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Synthesis of Isomeric Azo Disperse Dyes of Pyridobenzimidazole—Part II

D. V. Dikshit and K. D. Deodhar†

Department of Chemistry, Indian Institute of Technology,
Powai, Bombay 400 076, India

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SUMMARY

3-(4-Methoxyphenyl)-1-oxo-1H,5H-pyrido[1,2-a]benzimidazole (**1**) *was subjected to demethylation generating additional nucleophilic centres on the 3-phenyl ring. However, on coupling with an aryldiazonium salt it gave a mixture of a pair of positionally isomeric azo dyes with coupling in the pyridone ring. Compound* **1** *was converted to an acetylated pyridobenzimidazole derivative, which, on azo-coupling gave a pair of positionally isomeric acetylated pyridobenzimidazole dyes. The dyes were tested on polyamide (PA) and polyester (PES) fibres.*

1. INTRODUCTION

In our earlier communication[1] we reported the preparation of a new pyridobenzimidazole coupler which gave, on azo-coupling reaction, a pair of positionally isomeric azo disperse dyes. The observation which prompted us to undertake the present work was that, even with a large excess of aryldiazonium salt, pyridobenzimidazole **1** never underwent bisazo coupling, which would have resulted in a more intense shade. In order to obtain additional positions for azo coupling, **1** was demethylated to give the corresponding hydroxy derivative (**2**) (Scheme 1). The azo-coupling reaction on **2** however, gave a pair of positionally isomeric azo dyes in which coupling had taken place solely on the pyridone ring.

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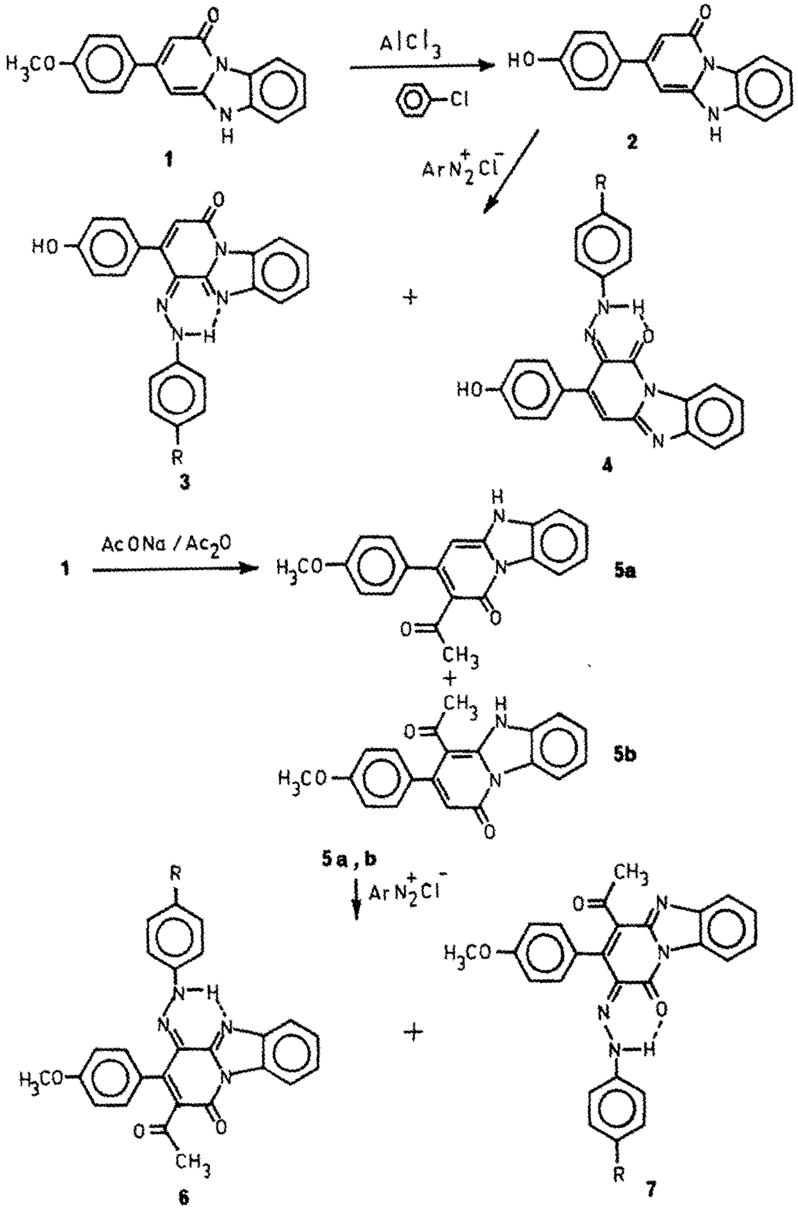
† To whom all correspondence should be addressed.



