd for $C_{30}H_{20}N_2O_2$: C, 81·80; H, 4·58; N, 6·36. Found: C, 82·00: H, 4·78: N, 6·25%.

*4,5-Dibenzoyl-3,6-di(*p-*phenyl)phenylpyridazine (**12b**).* Yield 72%; skin-colored prisms (ethanol); m.p. 229–232°C; M^+ 592. Calcd for $C_{42}H_{28}N_2O_2$: C, 85·11; H, 4·76; N, 4·73. Found: C, 84·76; H, 4·96; N, 4·63%.

3.5 Preparation of 6 and 7

Typical procedure: a mixture of **1a** (1·00 g, 2·70 mmol) and potassium hydroxide (25 g) in ethanol (250 ml) was heated under reflux for 24 h. The liquor was cooled, poured into dilute hydrochloric acid and neutralized with aqueous sodium hydrogen carbonate. The mixture was extracted with dichloromethane, dried, and evaporated *in vacuo* to leave a residue which was then chromatographed. A trace amount of unchanged **1a** was eluted with a 95:5 mixture of benzene and ethyl acetate, then the desired amide **6a** (917 mg, 88%) and carboxylic acid (40 mg, 4%) were eluted with 4:1 and 3:2 mixtures of the two solvents respectively.

*2-Methyl-1,3,4,7-tetraphenylpyrrolo[3,4-c]pyridine-6-ylcarboxamide (**6a**).* Green prisms (ethanol); m.p. 315·5–318°C; M^+ 479. Calcd for $C_{33}H_{25}N_3O$: C, 82·65; H, 5·25; N, 8·76. Found: C, 82·66; H, 5·34; N, 8·75%.

*2-Methyl-1,3,4,7-tetraphenylpyrrolo[3,4-c]pyridine-6-ylcarboxylic acid (**7a**).* Yellow prisms (hexane); m.p. 246–249°C; M^+ 480. Calcd for $C_{33}H_{24}N_2O_2$: C, 82·48; H, 5·03; N, 5·83. Found: C, 82·52; H, 5·15; N, 5·63%.

*4,7-Di(*p-*butoxyphenyl)-2-methyl-1,3-diphenylpyrrolo[3,4-c]pyridine-6-ylcarboxamide (**6b**).* Yield 69%; yellow needles (methanol); m.p. 265–269°C; M^+ 623. Calcd for $C_{41}H_{41}N_3O_3$: C, 78·94; H, 6·63; N, 6·74. Found: C, 78·94; H, 6·56; N, 6·82%.

*4,7-Di(*p*-butoxyphenyl)-2-methyl-1,3-diphenylpyrrolo[3,4-c]pyridine-6-ylcarboxylic acid (**7b**)*. Yield 6%; lemon-yellow plates (hexane); m.p. 187–190°C; M^+ 624. Calcd for $C_{41}H_{40}N_2O_4$: C, 78·82; H, 6·45; N, 4·48. Found: C, 78·72; H, 6·40; N, 4·56%.

*4,7-Di(*p*-phenylphenyl)-1,3-diphenylpyrrolo[3,4-c]pyridine-6-ylcarboxamide (**6c**)*. Yield 31%; yellow plates (a 1:4 mixture of hexane and benzene); m.p. >300°C; M^+ 631. Calcd for $C_{45}H_{33}N_3O$: C, 85·55; H, 5·27; N, 6·65. Found: C, 85·72; H, 5·41; N, 6·45%.

*4,7-Di(*p*-phenylphenyl)-1,3-diphenylpyrrolo[3,4-c]pyridine-6-ylcarboxylic acid (**7c**)*. Yield 8%; lemon-yellow plates (ethanol); m.p. 286–289°C; M^+ 632. Calcd for $C_{45}H_{32}N_2O_2$: C, 85·42; H, 5·10; N, 4·43. Found: C, 85·07; H, 5·30; N, 4·29%.

