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# Synthesis of Oxazolo[4′,5′:5,6]Pyrido[1,2-*a*]-Benzimidazole Derivatives and Study of Their Fluorescent Properties

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## *SUMMARY*

*2-Amino-3-methyl-1-oxo-1H,4H-pyrido[1,2-a]benzimidazole-4-carbonitrile* (**4**), *the key compound in the synthesis of oxazolo[4′,5′:5,6]pyrido [1,2-a]benzimidazole derivatives, was prepared by reduction of the azo dye obtained from phenyldiazonium-4-sulphonic acid salt* (**2**) *coupled with 3-methyl-1-oxo-1H,5H-pyrido[1,2-a]benzimidazole-4-carbonitrile* (**1**). *The condensation of* **4** *with acetic anhydride yielded 2,4-dimethyloxazolo [4′,5′:5,6]pyrido[1,2-a]benzimidazole-5-carbonitrile* (**5**) *and condensation of* **4** *with ethyl benzoate* (**6a**) *and ethyl 4-methoxybenzoate* (**6b**) *in PPA afforded the corresponding 2-aryl-4-methyloxazolo[4′,5′:5,6]pyrido [1,2-a]benzimidazole-5-carbonitrile* (**7a–7b**). *Bis-1,2-{4-methyl oxazolo-[4′,5′:5,6]pyrido[1,2-a]benzimidazol-2-yl-5-carbonitrile}ethylene* (**9a**) *and bis-1,4-{4-methyloxazolo[4′,5′:5,6]pyrido[1,2-a]benzimidazol-2-yl-5-carbonitrile}benzene* (**9b**) *were similarly obtained by condensation of two moles of* **4** *with 1 mole of fumaric acid* (**8a**) *and diethyl terephthalate* (**8b**), *respectively in PPA and phosphorus oxychloride. The fluorescence properties of the compounds* **5**, **7a–7b** *and* **9a–9b** *were studied. Some of the compounds were evaluated as fluorescent whitening agents for polyester fibres.*

## 1. INTRODUCTION

Fused heterocyclic systems are particularly useful in the synthesis of fluorescent whitening agents, providing the extension of conjugation

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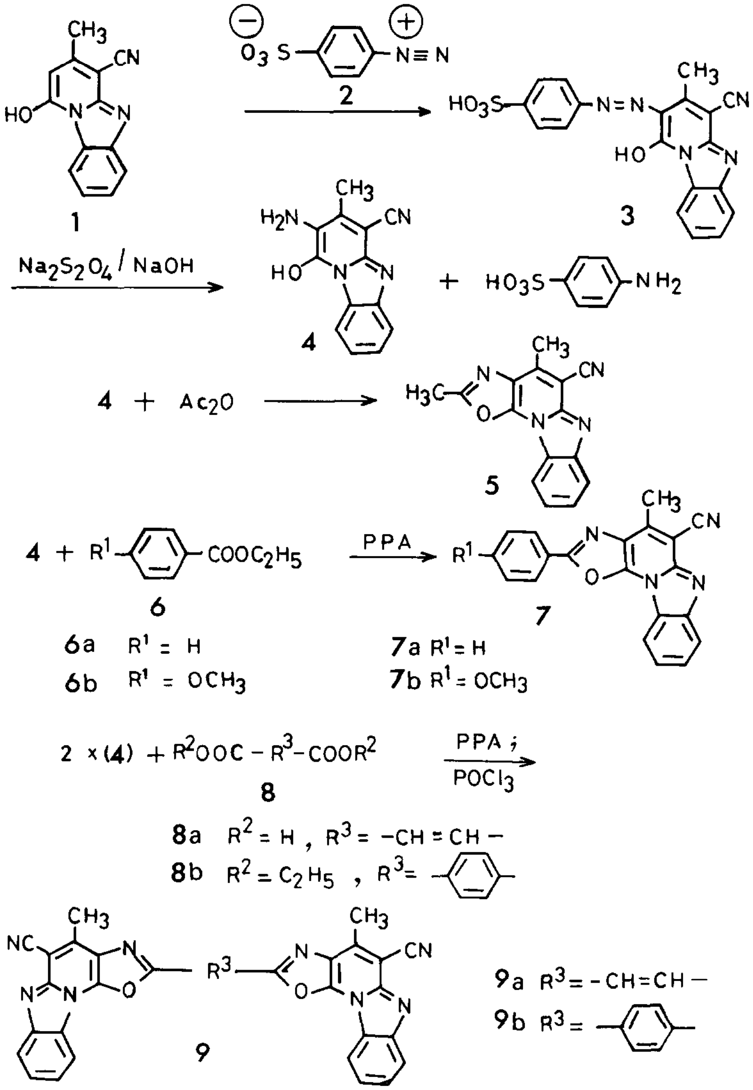
and rigidity of structure particularly suitable for such compounds. Pyrido[1,2-*a*]benzimidazole has been previously used in the synthesis of a variety of dyes[1-10] and pigments[11,12] and in the present work we describe the use of this heterocyclic system in the synthesis of fluorescent whitening agents.