Scheme 1

To block one of the nucleophilic centres in the pyridone residue, **1** was acetylated under Perkin reaction conditions to form the corresponding acetyl derivative (**5**). Azo-coupling reaction on **5**, however, also gave a pair of isomeric dyes.

2. RESULTS AND DISCUSSION

The pyridobenzimidazole nucleus **1** contains two nucleophilic sites which could undergo azo-coupling reactions. However, bis-coupling was not observed. In **1** the phenyl ring at the 3-position was incapable of undergoing azo-coupling reaction due to insufficient activation by the methoxy group. Hence, compound **1** was demethylated using anhydrous $AlCl_3$ and chlorobenzene in order to regenerate the hydroxy derivative which could activate the ring more extensively and make azo-coupling feasible in the phenyl ring. Thus, a new coupling component, 3-(4-hydroxyphenyl)-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole (**2**) possessing two active centres for the azo-coupling reaction, was prepared. Compound **2** was soluble in NaOH and gave a typical blue fluorescence.[2,3] Its structure was confirmed by the spectral analysis: IR (KBr) 3000–3460 (benzimidazole NH and phenolic OH), 1670 (CO); PMR (DMSO-d_6) 5·85 (1H, s, $C_2\underline{H}$), 6·1 (1H, s, $C_4\underline{H}$), 6·5–7·5 (7H, m, Ar$\underline{H}$ and $C_7\underline{H}$, $C_8\underline{H}$, $C_9\underline{H}$), 8·35 (1H, m, $C_{10}\underline{H}$), 9·35 (1H, bs, O$\underline{H}$, exchangeable) and 12·29 (1H, bs, N$\underline{H}$, exchangeable).

Compound **2** when coupled with an equimolar quantity of 4-chlorobenzenediazonium chloride in acetone, gave an intensely coloured substance which was found to be a mixture of two major constituents **3a** and **4a**. The same mixture of dyes **3a** and **4a** was obtained when the coupling was carried out in NaOH. The mixture was separated by column chromatography (silica gel, 60–120 mesh) using chloroform as an eluent to obtain a yellow dye (**3a**). After the removal of **3a** from the column, acetone was used as an eluent to obtain the red dye (**4a**).

The yellow dye was shown to be 3-(4-hydroxyphenyl)-4-(4-chlorophenylhydrazono)-1-oxo-1*H*-pyrido[1,2-*a*]benzimidazole (**3a**) on the basis of the spectral data: MS, m/e 414 (M^+); IR (KBr) 2900–3400 (hydrazono NH and phenolic OH), 1670 (CO), 1510 ($>C{=}N{-}$); PMR (DMSO-d_6), 6·49 (1H, s, $C_2\underline{H}$), 7–7·7 (11H, m, ArH), 8·4 (1H, m, $C_{10}\underline{H}$), 9·35 (1H, bs O$\underline{H}$, exchangeable) and 14·6 (1H, bs, NH, exchangeable). Similarly the red dye was identified as 2-(4-chlorophenylhydrazono)-3-(4-hydroxyphenyl)-1-oxo-1*H*-pyridol[1,2-*a*]benzimidazole (**4a**): MS, m/e 414 (M^+); IR (KBr) 2900–3350 (hydrazono NH and phenolic OH), 1650 (CO), 1505 ($>$C=N—); PMR (DMSO-d_6) 6·8–7·8 (12H, m, Ar$\underline{H}$ and $C_4\underline{H}$), 8·42 (1H, m, $C_{10}\underline{H}$), 9·38 (1H, bs, OH, exchangeable) and 14·9 (1H, bs, N$\underline{H}$, exchangeable).

