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Synthesis of Benzimidazole Substituted Pyridone Azo Disperse Dyes

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SUMMARY

Benzimidazole substituted couplers containing pyridone as a basic moiety were prepared by the condensation of appropriate amines with glutaconic anhydride (**1**). *The resulting glutaconimides were coupled with diazotized arylamines to form azo disperse dyes, the fastness properties of which were evaluated.*

INTRODUCTION

We have previously[1] described studies to incorporate a benzimidazole moiety into some new pyridobenzimidazole couplers, and azo disperse dyes derived from them. In continuation of this work we now report the effect of separating the benzimidazole ring from the pyridone skeleton and using it as a substituent on the N-atom of the pyridone framework, and also the effect of the benzimidazole moiety, when separated from the imide N-atom of an alkylene and an aryl ring, on the colour and fastness properties on polyamide (PA) and polyester (PES) fibres of the resultant azo dyes.

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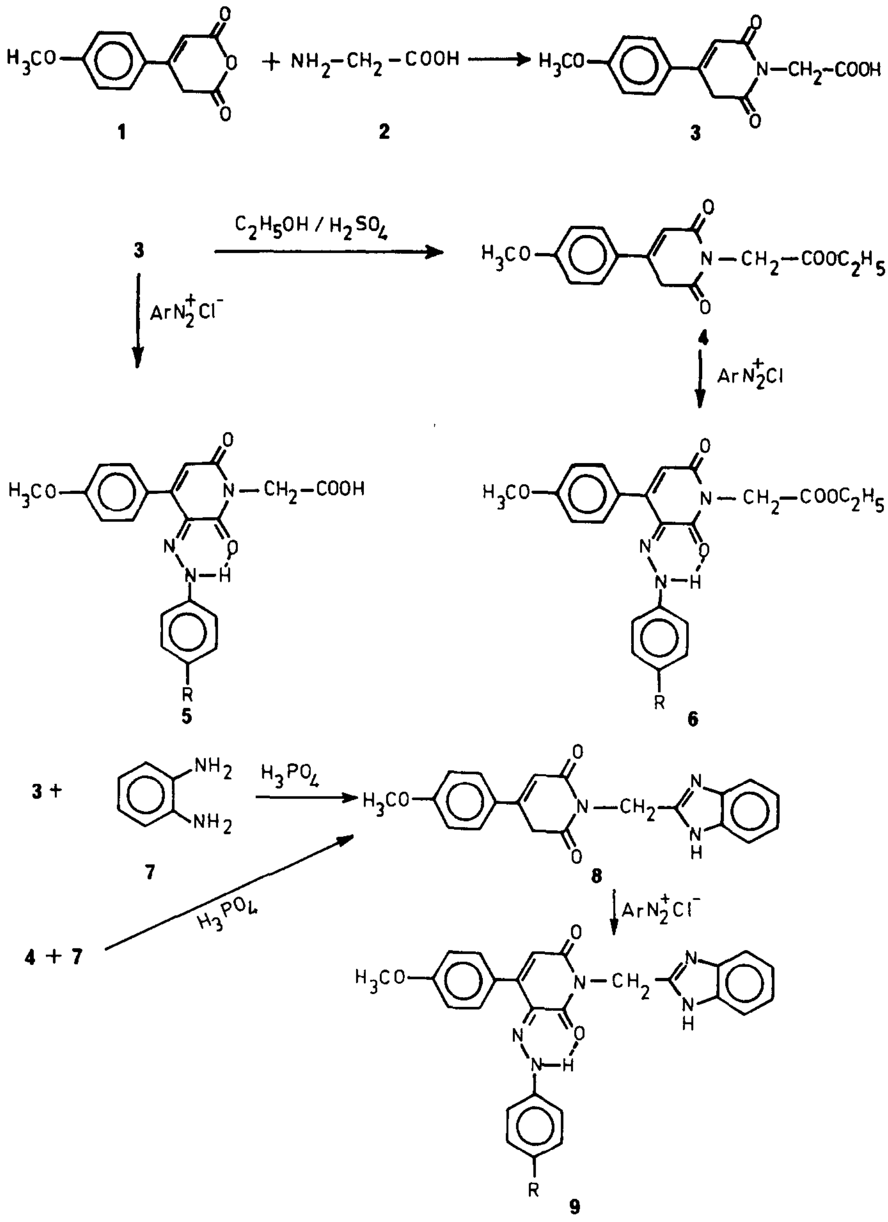
RESULTS AND DISCUSSION

