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# Synthesis of Triazolo[4,5-*b*]pyrido[1′,2′-*a*]benzimidazole Derivatives as Fluorescent Disperse Dyes and Whiteners for Polyester Fibre

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## ABSTRACT

*Diazotised arylamines were coupled with the sodium salt of acetonitrile dimer to give α-arylazoacetonitrile dimers, which on condensation with 2-cyanomethylbenzimidazole gave the corresponding 1-amino-2-arylazo-4-cyano-3-methylpyrido[1,2-*a*]benzimidazoles. These were further converted into the respective 2-aryl-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*] pyrido(1′,2′-*a*]benzimidazoles. The 2-(4′-nitrophenyl)-, 2-(4′-methylphenyl)-, and 2-(4′-methoxyphenyl)- derivatives were applied as fluorescent disperse dyes and gave satisfactory results, and the 2-(4′-nitrophenyl)-derivative, which was also converted to the 2-(4′-acetamidophenyl)-derivative, was evaluated as a fluorescent whitener for polyester.*

## 1 INTRODUCTION

Several reports describing the utility of condensed nitrogen containing heterocycles as fluorescent dyes and as fluorescent brighteners have appeared. Pyrido[1,2-*a*]benzimidazoles form an important class of such compounds, having widespread use as components of azomethine,[1] azo[2] and cyanine[3] dyestuffs and as photographic sensitising agents.[4] However, there are few references in the literature describing the introduction of heterocycles in the 1,2-position of pyrido[1,2-*a*]benzimidazole.

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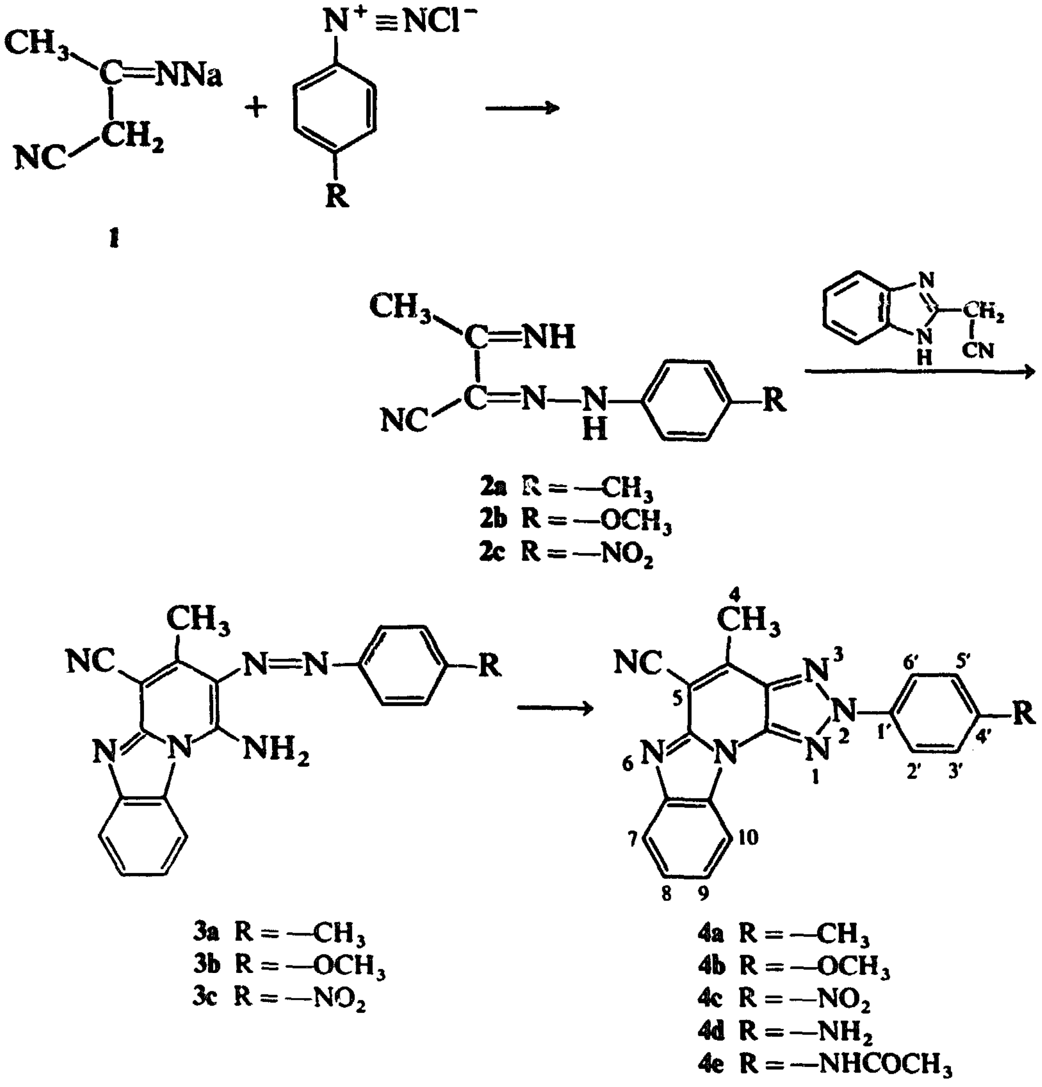
Pyrimido[5′,4′:5,6]pyrido(1,2-*a*]benzimidazoles have been reported[5] to be useful as fluorescent dyes and photoconductors and we have previously reported[6] the use of oxazolo[4′,5′:5,6]pyrido[1,2-*a*]benzimidazoles as optical whiteners for polyester fibres. In this present work, we report the synthesis of triazolo[4,5-*b*]pyrido[1′,2′-*a*]benzimidazoles from 1-amino-2-arylazo-4-cyano-3-methylpyrido[1,2-*a*]benzimidazoles, such compounds having application in the field of disperse dyes.