Changing both the coupling medium and the molar proportion of 4-chlorobenzenediazonium chloride resulted in the same mixture being obtained and no significant change in the composition of the mixture. The dyes **3a** and **4a** were obtained (mixed up, co-TLC and superimposable IR) when the isomeric dyes derived from azo-coupling **1** with 4-chlorobenzenediazonium chloride were demethylated according to the same procedure. This alternate route substantiated the proposed structures **3a** and **4a**. It clearly indicated that the azo-coupling reaction on **2** had taken place on the pyridone ring and bisazo-coupled dyes had not been formed.

The comparable nucleophilicities of the 2- and 4-positions in compounds **1** and **2** were mainly responsible for the formation from them of equivalent amounts of the two positionally isomeric azo dyes. An attempt was therefore made to obtain a single azo dye by blocking one of the two reactive positions. Hence, compound **1** was acetylated to obtain **5**. Compound **5** gave the following spectral data: MS, m/e 322 (M^+); IR (KBr), 1695 ($COCH_3$), 1650 (CO); PMR ($CDCl_3$), 2·78 (3H, s, —$COC\underline{H}_3$), 3·8 (3H, s, $OC\underline{H}_3$), 6·45 (1H, s, =C$\underline{H}$—CO), 6·7–7·8 (7H, m, Ar$\underline{H}$), 8·66 (1H, m, $C_{10}\underline{H}$) and a D_2O-exchangeable NH. These spectral data are in accord with the positional isomers 2-acetyl-3-(4-methoxyphenyl)-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole (**5a**) and 4-acetyl-3-(4-methoxyphenyl)-1-oxo-1*H*,5*H*-pyrido[1,2-*a*]benzimidazole (**5b**).

Compound **5** was freely soluble in chloroform and hence a mixture of chloroform and acetic acid (1:1 v/v) was found to be a better solvent for the azo-coupling reaction. Compound **5** was thus coupled with an equimolar amount of 4-chlorobenzenediazonium chloride to obtain a vividly coloured substance which was found to be again a mixture of two dyes **6a** and **7a**. The mixture was separated by column chromatography to obtain the bright yellow **6a** using benzene as eluent and the red **7a** when the column was eluted with chloroform. Both **6a** and **7a** gave the same empirical formula indicating that they were the positional isomers of each other.

The bright yellow dye was identified as 2-acetyl-4-(4-chlorophenylhydrazono)-3-(4-methoxyphenyl)-1-oxo-1*H*-pyrido[1,2-*a*]benzimidazole (**6a**) on the basis of spectral data: IR (KBr), 2800–3200 (hydrazono NH), 1680 (acetyl CO), 1670 (CO), 1510 (hydrazono C═N); PMR ($CDCl_3$), 2·8 (3H, s, $CO\underline{CH_3}$), 3·83 (3H, s, $O\underline{CH_3}$), 6·85–7·9 (11H, m, $Ar\underline{H}$), 8.4 (1H, m, $C_{10}\underline{H}$) and 16.0 (1H, bs, $N\underline{H}$, exchangeable). Similarly the bright red dye was assigned the structure 4-acetyl-2-(4-chlorophenylhydrazono)-3-(4-methoxyphenyl)-1-oxo-1*H*-pyrido[1,2-*a*]-benzimidazole (**7a**). IR (KBr), 2800–3200 (hydrazono NH), 1640 (acetyl CO), 1615 (CO), 1500 (hydrazono C═N); PMR ($CDCl_3$), 2·75 (3H, s, $CO\underline{CH_3}$), 3·9 (3H, s, $O\underline{CH_3}$), 6·9–7·9 (11H, m, $Ar\underline{H}$), 8·35 (1H, m, $C_{10}\underline{H}$) and 15·88 (1H, bs, $N\underline{H}$, exchangeable).

These observations, i.e. acetylation of compound **1** and azo-coupling reaction on compound **5**, could be explained as follows. In the previous paper we have established the presence of two compatible nucleophilic sites in compound **1**. Similarly to the azo-coupling reaction on compound **1**, the acetylation reaction could also take place at positions 2 and 4 giving rise to the mixture of two positionally isomeric acetylated derivatives **5a** and **5b**. However, the two isomers could not be separated by traditional methods. Both the isomers **5a** and **5b** retained one nucleophilic site in their structures which could undergo azo-coupling reaction. Hence, the reaction of **5** with aryldiazonium salt gave two isomeric dyes **6** and **7** from **5a** and **5b**, respectively.