4-(4-Methoxyphenyl)-5*H*-pyran-2,6-dione (**1**) was fused with equimolar quantity of aminoacetic acid (**2**) to give 4-(4-methoxyphenyl)-1*H*,5*H*-pyridine-2,6-dione-1-acetic acid (**3**) (Scheme 1). The structure of compound **3** was confirmed on the basis of its spectral data: IR (KBr), 3260–3640 (carboxylic OH), 1725 and 1705 (cyclic imide CO), 1665 (carboxy CO); PMR (DMSO-d_6), 3·85 (3H, s, OC$\underline{H}_3$), 4·1 (2H, s, —C$\underline{H}_2$—CO), 4·5 (2H, s, N—C$\underline{H}_2$—CO) 5·95 (1H, bs, O$\underline{H}$, exchangeable), 6·65 (1H, s, =C$\underline{H}$—CO) and 6·9–7·9 (4H, m, Ar$\underline{H}$).

The acid **3** was esterified with ethyl alcohol in presence of H_2SO_4 to obtain ethyl 4-(4-methoxyphenyl)-1*H*,5*H*-pyridine-2,6-dione-1-acetate (**4**); MS, m/e 303 (M^+); IR (KBr), 1755 and 1725 (cyclic imide CO), 1675 (ester CO); PMR ($CDCl_3$), 1·3 (3H, t, O—CH_2—C$\underline{H}_3$), 3·85 (5H, s, OC$\underline{H}_3$ and —C$\underline{H}_2$—CO), 4·2 (2H, q, O—C$\underline{H}_2$—CH_3), 4·63 (2H, s, N—C$\underline{H}_2$—CO), 6·55 (1H, s, =C$\underline{H}$—CO) and 6·75–7·6 (4H, m, Ar$\underline{H}$).

The acid **3** and its ethyl ester **4** when coupled with 4-chlorobenzenediazonium chloride gave, respectively, the dyes 4-(4-methoxyphenyl)-5-(4-chlorophenylhydrazone)-1*H*-pyridine-2,6-dione-1-acetic acid (**5a**) [IR (KBr), 3300–3620 (carboxy OH), 2800–3200 (hydrazono —NH—), 1755 and 1725 (cyclic imide CO), 1680 (carboxy CO), 1505 ($>$C=N); PMR (DMSO-d_6), 3·95 (3H, s, —OCH_3), 4·65 (2H, s, N—CH_2—CO—), 6·4 (1H, s, =C$\underline{H}$—CO), 7·05–7·85 (8H, m, Ar$\underline{H}$)] and ethyl-4-(4-methoxyphenyl)-5-(4-chlorophenylhydrazono)-1*H*-pyridine-2,6-dione-1-acetate (**6a**) [IR (KBr), 2900–3200 (hydrazono —NH—), 1725 (ester CO), 1660 and 1620 (imide CO), 1500 ($>$C=N—); PMR ($CDCl_3$), 1·3 (3H, t, —O—CH_2—C$\underline{H}_3$), 3·95 (3H, s, —OC$\underline{H}_3$), 4·28 (2H, q, —O—C$\underline{H}_2$—CH_3), 4·8 (2H, s, N—C$\underline{H}_2$—CO—), 6·35 (1H, s, =C$\underline{H}$—CO), 6·8–7·55 (8H, m, Ar$\underline{H}$) and 14·7 (1H, bs, hydrazono —N$\underline{H}$—, exchangeable).