## 2. RESULTS AND DISCUSSION

Oxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole derivatives were synthesised from 2-amino-3-methyl-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole-4-carbonitrile (**4**); see Scheme 1. The starting compound **4** was prepared from 3-methyl-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole-4-carbonitrile (**1**), which was obtained by condensation of benzimidazole-2-acetonitrile and ethyl acetoacetate. Thus, sulphanilic acid was diazotised by reverse diazotisation and coupled with **1** under alkaline pH to give 2-(4-sulphophenyl azo)-3-methyl-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole-4-carbonitrile (**3**). The resulting azo dye **3** was reduced with an alkaline mixture of sodium hydrosulphite and sodium hydroxide solution and then neutralised to pH 7 to give the water-insoluble compound **4** together with the water-soluble sulphanilic acid, which were separated by filtration. Compound **4** was used to synthesise various oxazolo-[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole derivatives (**5**, **7a**–**7b** and **9a**–**9b**). To obtain compounds which it was anticipated would possess fluorescent properties, the synthesis of 2-alkyl and 2-aryl derivatives was effected. Thus, 2,4-dimethyloxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole-5-carbonitrile (**5**) was synthesised by refluxing compound **4** with acetic anhydride. 2-Phenyl-3-methyloxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole-5-carbonitrile (**7a**) and 2-(4-methoxyphenyl)-3-methyloxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole-5-carbonitrile (**7b**) were synthesised by the condensation of **4** with ethyl benzoate (**6a**) and ethyl 4-methoxybenzoate (**6b**) respectively, using polyphosphoric acid (PPA) as condensing agent.

In order to obtain compounds in which the conjugation was further extended, the synthesis of compounds containing two oxazolo-[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole systems linked to each other at the 2-positions was also carried out. Thus, bis-1,2-{4-methyloxazolo-[4′,5′:5,6]pyrido[1,2-*a*]benzimidazol-2-yl-5-carbonitrile}ethylene (**9a**) and bis-1,4-{4-methyloxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazol-2-yl-5-carbonitrile}benzene (**9b**) were synthesised by the condensation of two


1
2
3
4
5
6
7
8
9
Na2S2O4 / NaOH
4 + Ac2O
4 + R1
COOC2H5
PPA
6a R1 = H
6b R1 = OCH3
7a R1 = H
7b R1 = OCH3
2 × (4) + R2OOC − R3−COOR2
PPA ; POCl3
8a R2 = H , R3 = −CH = CH −
8b R2 = C2H5 , R3 =
9a R3 = −CH=CH−
9b R3 =

**Scheme 1.**

moles of **4** with one mole of fumaric acid (**8a**) and diethyl terephthalate (**8b**) respectively, using both PPA and phosphorus oxychloride as condensing agents.

The PMR spectrum of the compound **7b** recorded in trifluoroacetic acid (TFA) showed a sharp singlet centred at 3·2 attributed to the methyl group at $C_4$ (3H, aliphatic); a sharp singlet centred at 4·1 attributed to the methoxy group of the 4-methoxyphenol substituent at $C_2$ (3H, aliphatic); a broad multiplet centred between 7·0 and 8·2 attributed to the aromatic protons and corresponding to four protons of the phenyl ring of the 4-methoxyphenyl residue at $C_2$ and two protons of the phenyl ring away from the imidazole moiety of the benzimidazole ring (6H, aromatic) and a multiplet centred between 8·3 and 8·8 attributed to aromatic protons, corresponding to 2-protons of the phenyl ring adjacent to the imidazole moiety of the benzimidazole ring (2H, aromatic).