3.6 Ethyl 2-methyl-1,3,4,7-tertraphenylpyrrolo[3,4-c]pyridine-6-ylcarboxylate (8)

The acid chloride of **7a** was prepared by treating **7a** (500 mg, 1·04 mmol) in refluxing thionyl chloride (5 ml) for 4 h and then evaporating thionyl chloride *in vacuo*. The crude acid chloride was dissolved in a mixture of ethanol (6 ml) and benzene (6 ml) and the mixture was heated under reflux for 14·5 h. It was poured into water, extracted with dichloromethane, dried, and evaporated *in vacuo* to leave a residue which was chromatographed using a 9:1 mixture of benzene and ethyl acetate, giving **8** (318 mg, 60%) as yellow-green needles (hexane and benzene): m.p. 230–232°C; IR ν, 1720 cm^{-1}; ^{1}H-NMR δ, 0·88 (3H, t, J = 8 Hz), 3·52 (3H, s), 3·98 (2H, q, J = 8 Hz), 6·80–7·30 (20H, m); M^+ 508. Calcd for $C_{35}H_{28}N_2O_2$: C, 82·65; H, 5·55; N, 5·51. Found: C,. 82·77; H, 5·79; N, 5·63%.

The fraction eluted with a 3:2 mixture of benzene and ethyl acetate gave **7a** (151 mg, 30%).

3.7 1,2-Bis(2-methyl-1,3,4,7-tertraphenylpyrrolo[3,4-c]pyridine-6-ylcarbohydrazide) (9)

A mixture of the acid chloride, which was obtained from **7a** (500 mg, 1·04 mmol) and thionyl chloride (5 ml) as described above, in dichloromethane (10 ml) was added dropwise to an ice-cold mixture of sodium hydroxide (105 mg) and hydrazine dihydrochloride (55 mg) in water (8 ml). The mixture was stirred in an ice bath for 15 min and then at room temperature for 2 h. The precipitated $9 \cdot H_2O$ (67 mg) was filtered. The filtrate was poured into water, extracted with dichloromethane, dried, and evaporated *in vacuo* to leave a residue which, on trituration with methanol, afforded $9 \cdot H_2O$ (140 mg): yield 42%; dark green powder (benzene); m.p. 370°C (decomp.); IR ν, 3390, 1680,

1630 cm^{-1}; ^{1}H-NMR δ, 3·45 (6H, s), 6·86–7·19 (40H, m), 10·61 (2H, s, D_2O-exchanged); M^+ 956. Calcd for $C_{66}H_{48}N_6O_2 + H_2O$): C, 81·29; H, 5·17; N, 8·62. Found: C, 81·59; H, 5·08; N, 8·38%.

3.8 2-Methyl-1,3,4,7-tertraphenylpyrrolo[3,4-c]pyridine (10)

The pyrolysate of **7a** (300 mg, 0·625 mmol) at 260°C for 40 min was chromatographed using a 99:1 mixture of benzene and ethyl acetate as an eluent, giving **10** (252 mg, 92%): yellow prisms (toluene); m.p. 309–312°C; ^{1}H-NMR δ, 3·62 (3H, s), 6·92–7·32 (20H, m), 7·97 (1H, s); M^+ 436. Calcd for $C_{30}H_{24}N_2$: C, 88·04; H, 5·54; N, 6·42. Found: C, 88·22; H, 5·74; N, 6·09%.

3.9 Preparation of 11 and 13

A mixture of diketone and ten equivalents of hydrazine in acetic acid was heated under reflux, giving the desired **11** and **13**.

*2-Methyl-1,3,4,7-tetraphenylpyrrolo[3,4-c]pyridazine (**11a**).* Quantitative yield; pale yellow plates (ethanol); m.p. 356–358°C; ^{1}H-NMR δ, 3·61 (3H, s), 6·86–7·32 (20H, m); M^+ 437. Calcd for $C_{31}H_{23}N_3$: C, 85·10; H, 5·29; N, 9·61. Found: C, 85·24; H, 5·54; N, 9·58%.

*2-Methyl-1,3-diphenyl-4,7-di-*p*-phenylphenyl)pyrrolo[3,4-c]pyridazine (**11b**).* Quantitative yield; pale yellow needles (ethanol); m.p. 350–355°C; ^{1}H-NMR δ, 3·66 (3H, s), 7·02–7·50 (28H, m); M^+ 589. Calcd for $C_{43}H_{31}N_3$: C, 87·58; H, 5·30; N, 7·13. Found: C, 87·51; H, 5·53; N, 7·06%.