## 2 RESULTS AND DISCUSSION

The object of this present study was the synthesis of fused heterocyclic compounds containing the triazolo[4,5-*b*]pyrido[1′,2′-*a*]benzimidazole system and their possible use as fluorescent disperse dyes. The sodium salt of acetonitrile dimer (**1**) was used as a coupling component for preparing various α-arylazoacetonitrile dimer dyes (**2**), which were then condensed with 2-cyanomethyl-benzimidazole to give the corresponding 1-amino-2-arylazopyrido[1,2-*a*]benzimidazoles (**3a**–**3c**). These *o*-aminoarylazo dyes were oxidised to the triazolo[4,5-*b*]pyrido[1′,2′-*a*]benzimidazoles (**4a**–**4c**), which have extended conjugation and a planar rigidity and should thus be suitable as fluorescent compounds. Thus, *p*-toluidine, *p*-anisidine and *p*-nitroaniline were diazotised and coupled with **1** to give the α-*p*-toluylazoacetonitrile dimer (**2a**), the α-*p*-methoxyphenylazoacetonitrile dimer (**2b**) and the α-*p*-nitrophenylazoacetonitrile dimer (**2c**) respectively. These α-arylazoacetonitrile dimers were condensed with 2-cyanomethyl-benzimidazole in acetic acid to give the corresponding 1-amino-2-*p*-toluylazo-4-cyano-3-methylpyrido[1,2-*a*]benzimidazole (**3a**), 1-amino-2-*p*-methoxyphenylazo-4-cyano-3-methylpyrido[1,2-*a*]benzimidazole (**3b**) and 1-amino-2-*p*-nitrophenylazo-4-cyano-3-methylpyrido[1,2-*a*]benzimidazole (**3c**). Compounds **3a**–**3c** were oxidised using cupric acetate and DMF in a current of air to give 2-(4′-toluyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo-[4,5-*b*]-pyrido[1′,2′-*a*]benzimidazole (**4a**), 2-(4′methoxyphenyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]pyrido[1′,2′-*a*]benzimidazole (**4b**) and 2-(4′-nitrophenyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]pyrido[1′,2′-*a*]-benzimidazole (**4c**) respectively. The nitro group in **4c** was reduced with zinc and acetic acid to give the amino derivative (**4d**) which was acetylated with acetic anhydride to give 2-(4′-acetamidophenyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]pyrido[1′,2′-*a*]benzimidazole (**4e**).