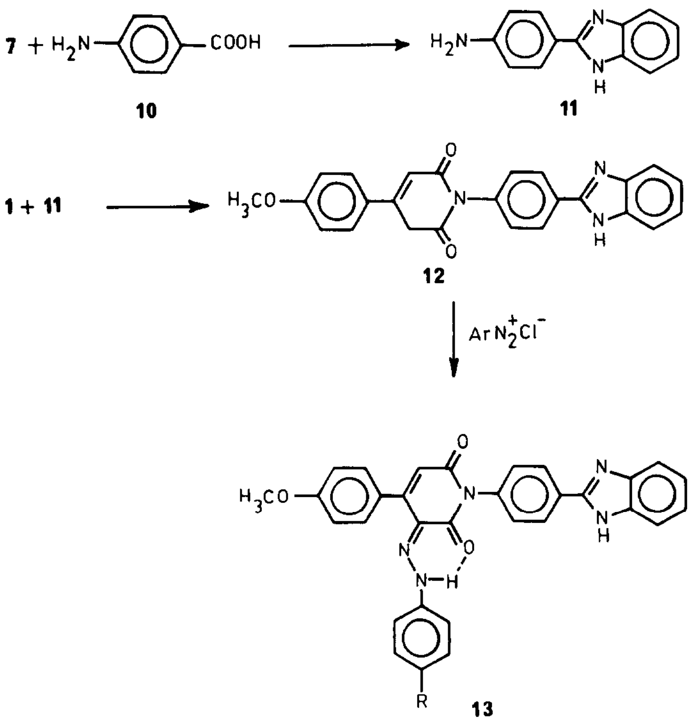
Phosphoric acid (H_3PO_4) is known to be a good condensing agent for the preparation of 2-alkyl substituted benzimidazole derivatives.[2] A mixture of **3** and 1,2-diaminobenzene (**7**) was heated in phosphoric acid to give 1-(benzimidazol-2-ylmethyl)-4-(4-methoxyphenyl)-1*H*,5*H*-pyridine-2,6-dione (**8**). IR (KBr), 3000–3600 (benzimidazole —NH—), 1720 and 1710 (imide CO). Compound **8** was also obtained by similar reaction of compounds **4** and **7**. The PMR spectrum of **8** could not be run due to its poor solubility in the common organic solvents. Compound **8**


H3CO
+ NH2–CH2–COOH
N–CH2–COOH
1
2
3
C2H5OH / H2SO4
ArN2+Cl−
N–CH2–COOC2H5
4
5
6
R
3 +
NH2
H3PO4
N–CH2
7
8
4 + 7
9

Scheme 1

was coupled with 4-chlorobenzenediazonium chloride to furnish a yellow dye 1-(benzimidazol-2-ylmethyl)-4-(4-methoxyphenyl)-5-(4-chlorophenylhydrazone)-1*H*-pyridine-2,6-dione (**9a**): IR (KBr), 3300 (hydrazono —NH—), 2900 (benzimidazolo —NH—), 1500 (hydrazono $>C{=}N-$); PMR (DMSO-d_6), 3·93 (3H, s, $OC\underline{H}_3$), 5·55 (2H, s, $>N{-}C\underline{H}_2{-}C<$), 6·4 (1H, s, $={C\underline{H}}{-}CO$), 6·95–7·8 (12H, m, $Ar\underline{H}$), 14·0 (1H, bs, hydrazono $-N\underline{H}-$, exchangeable).

While conventional methods of condensation work well for the preparation of 2-alkyl substituted benzimidazole derivatives, they frequently fail or give low yields in the preparation of certain 2-aryl substituted benzimidazoles. Polyphosphoric acid (PPA) was found to be a remarkably effective condensing agent for the formation of 2-aryl substituted benzimidazoles.[3] 1,2-Diaminobenzene (**7**) was condensed with 4-aminobenzoic acid (**10**) in polyphosphoric acid according to the procedures given in the literature[4,5] to obtain 2-(4-aminophenyl) benzimidazole (**11**),



Scheme 2

which, on fusion with **1** gave the coupling component 1-[4-(benzimidazol-2-yl)phenyl]-4-(4-methoxyphenyl)-1*H*,5*H*-pyridine-2,6-dione (**12**) (Scheme 2): IR (KBr), 2800 (benzimidazole —NH—), 1710 and 1670 (imide CO). The PMR spectrum of **12** could not be run due to its poor solubility in the common organic solvents. Compound **12** was coupled with 4-chlorobenzenediazonium chloride to give the dye 1-[4-(benzimidazol-2-yl)phenyl]-4-(4-methoxyphenyl)-5-(4-chlorophenylhydrazono)-1*H*-pyridine-2,6-dione (**13a**): IR (KBr), 3300 (hydrazono —NH—) 1670 and 1625 (imide CO), 1500 (hydrazono $>C{=}N-$); PMR (TFA-d_1) 3·9 (3H, s, $-OC\underline{H}_3$), 6·5 (1H, s, $=C\underline{H}-CO$), 6·85–8 (16H, m, ArH).