The mass spectrum of compound **5** showed the molecular ion peak ($m^+/e$) at 262, in agreement with its molecular formula $C_{15}H_{10}N_4O$.

The IR spectrum of compound **4** recorded in Nujol mull showed peaks at 3350 $cm^{-1}$ and 3400 $cm^{-1}$ corresponding to the primary amino group, whereas the IR spectra of compounds **5**, **7a–7b** and **9a–9b** recorded in Nujol mull showed the absence of primary amino and hydroxy groups. The IR spectra of all compounds **4**, **7a–7b** and **9a–9b** showed a sharp peak at 2220 $cm^{-1}$ and the IR spectrum of compound **5** showed a sharp peak at 2240 $cm^{-1}$, corresponding to the presence of a cyano group.

The absorption and fluorescence emission maxima of the compounds

TABLE 1
Absorption and Fluorescence Emission Spectra of Oxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole Derivatives

| *Compound* | *Absorption max (nm)* | *Molar extinction coefficient* $\times 10^{-4}$ | *Fluorescence emission max (nm)* |
|---|---|---|---|
| **5** | 332 | 1·245 | 460 |
| **7a** | 341 | 1·318 | 463 |
| **7b** | 343 | 1·357 | 457 |
| **9a** | 357 | 2·188 | 465 |
| **9b** | 348 | 2·788 | 461 |

are shown in Table 1. The absorption maxima of a good fluorescent whitener is in the region 350–400 nm and the oxazolo[4′,5′: 5,6]pyrido[1,2-*a*]benzimidazole derivatives **5, 7a–7b** and **9a–9b** had absorption maxima in the range 332–357 nm. The fluorescence emission maxima of the compounds were in the greenish-blue region, i.e. 457–465 nm, whereas that of a good fluorescent whitener is in the region close to the blue, i.e., 420–440 nm. When applied to polyester fibres as fluorescent whiteners, compound **5** gave a poor whitening effect, compounds **7a–7b** a fairly good whitening effect and compounds **9a–9b** a yellow colouration to the fibre.

## 3. EXPERIMENTAL

All melting points are uncorrected and are in °C. Absorption and fluorescence emission spectra in DMF solutions were recorded on a Beckman Model 25 spectrophotometer and Aminco Bowman spectrophotofluorimeter respectively. Infrared spectra were recorded on a Perkin-Elmer Model 397 spectrometer. The PMR spectrum was recorded on a Varian 60 MHz instrument EM-360-L using TMS as internal standard and the chemical shifts are cited on a $\delta$ (ppm) scale.

### 3.1. Preparation of starting materials

3-Methyl-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole-4-carbonitrile (**1**), m.p. 300° (decomp.), lit.[13] m.p. 300° (decomp.) was prepared by the known method.

### 3.2. 2-Amino-3-methyl-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole-4-carbonitrile (4)

Sulphanilic acid (2·1g; 0·012 mol) was dissolved in water (12 ml) containing sodium carbonate (0·64g) by warming to 45°C. A solution of sodium nitrite (0·84g; 0·0122 mol) in water (12 ml) was added to the above solution at 0–10°C and the mixture slowly added with stirring to hydrochloric acid (30%; 3–5 ml) diluted with water (8·5 ml) at 0–5°C. Stirring was continued for about 1·5–2 h to obtain a fine suspension of the pinkish coloured phenyldiazonium-4-sulphonic acid salt (**2**), which was then slowly added to a cold slurry of **1** (2·23g; 0·01 mol) in water (50 ml) containing sodium carbonate (12 g) at 5–10°C. Stirring was continued for 4 h at 5–10°C and then at room temperature (30–32°C) for about 1 h and the mixture was then neutralised with acetic acid (10–12 ml) to pH 7, cooled and filtered to give the orange yellow dye, 2-(4-sulphophenylazo)-3-methyl-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole-4-carbonitrile (**3**) (71%). The crude dye was used as such for reduction.