The structures of these new compounds were established by spectral data. IR spectra confirmed the absence of —NH$_2$ groups in compounds **4a**, **4b**, **4c** and the spectra showed peaks at 3450 cm$^{-1}$, 2220 cm$^{-1}$, 1700 cm$^{-1}$, 1690 cm$^{-1}$ corresponding to —NH stretching, C≡N stretching, —NH



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2a R = —$CH_3$
2b R = —$OCH_3$
2c R = —$NO_2$

3a R = —$CH_3$
3b R = —$OCH_3$
3c R = —$NO_2$

4a R = —$CH_3$
4b R = —$OCH_3$
4c R = —$NO_2$
4d R = —$NH_2$
4e R = —$NHCOCH_3$

deformation and C═O stretching of the amide group, respectively, for compound **4e**.

The PMR spectrum of **4b** in trifluoroacetic acid showed a sharp singlet at 3·0, corresponding to three protons of the methyl residue of the 4′-methoxy group in the phenyl group at N-2, a split doublet centred at 7·2 corresponding to two aromatic protons in the 3′,5′-positions of the phenyl group at N-2, a multiplet between 8·0 and 8·3 corresponding to four aromatic protons at C-7, C-8, C-9, C-10 and a split doublet at 8·8 corresponding to two aromatic protons in the 2′,6′-positions of phenyl group at N-2.

The absorption and the fluorescence emission maxima of compounds **4a**–**4e** are shown in Table 1. Compounds **4a**–**4e** showed fluorescence emission maxima close to the blue to greenish blue and green region. The

**TABLE 1**
Absorption and Fluorescence Emission spectra of Triazolo[4,5-*b*]pyrido[1′,2′-*a*]-benzimidazoles

| *Compound* | *Absorption max. (nm)* | *Fluorescence emission max. (nm)* | *Molar extinction coeff.* × $10^{-4}$ |
|---|---|---|---|
| **4a** | 398 | 530 | 1·0272 |
| **4b** | 412 | 517 | 1·5674 |
| **4c** | 421 | 520 | 2·2535 |
| **4d** | 416 | 498 | 1·4678 |
| **4e** | 398 | 448 | 1·0760 |
| Standard[a] | 376 | 458 | 2·5540 |

[a] 7-Diethylamino-4-methylcoumarin.

yellow-coloured 2-(4′-nitrophenyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]pyrido[1′,2′-*a*]benzimidazole (**4e**) dyed polyester fibre in lemon yellow shades having good light and sublimation fastness. The pale yellow coloured 2-(4′-acetamidophenyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]pyrido[1′,2′-*a*]-benzimidazole (**4e**) had a moderate fluorescent activity on polyester fibre. Compounds **4a** and **4b** dyed polyester in yellowish brown shades with moderate tinctorial power and sublimation fastness.

## 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 an Aminco–Bowman spectrofluorimeter respectively. Infrared spectra were recorded on a Perkin–Elmer Model 397 spectrometer. The PMR spectra were recorded on a Varian 60-MHz and 100-MHz instrument EM-360-L using TMS as internal standard; the chemical shifts are given in $\delta$ (ppm).

### 3.1 Preparation of starting materials

2-Cyanomethyl-benzimidazole,[7] m.p. 212° (lit.[7] m.p. 210°) and the sodium salt of acetonitrile dimer[8] (**1**) were prepared by known methods.