The dyes **3**, **4**, **6** and **7** were tested on polyamide (PA) and polyester (PES) fibres. In the four series of the two pairs of isomeric pyridobenzimidazole hydrazone dyes (**3**, **4**, **6** and **7**) dyes **4** and **7** were more intense and showed bathochromic shifts compared with **3** and **6**. This is possibly due to the *trans*-orientation of the arylhydrazone chromophore with respect to the benzimidazole moiety in **4** and **7**, lengthening the conjugated system, compared with the crossed conjugation present in **3** and **6**. Acetylated pyridobenzimidazole hydrazone dyes **6** and **7** were found to be much brighter than **3** and **4**, indicating the influence of the acetyl group directly attached to the heterocyclic coupler and also indicating that substitution on the pyridoimidazole skeleton would have profound effect on the shade of the resultant dye as it has an ability to modify the chromophoric structure.

The overall lightfastness of the dyes under study was good. Sublimation fastness for all the dyes was also good. Washing fastness for dyes **6** and **7** was better than for dyes **3** and **4** probably because of the solubilizing phenolic group present in the latter.

3. EXPERIMENTAL

Melting points were recorded on a Metler FP 15 model. Infrared spectra, in KBr, were run on a Beckmann Acculab-10 infrared spectrophotometer, PMR spectra on a Varian T-60 spectrometer and mass spectra on a Varian Mat 112S (70 eV) instrument.

3.1. 3-(4-Hydroxyphenyl)-1-oxo-1*H*,5*H*-pyrido|1,2-*a*|benzimidazole (2)

A mixture of **1** (2.90 g, 0·01 mol) and anhydrous $AlCl_3$ (5.40 g, 0·04 mol) was refluxed in chlorobenzene (50 ml) for 6 h under anhydrous conditions. The reaction mixture was cooled, treated with dilute HCl, and steam distilled to remove chlorobenzene. The aqueous solution was filtered giving the compound **2**; m.p. > 310 °C. Calc.: C, 69·56; H, 4·34: N, 10·14. Found: C, 69·21; H, 4·42; N, 10·15%. Yield 2·00 g (70%).

3.2. Azocoupling reaction on 2

The coupling was carried out by the two general methods outlined below:

Method A

Finely powdered **2** (2·76 g, 0·01 mol) was added to acetone (150 ml) with vigorous stirring to obtain a good suspension. A solution of 4-chlorobenzenediazonium chloride [prepared by diazotizing 4-chloroaniline (1·28 g, 0·01 mol) dissolved in 6 ml of 1:1 HCl with $NaNO_2$ (0·69 g, 0·01 mol) in 5 ml water] was added with constant stirring to the above suspension. The coloured product thus obtained was filtered, washed with water and dried.

Method B

Compound **2** (2·76 g, 0·01 mol) was dissolved in NaOH solution (2%, 100 ml). A solution of 4-chlorobenzenediazonium chloride (prepared as above) was added to the alkaline solution with stirring. The pH of the solution was maintained at 9–9·5. The solution was neutralized to obtain the product.

The above mixture was chromatographed using a column of activated silica gel (60–120 mesh). On elution with chloroform the yellow dye **3a**, m.p. 260 °C, was obtained. Acetone was then used as an eluent to obtain the red dye **4a**, m.p. 263 °C.