*2-Methyl-1,3-diphenyl-4,7-di-(*p*-butoxyphenyl)pyrrolo[3,4-d]pyridazine (**11c**).* Quantitative yield; pale yellow plates (a 1:1 mixture of hexane and benzene); m.p. 259–262°C; ^{1}H-NMR δ, 1·00 (6H, t, J = 6 Hz), 1·30–1·80 (m, 8H), 3·64 (3H, S), 3·88 (4H, t, J = 6 Hz), 6·52 (4H, d, J = 9 Hz), 6·96–7·28 (14H, m); M^+ 581. Calcd for $C_{39}H_{39}N_3O_2$: C, 80·52; H, 6·76; N, 7·22. Found: C, 80·44; H, 6·71; N, 7·24%.

*7-Cyano-1,4-diphenyl-5,8-di-(*p*-phenylphenyl)pyridino[3,4-d]pyridazine (**13**).* Yield 70%; yellow prisms (ethanol); m.p. 332–336°C; IR ν, 3070, 3050, 2750, 1610, 1480 cm^{-1}; ^{1}H-NMR δ, 7·02–7·54 (28H, m); M^+ 612. Calcd for $C_{44}H_{28}N_4$: C, 86·27; H, 4·58; N, 9·15. Found: C, 85·85; H, 4·78; N, 9·12%.

3.10 Preparation of 14

Typical procedure: a mixture of **12a** (300 mg, 0·68 mmol) and hydrazine hydrate (1·70 g, mmol) in acetic acid (30 ml) was heated under reflux for

24 h. The liquor was cooled and filtered to give **14a** (226 mg, 76%). The filtrate was poured into water, neutralized with sodium hydrogen carbonate, extracted with dichloromethane, dried, and evaporated *in vacuo* to leave a residue which was chromatographed. The fraction eluted with a 9:1 mixture of benzene and ethyl acetate afforded additional **14a** (26 mg, 9%).

*2,3,6,7-Tetraphenylpyridazino[4,5-d]pyridazine (**14a**).* Yellow prisms (benzene); m.p. >300°C; ^{1}H-NMR δ, 7·08–7·54 (20 m); M^+ 436. Calcd for $C_{30}H_{20}N_4$: C, 82·54; H, 4·62; N, 12·84. Found: C, 82·96; H, 4·84; N, 12·75%.

*2,3-Diphenyl-6,7-di-(*p*-phenyl)phenylpyridazino[4,5-d]pyridazine (**14b**).* Yield 79%; yellow prisms (a 2:3 mixture of hexane and benzene); m.p. >300°C; ^{1}H-NMR δ, 7·08–7·54 (28H, m); M^+ 588. Calcd for $C_{42}H_{28}N_4$: C, 85·69; H, 4·79; N, 9·52. Found: C, 85·79; H, 5·11; N, 9·16%.

3.11 Preparation of 17

Compounds **17** were obtained by the reported method,[8] giving:

*3,4-Dibenzoyl-1-methylpyrrolidine (**17a**).* Yield 70%; colourless prisms (hexane); m.p. 110–113°C; M^+ 293. Calcd for $C_{19}H_{19}NO_2$: C, 77·79; H, 6·53; N, 4·77. Found: C, 77·85; H, 6·54; N, 4·86%.

*3,4-Di-(*p*-butoxybenzoyl)-1-methylpyrrolidine (**17b**).* Yield 86%; pale-yellow prisms (hexane); m.p.103–104°C; M^+ 437. Calcd for $C_{27}H_{35}NO_4$: C, 74·11; H, 8·06; N, 3·20. Found: C, 73·99; H, 8·09; N, 2·71%.

*3,4-Di-(*p*-bromobenzoyl)-1-methylpyrrolidine (**17c**).* Yield 76%; colourless needles (hexane); m.p. 148–150°C; M^+ 453, 451, 449. Calcd for $C_{19}H_{17}NO_2Br_2$: C, 50·58; H, 3·80; N, 3·10. Found: C, 50·74; H, 3·85; N, 2·76%.

3.12 Preparation of 15

Typical procedure: a mixture of **17a** (500 mg, 1·71 mmol) and chloranil (841 mg, 3·42 mmol) in xylene (20 ml) was heated under reflux for 1 h. After cooling, ether (60 ml) was added. The mixture was washed with 4% aqueous sodium hydroxide (100 ml) containing sodium bisulfite (1·0 g) and then with water. It was dried and evaporated *in vacuo* to leave a residue which, on chromatography, using a mixture of benzene and ethyl acetate as eluent, gave:

*3,4-Dibenzoyl-1-methylpyrrol (**15a**)* (211 mg). Yield 43%; colorless plates (a mixture of benzene and hexane); m.p. 156–158°C; M^+ 289.