### 3.2 α-*p*-Toluylazoacetonitrile dimer (2a)

*p*-Toluidine (2·14 g, 0·02 mol) was diazotised at 0–5°C using sodium nitrite (1·52 g, 0·022 mol) and 1:1 hydrochloric acid (20 ml). The excess of nitrous acid was destroyed by addition of urea (0·5 g). The diazo solution was stirred slowly into a solution of the sodium salt of acetonitrile dimer 1 (2·08 g, 0·02 mol) in 20 ml dilute hydrochloric acid (12 ml conc. hydrochloric acid + 8 ml water) at 0–5° and stirring was continued for a further 3·5 h. During coupling, the pH of the mixture was maintained between 6 and 7 by addition of 20% sodium carbonate solution. The reaction mixture was kept overnight in a refrigerator and the yellowish-brown coloured product which separated was filtered, washed with water and dried. It was recrystallised from ethanol (85%), m.p. 162°. Calculated for $C_{11}H_{12}N_4$: C, 66·0; H, 6·0; N, 28·0. Found: C, 65·5; H, 5·9; N, 27·6%.

The other α-arylazoacetonitrile dimers (**2b**, **2c**) were prepared in the same manner.

### 3.3 α-*p*-Methoxyphenylazoacetonitrile dimer (2b)

Crystallised from ethanol as yellowish-brown crystals (87%), m.p. 115°. Calculated for $C_{11}H_{12}N_4O$: C, 61·1; H, 5·55; N, 25·9. Found: C, 60·7; H, 5·5; N, 25·8%.

### 3.4 α-*p*-Nitrophenylazoacetonitrile dimer (2c)

Crystallised from ethanol as brown crystals (91%), m.p. 132–135°C. Calculated for $C_{10}H_9N_5O_2$: C, 51·9; H, 3·9; N, 30·3. Found: C, 50·2; H, 3·8; N, 30·8%.

### 3.5 1-Amino-2-*p*-toluylazo-4-cyano-3-methylpyrido[1,2-*a*]benzimidazole (3a)

2-Cyanomethylbenzimidazole (3·14 g, 0·02 mol) and the α-*p*-toluylazoacetonitrile dimer dye **2a** (4·00 g, 0·02 mol) were refluxed in 20 ml acetic acid for 5 h and after standing overnight at room temperature the product was filtered, washed with a little methanol and dried. A second crop of product was obtained by pouring the filtrate into water (20 ml). The product was recrystallised from ethanol (82%), m.p. 169°. Calculated for $C_{20}H_{16}N_5$: C, 67·4; H, 4·5; N, 23·6. Found: C, 67·15; H, 4·2; N, 22·9%.

The other 2-arylazopyrido[1,2-*a*]benzimidazoles (**3b**, **3c**) were prepared in the same manner.

### 3.6 1-Amino-2-*p*-methoxyphenylazo-4-cyano-3-methylpyrido[1,2-*a*]-benzimidazole (3b)

Crystallised from ethanol (69%), m.p. 123°. Calculated for $C_{20}H_{16}N_5O$: C, 70·6; H, 4·7; N, 24·7. Found: C, 70·2; H, 4·3; N, 24·45%.

### 3.7 1-Amino-2-*p*-nitrophenylazo-4-cyano-3-methylpyrido[1,2-*a*]-benzimidazole (3c)

Crystallised from acetic acid (90%), m.p. >360°. Calculated for $C_{19}H_{13}N_6O_2$: C, 61·45; H, 3·5; N, 26·4. Found: C, 60·1; H, 3·2; N, 25·05%.