The dyes **5** and **6** dyed polyamide (PA) and polyester fibres (PES) in yellow shades. The presence of the carboxylic acid group in **5** was found to make these dyes more suitable than dyes **6** for PA, although dyes **6** gave more intense dyeings on PES.

Dyes **9** and **13** also gave yellow dyeings, the presence in dyes **13** of the bulky phenyl bridge between the benzimidazole and pyridone rings resulting in much weaker dyeings than the alkylene bridged dyes **9**. This observation is in agreement with previous reports on *N*-CH_3 and *N*-aryl glutaconimide hydrazone dyes,[6] where the former were found to be the better disperse dyes.

The overall lightfastness of the dyes was good and sublimation fastness of all dyes was excellent. Washing fastness for dyes **6**, **9** and **13** was better than that of dyes **5** probably because of the solubilizing carboxylic group present in the latter.

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.

4-(4-Methoxyphenyl)-1*H*,5*H*-pyridine-2,6-dione-1-acetic acid (3)

A mixture of **1** (2·18 g, 0·01 mol) and **2** (0·75 g, 0·01 mol) were fused for 2 h at 200 °C. The fused mass was cooled, extracted with aqueous $NaHCO_3$ and acidified to give **3** (2·36 g, 86 %), m.p. 246 °C (acetic acid). Calc.: C, 61·09; H, 4·72; N, 5·09. Found: C, 60·98; H, 4·70; N, 5·05 %.

Ethyl 4-(4-methoxyphenyl)-1*H*,5*H*-pyridine-2,6-dione-1-acetate (4)

Compound **3** (2 g) was refluxed in absolute ethanol (40 ml) with concentrated H_2SO_4 (0·2 ml) for 8 h. The solution was concentrated, cooled, added to cold water and filtered, to give **4**, m.p. 132 °C (50 % aq. alcohol). Calc.: C, 63·36; H, 5·61; N, 4·62. Found: C, 63·35; H, 5·60; N, 4·65 %.

Azocoupling reactions on 3 and 4

Finely powdered **3** (2·75 g, 0·01 mol) was added to acetone (200 ml) with vigorous stirring to obtain a fine 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 product was filtered, washed with water, dried and crystallized from acetic acid to give the yellow dye **5a**, m.p. 243 °C. Dyes **5b–5d** were similarly prepared using other aryl amines.

Following the same procedure, **4** (3·03 g, 0·01 mol) was coupled with 4-chlorobenzenediazonium chloride to give **6a**, m.p. 163 °C (alcohol). Dyes **6b–6d** were similarly prepared using other aryl amines. Relevant data for dyes **5** and **6** are given in Table 1.

TABLE 1
Characterisation Data of Dyes 5 and 6

Dye	*R*	*Molecular formula*	*Yield (%)*	*Melting point (°C)*	*Analysis (%)*					
					C		*H*		*N*	
					Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
5a	Cl	$C_{20}H_{16}ClN_3O_5$	92	243	58·04	57·69	3·86	4·00	10·15	9·92
5b	H	$C_{20}H_{17}N_3O_5$	94	233	63·32	62·91	4·48	4·41	11·08	10·86
5c	CH_3	$C_{21}H_{19}N_3O_5$	93	217	64·12	63·64	4·83	4·74	10·68	10·42
5d	OCH_3	$C_{21}H_{19}N_3O_6$	94	198	61·61	62·12	4·64	4·69	10·26	10·44
6a	Cl	$C_{22}H_{20}ClN_3O_5$	94	163	59·79	59·10	4·53	4·52	9·51	9·38
6b	H	$C_{22}H_{21}N_3O_5$	93	197	64·86	63·98	5·15	5·00	10·31	10·30
6c	CH_3	$C_{23}H_{23}N_3O_5$	92	167	65·55	65·69	5·46	5·40	9·97	10·00
6d	OCH_3	$C_{23}H_{23}N_3O_6$	92	124	63·15	62·81	5·26	4·12	9·61	9·48