Calcd for $C_{19}H_{15}NO_2$: C, 78·87; H, 5·23; N, 4·84. Found: C, 79·06; H, 5·31; N, 4·74%.

*3,4-Di-(*p-*butoxybenzoyl)-1-methylpyrrolidine (**15b**).* Yield 51%; colourless plates (a mixture of benzene and hexane); m.p. 111–114°C; M^+ 433. Calcd for $C_{27}H_{31}NO_4$: C, 74·80; H, 7·21; N, 3·23. Found: C, 74·50; H, 7·26; N, 2·85%.

*3,4-Di-(*p-*bromobenzoyl)-1-methylpyrrole (**15c**).* Yield 25%; colourless plates (benzene); m.p. 220–223°C; M^+ 449, 447, 445. Calcd for $C_{19}H_{13}NO_2Br_2$: C, 51·04; H, 2·93; N, 3·13. Found: C, 51·09; H, 3·04; N, 2·79%.

3.13 Preparation of 16

Typical procedure: a mixture of **15a** (145 mg, 0·50 mmol) and cyanomethylammonium sulfate (528 mg, 2·51 mmol) in butanol (20 ml) was heated under reflux for 6 h. Insoluble materials were filtered and the filtrate was evaporated *in vacuo* to leave a residue which was chromatographed. The fraction eluted with a mixture of toluene and ethyl acetate afforded **16a**, which was recrystallized to give:

*6-Cyano-2-methyl-4,7-diphenylpyrrolo[3,4-c]pyridine (**16a**)* (14 mg, 9%). Yellow prisms (a mixture of hexane and ethanol); m.p. 233°C (decomp.): IR ν, 2215 cm^{-1}; ^{1}H-NMR δ, 4·06 (3H, s), 7·18 (1H, d, J = 1·8 Hz), 7·50–7·58 (7H, m), 7·70–7·71 (1H, m), 8·01–8·05 (2H, m); M^+ 309.

*6-Cyano-2-methyl-4,7-di-(*p-*bromo)phenylpyrrolo[3,4-c]pyridine (**16c**).* Yield 11%; yellow needles (ethanol); m.p. 260°C (decomp.): IR ν, 2220 cm^{-1}; ^{1}H-NMR δ, 4·08 (3H, s), 7·17 (1H, d, J = 1·8 Hz), 7·52 (1H, d, J = 1·8 Hz), 7·58 (2H, d, J = 8·6 Hz), 7·67 (2H, d, J = 8·6 and 2·0 Hz), 7·69 (2H, d, J = 8·6 and 2·0 Hz), 7·92 (2H, d, J = 8·6 Hz); M^+ 469, 467, 465.

ACKNOWLEDGEMENT

This work was partially supported by Grant-in-Aid for Scientific Research No. 04650758 (S.M.) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. Tsutsui, T., Adachi, C., & Saito, S., *Senryo to Yakuhin* (Dyestuffs and Chemicals), **36** (1991) 121.
2. Saito, S., Tsutsui, T., Adachi, C., Tashiro, M. & Mataka, S., Kokai Tokkyo Kogo (Japanese Patent) 3-37292 (1991).

3. Tashiro, M. Mataka, S., Takahashi, K., Sato, Y. & Maeda, S., Kokai Tokkyo Kogo (Japanese Patent) 3-37293 (1991).
4. Mataka, S., Takahashi, K. & Tashiro, M., *J. Heterocycl. Chem.*, **18** (1981) 1073.
5. Mataka, S., Takahashi, K. & Tashiro, M., *J. Heterocyl. Chem.*, **20** (1983) 971.
6. Mataka, S., Lin, W. H., Tashiro, M., Takahashi, K., Hatta, T. & Tori-i, A., *Kyushu Daigaku Sogorikougaku Kenkyuka Houkoku* (Eng. Sci. Report, Hyushu University, 12 (1990) 183.
7. Potts, K. T. & McKeough, D., *J. Am. Chem. Soc.*, **96** (1974) 4268.
8. Tsuge, O., Kanemasa, S., Ohe, M & Takenaka, S., *Bull. Chem. Soc., Jpn*, **60** (1987) 4079.