### 3.8 2-4′-Toluyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]pyrido[1′,2′-a]-benzimidazole (4a)

A mixture of the α-*p*-toluylazoacetonitrile dimer **3a** (3·4 g, 0·01 mol) and cupric acetate (1 g, 0·0052 mol) in dimethylformamide (15 ml) was stirred in a continuous current of air and the temperature raised to 90°C. The reaction was continued until the colour of the original dye disappeared (about 1 h). The reaction mixture was cooled and slowly added with stirring to ice-cold dilute (5%) hydrochloric acid (50 ml). The product so obtained was filtered, washed acid-free and dried. Residual traces of **3a** was removed during recrystallisation from *N*,*N*-dimethylformamide by the addition of zinc dust (0·05 g). The product was obtained as pale yellow crystals (76%), m.p. 166°. Calculated for $C_{20}H_{14}N_6$: C, 71·0; H, 3·95; N, 23·7. Found: C, 70·1; H, 3·9; N, 23·6%.

The other triazoles **3b**, **3c** were synthesised by following this typical procedure.

### 3.9 2-(4′-methoxyphenyl)-5-cyano-4-methyl-2*H*-1,2,3 triazolo[4,5-*b*]-pyrido[1′,2′-*a*]benzimidazole (4b)

Crystallised from *N*,*N*-dimethylformamide as yellowish-brown needles (71%), m.p. 278°. Calculated for $C_{20}H_{14}N_6O$: C, 67·8; H, 3·95; N, 23·7. Found: C, 67·8; H, 3·9; N, 23·6%.

### 3.10 2-(4′-nitrophenyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]-pyrido[1′,2′-*a*]benzimidazole (4c)

Crystallised from *N*,*N*-dimethylformamide (86%), m.p. >360°. Calculated for $C_{19}H_{11}N_7O_2$: C, 61·8; H, 3·0; N, 26·55. Found: C, 61·6; H, 2·75; N, 26·2%.

### 3.11 2-(4′-aminophenyl)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]-pyrido[1′,2′-*a*]benzimidazole (4d)

Powdered zinc (2·6 g, 0·04 g atom) was added portionwise over 1 h with stirring to a refluxing solution of the nitro compound **4c** (3·69 g, 0·01 mol) in glacial acetic acid (20 ml). Heating was continued for 3 h at reflux and the reaction mixture was filtered hot. The filtrate was cooled and stirred into ice-cold water (50 ml) and the brown solid filtered, washed acid-free and dried. It was recrystallised from acetic acid as pale brown crystals (69%) m.p. 334–335°. Calculated for $C_{19}H_{13}N_7$: C, 67·25; H, 3·8; N, 28·9. Found: C, 67·15; H, 3·7; N, 28·7%.

### 3.12 2-(4'-acetamido)-5-cyano-4-methyl-2*H*-1,2,3-triazolo[4,5-*b*]pyrido[1',2'-*a*]benzimidazole (4e)

The amino compound **4d** (3·39 g, 0·01 mol) and acetic anhydride (10 ml) were refluxed for 3·5 h. After cooling overnight at room temperature, the white crystalline product was filtered, washed with methanol and dried (77%), m.p. 242°. Calculated for $C_{21}H_{15}N_7O$: C, 66·1; H, 3·9; N, 25·7. Found: C, 65·9; H, 3·9; N, 25·4%.

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## REFERENCES

1. Eastman Kodak, French Patent 2 228 090; *Chem. Abstr.*, **83** (1975) 81245.
2. Ciba-Geigy, German Patent 2 542 408; *Chem. Abstr.*, **85** (1976) 22749.
3. Agfa-Gevaert, US Patent 3 931 156, *Chem. Abstr.*, **85** (1976) 64804.
4. Alpermann, H. G., *Arzneim. Forsch.*, **16** (1966) 1641; *Chem. Abstr.*, **66** (1967) 64072.
5. F. H., Ger. Offen. 2 929 414; *Chem. Abstr.*, **95** (1981) 44732.
6. Rajadhyaksha, D. D. & Rangnekar, D. W., *Dyes and Pigments*, 7 (1986) 365.
7. Elnageli, M. H., *Helv. Chim. Acta*, **59**(2) (1976) 551.
8. Copeland, R. A. B. & Cason, J., *J. Amer. Chem. Soc.*, **21** (1954) 72.