1-(Benzimidazol-2-ylmethyl)-4-(4-methoxyphenyl)-1*H*,5*H*-pyridine-2,6-dione (8) and derived dyes

A mixture of **3** (2·75 g, 0·01 mol) and **7** (1·08 g, 0·01 mol) in phosphoric acid (85 %, 50 ml) was heated for 2 h at 170–180 °C. The liquor was cooled and added to water (500 ml) when a white solid separated. This was filtered washed with water and with acetone to remove unreacted **7** and treated with $NaHCO_3$ to remove **3**, giving **8**, m.p. 214 °C, yield 2·3 (68 %). Calc.: C, 69·16; H, 4·89; N, 12·10. Found: C, 68·45; H, 4·91; N, 12·40 %.

Finely powdered **8** (0·347 g, 0·001 mol) was coupled with 4-chlorobenzenediazonium chloride following the same procedure as described earlier to obtain the yellow dye **9a**, m.p. 199 °C. Compounds **9b**–**9d** were prepared using other aryl amines by a similar procedure. Characteristic data are summarised in Table 2.

1-[4-(Benzimidazol-2-yl)phenyl]-4-(4-methoxyphenyl)-1*H*,5*H*-pyridine-2,6-dione (12) and derived dyes

A mixture of **1** (2·18 g, 0·01 mol) and **11** (2·09 g, 0·01 mol) was fused at 210–220 °C for 4 h. The fused mass was cooled to room temperature and washed with acetone and 1:1 HCl to remove unreacted **1** and **11** respectively. The product thus obtained was **12**, m.p. 303 °C, yield 2·37 g

TABLE 2
Characterisation Data of Dyes 9 and 13

Dye	*R*	*Molecular formula*	*Yield (%)*	*Melting point (°C)*	*Analysis (%)*					
					C		*H*		*N*	
					Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
9a	Cl	$C_{26}H_{20}ClN_5O_3$	82	199	64·26	64·81	4·11	4·00	14·41	14·93
9b	H	$C_{26}H_{21}N_5O_3$	87	227	69·17	68·12	4·65	4·78	15·52	15·10
9c	CH_3	$C_{27}H_{23}N_5O_3$	88	189	69·67	70·91	4·94	5·12	15·05	14·68
9d	OCH_3	$C_{27}H_{23}N_5O_4$	85	192	67·35	66·12	4·78	4·98	14·55	14·90
13a	Cl	$C_{31}H_{22}ClN_5O_3$	90	273	67·94	66·49	4·01	4·12	12·78	12·89
13b	H	$C_{31}H_{23}N_5O_3$	88	280	72·51	73·81	4·48	4·28	13·64	13·81
13c	CH_3	$C_{32}H_{25}N_5O_3$	92	269	73·14	72·40	4·76	4·69	13·33	13·51
13d	OCH_3	$C_{32}H_{25}N_5O_4$	87	259	70·71	71·68	4·60	4·50	12·89	12·96

(58%). Calc.: C, 73·34; H, 4·64; N, 10·26. Found: C, 72·19; H, 4·78; N, 10·10%.

Following the same procedure as described above, **12** (0·409 g, 0·001 mol) was coupled with an equimolar quantity of 4-chlorobenzenediazonium chloride to obtain a yellow dye **13a**, m.p. 273 °C. Dyes **13b**–**13d** were prepared using other aryl amines by a similar procedure. Characteristic data are summarised 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. E. Faith, U.S. Patent 3557121 (19 January 1971); *Chem. Abs.*, **75**, 5887c (1971).
3. D. W. Hein, R. J. Alheim and J. J. Leavitt, *J. Am. Chem. Soc.*, **79**, 427 (1957).
4. Ebana Takaaki, Yokota Kazuaki and Takada Yoshiyuki, *Hokkaido Daigaku Kogakubu Kenkyu Hokoku*, **89**, 131 (1978).
5. M. G. Pavlov, V. V. Korshak and I. Zugravescu, *Rev. Roum. Chim.*, **19**(11), 1783 (1974).
6. G. W. Joshi, M.Sc. Thesis, Bombay University (1980).