TABLE 1
Characterization Data of Dyes **3** and **4**

Dye	*R*	*Molecular formula*	*Yield*[a] (%)	*Melting point* (°C)	*Analysis* (%)					
					C		*H*		*N*	
					Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
3a	Cl	$C_{23}H_{15}ClN_4O_2$	40	260	66·58	66·98	3·61	3·64	13·51	13·11
3b	H	$C_{23}H_{16}N_4O_2$	40	248	72·63	71·95	4·21	4·20	14·73	14·80
3c	CH_3	$C_{24}H_{18}N_4O_2$	42	237	73·09	74·21	4·56	4·61	14·21	14·10
3d	OCH_3	$C_{24}H_{18}N_4O_3$	41	280	70·24	70·10	4·39	4·42	13·65	13·63
4a	Cl	$C_{23}H_{15}ClN_4O_2$	41	263	66·58	67·12	3·61	3·58	13·51	13·12
4b	H	$C_{23}H_{16}N_4O_2$	40	265	72·63	72·60	4·21	4·19	14·73	14·44
4c	CH_3	$C_{24}H_{18}N_4O_2$	41	266	73·09	73·41	4·56	4·50	14·21	14·34
4d	OCH_3	$C_{24}H_{18}N_4O_3$	40	264	70·24	70·29	4·39	4·43	13·65	13·90

[a] Yield is based on the weight of **2**.

Compounds **3b**–**3d** and **4b**–**4d** were prepared by a similar procedure using other aryl amines. Characteristic data are summarized in Table 1.

3.3. Acetylation of 1

A mixture of **1** (3 g) and fused sodium acetate (3 g) was refluxed in acetic anhydride (25 ml) under anhydrous conditions for 2 h. The solution was cooled, filtered and the residue crystallized from absolute ethanol to give colourless needles of **5**, m.p. 195–197 °C. Calc.: C, 72·28; H, 4·81; N, 8·43. Found: C, 72·30; H, 4·90; N, 8·38%. The product was a mixture of positional isomers **5a** and **5b** and showed a single spot on TLC (chloroform, ethyl acetate and acetone).

3.4. Azocoupling reaction on 5

Compound **5** (3·32 g, 0·01 mol) was dissolved in a mixture of chloroform and acetic acid (200 ml, 1:1 v/v). The solution of 4-chlorobenzenediazonium chloride (prepared as described earlier) was added to the above solution. After stirring for 12 h, the solution had assumed a dark colour. When water (200 ml) was added, the dark red coloured chloroform layer separated. This was washed with water to remove acetic acid and the

TABLE 2
Characterization Data of Dyes **6** and **7**

Dye	*R*	*Molecular formula*	*Yield*[a] (%)	*Melting point* (°C)	*Analysis* (%) *C*		*H*		*N*	
					Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
6a	Cl	$C_{26}H_{19}ClN_4O_3$	40	258	66·31	65·92	4·03	4·10	11·90	11·78
6b	H	$C_{26}H_{20}N_4O_3$	40	193	71·55	71·56	4·58	4·65	12·84	12·40
6c	CH_3	$C_{27}H_{22}N_4O_3$	42	207	72·00	71·81	4·88	4·83	12·44	12·41
6d	OCH_3	$C_{27}H_{22}N_4O_4$	41	230	69·52	69·92	4·72	4·71	12·01	11·96
7a	Cl	$C_{26}H_{19}ClN_4O_3$	40	252	66·31	67·10	4·03	4·11	11·90	11·80
7b	H	$C_{26}H_{20}N_4O_3$	41	229	71·55	71·40	4·58	4·53	12·84	12·61
7c	CH_3	$C_{27}H_{22}N_4O_3$	41	236	72·00	71·58	4·88	4·71	12·44	12·12
7d	OCH_3	$C_{27}H_{22}N_4O_4$	42	224	69·52	69·69	4·72	4·76	12·01	11·80

[a] Yield is based on the weight of **5**.

chloroform evaporated to obtain a dark red coloured powder which was a mixture of two dyes.

The above mixture was chromatographed using a column of activated silica gel (60–120 mesh). On elution with benzene a bright yellow dye **6a** (m.p. 258 °C) was obtained. After removal of **6a** from the column chloroform was used as an eluent to obtain a bright red dye **7a** (m.p. 252 °C).

Compounds **6b**–**6d** and **7b**–**7d** were prepared by a similar procedure using other aryl amines. Characteristic data are summarized in Table 2.

REFERENCES

1. D. V. Dikshit, S. D. Samant, D. S. Kanekar and K. D. Deodhar, *Dyes and Pigments*, **4**, 35 (1983).
2. H. Farbacrke, French Patent 1575400 (11 July 1969); *Chem. Abs.*, **73**, 46694q (1970).
3. J. Arient and J. Marhan, *Collection Czech. Chem. Commun.*, **28**, 1292 (1962).