The above crude azo dye (**3**) (2·89 g; 0·0071 mol) in water (25 ml) containing sodium hydroxide (5 g; 0·125 mol) was warmed to 45°C and sodium hydrosulphite (3·5 g; 0·02 mol) was added at reflux in portions over 5h at pH above 10. The mixture was refluxed until the colour of the azo dye disappeared (2–2·5 h) and the reaction mixture was cooled to 0–5°C, carefully neutralised to pH 7, filtered, and the solid obtained was washed with water and dried. It was recrystallised from acetic acid to give **4** (65% based on **1**), m.p. > 340°C. Calculated for $C_{13}H_{10}N_4O$: C, 65·5; H, 4·2; N, 23·5. Found: C, 64·9; H, 4·4; N, 23·9%.

### 3.3. 2,4-Dimethyloxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole-5-carbonitrile (5)

A mixture of compound **4** (2·62 g; 0·01 mol) and acetic anhydride (5 ml) was refluxed for 3 h, cooled to room temperature and slowly added to cold aqueous methanol solution (1:1; 25 ml) with stirring. The mixture was neutralised with sodium carbonate and the product thus obtained was filtered, washed with water and dried. Recrystallisation from DMF–ethanol (1:1) yielded colourless crystals (68%), m.p. 327–9°. Calculated for $C_{14}H_{10}N_4O$: C, 68·7; H, 3·8; N, 21·4. Found: C, 67·95; H, 3·5; N, 21·2%.

### 3.4. 2-Phenyl-4-methyloxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole-5-carbonitrile (7a)

To polyphosphoric acid (PPA) prepared by heating a mixture of phosphorus pentoxide (14 g) and orthophosphoric acid (5·6 g) to 180°C for 1 h with efficient stirring was added at 120°C a mixture of compound **4** (2·0 g; 0·0084 mol) and ethyl benzoate (**6a**) (1·26 g; 0·0084 mol). The resultant mixture was heated to 200°C for 2 h with stirring, cooled to room temperature over 5 h and added to ice-cold water. The separated solid was filtered, washed free of acid and dried. It was recrystallised from DMF in colourless crystals of compound **7a** (74%), m.p. > 340°. Calculated for $C_{20}H_{12}N_4O$: C, 74·1; H, 3·7; N, 17·3. Found: C, 74·0; H, 3·4; N, 17·1%.

### 3.5. 2-(4-Methoxyphenyl)oxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazole-5-carbonitrile (7b)

The compound was prepared using the procedure described for **7a** above. It was crystallised from acetic acid as colourless crystals (67%), m.p. 321° (decomp.). Calculated for $C_{21}H_{14}N_4O_2$: C, 71·2; H, 3·95; N, 15·8. Found: C, 72·0; H, 3·6; N, 15·5%.

### 3.6. Bis-1,2-{4-methyloxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazol-2-yl-5-carbonitrile}ethylene (9a)

Compound **4** (4·0 g; 0·0168 mol) and fumaric acid (**8a**) (0·98 g; 0·0084 mol) were added at 120°C to a thick viscous mass of PPA prepared in the same manner as above for the synthesis of compound **7a**. The resultant mixture was heated to 200°C for 2–3 h with stirring, cooled to room temperature over 5 h and added to ice-cold water. The resultant solid was filtered, washed free of acid and dried. The dried product was heated on a water-bath at 80–90°C with phosphorus oxychloride (10 ml) for 3 h, cooled to room temperature (30–32°C) and the reaction mixture added to an ice–water mixture. The product thus obtained was filtered, washed free of acid and dried. It was recrystallised from DMF–ethanol (1:1) to give pale yellow crystals (64·5%), m.p. > 340°. Calculated for $C_{28}H_{16}N_4O_2$: C, 71·6; H, 3·15; N, 19·6. Found: C, 71·1; H, 3·3; N, 18·95%.

### 3.7. Bis-1,4-{4-methyloxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazol-2-yl-5-carbonitrile}benzene (9b)

Compound **9b** was synthesised by following the above procedure. It crystallised from DMF as pale yellow needles (74·0%), m.p. > 340°. Calculated for $C_{32}H_{18}N_8O_2$: C, 69·2; H, 3·1; N, 21·5. Found: C, 68·9; H, 3·1; N, 22·1%.

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