Dyes and Pigments **15** (1991) 69–82

Synthesis of Some Pyridone Azo Dyes from 1-Substituted 2-Hydroxy-6-pyridone Derivatives and their Colour Assessment

Chich Chien Chen & Ing Jing Wang

Department of Textile Engineering, National Taiwan Institute of Technology,
Taipei, Taiwan

(Received 5 March 1990; accepted 23 April 1990)

ABSTRACT

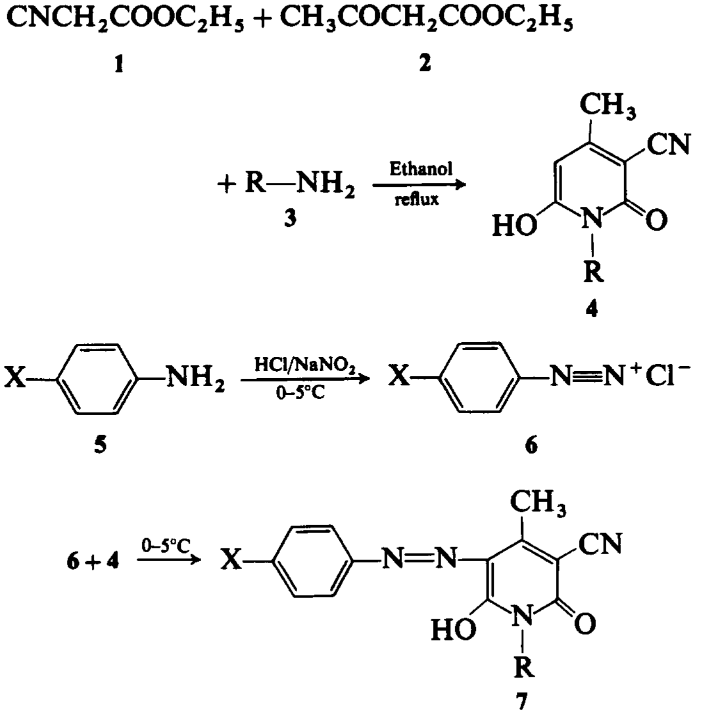
*The synthesis of a series of 3-(*p*-substituted phenylazo)-6-pyridone dyes, which are suitable for the dyeing of polyester fabrics, is described. Characterisation of the dyes was carried out by spectral and elemental analysis. The colour parameters of the dyed fabrics were measured. The assessment of colour was made in terms of CIE tristimulus values. The Helmholtz coordinates (λ_D, Y, $P\%$) and the position of colour in CIELAB coordinates (L^*, h^*_{ab}, C^*_{ab}) are reported. The correlation between colour and structure of the dyes is discussed.*

1 INTRODUCTION

Pyridone derivatives are relatively recent heterocyclic intermediates for the preparation of dyes. The azo pyridone dyes give bright hues and are therefore of investigative interest. In this paper some 3-(*p*-substituted phenylazo)-6-pyridone dyes were prepared by coupling the diazonium salts of *p*-substituted phenylamines with a 1-substituted 2-hydroxy-4-methyl-5-cyano-6-pyridone coupling component. The dyes were applied to polyester fabrics. We report here the spectral characteristics of the dyes and also a colorimetric evaluation of the dyes on polyester fabrics in order to examine the influence of substituents on the colour.

2 RESULTS AND DISCUSSION

1-Substituted-2-hydroxy-4-methyl-5-cyano-6-pyridones (**4a**–**4e**) were prepared from a mixture of ethyl cyanoacetate (**1**), ethyl acetoacetate (**2**) and amines (**3a**–**3e**) in ethanol under reflux with piperidine as catalyst. The *p*-substituted anilines (**5a**–**5c**) were diazotised using 1 M-hydrochloric acid and sodium nitrite at 0–5°C and the diazonium salts (**6a**–**6c**) were coupled with pyridone compounds (**4a**–**4e**) at pH 3–4 to give the 1-substituted 3-(*p*-substituted phenylazo)-6-pyridone dyes, **7a**–**7o**. The dyes were purified by recrystallisation from acetone and their purity examined by thin-layer chromatography.



Compound					*R*
3a	**4a**	**7a**	**7f**	**7k**	—H
3b	**4b**	**7b**	**7g**	**7l**	$—CH_3$
3c	**4c**	**7c**	**7h**	**7m**	$—CH_2CH_2OH$
3d	**4d**	**7d**	**7i**	**7n**	$—CH_2CH_2N(CH_3)_2$
3e	**4e**	**7e**	**7j**	**7o**	$—C_{12}H_{25}$

Compound			*X*
5a	**6a**	**7a–7e**	—H
5b	**6b**	**7f–7j**	$—CH_3$
5c	**6c**	**7k–7o**	$—NO_2$

Scheme 1

2.1 Spectroscopic analysis of dyes 7a–7o

The structures of dyes **7a**–**7o** were established by elemental analysis and spectral data. The IR spectra of dyes showed characteristic vibrational bands at 1624–1691 cm^{-1} for the carbonyl group and at 2218–2238 cm^{-1} for the nitrile group. The dyes **7k**–**7o**, which contain a nitro substituent showed two vibrational bands at 1509–1514 cm^{-1} and 1334–1341 cm^{-1}. The ^1H-NMR spectra of dyes showed a singlet at $\delta = 2{\cdot}54$–$2{\cdot}76$ ppm, which can be attributed to the methyl group linked to the heterocyclic ring at the 4-position. A multiplet at $\delta = 7{\cdot}55$ ppm is due to the 5H phenyl protons of dyes **7a**–**7e**. The *p*-substituted phenylazo compounds **7f**–**7o** showed two 2H doublets at $\delta = 7{\cdot}22$–$7{\cdot}50$ ppm and 7·78–8·22 ppm, which are attributed to the four protons of the *p*-substituted phenyl ring. The electronic absorption spectra of the dyes in DMSO showed absorption maxima in the range 431–445 nm and with high extinction coefficients. Comparing the absorption spectra of dyes **7a**–**7e**, it is observed that both the compounds with electron-donor groups (**7f**–**7j**) and with electron-withdrawing groups (**7k**–**7o**) show a bathochromic shift of the absorption maxima. IR and ^1H-NMR characterisation data are listed in Tables 1 and 2, respectively.

2.2 Colour assessment

The assessment of the colour of dyed fabrics was made in terms of tristimulus colorimetry.[1] Table 3 shows the values of the chromaticity coordinates, Helmholtz coordinates (λ_D, $Y\%$, $P\%$)[2] and the position of the colour in the CIELAB colour solid (L^*, a^*, b^*). The dominant wavelength shows a bathochromic shift, when the substituent X is CH_3, whereas when X is NO_2, there is little change in the dominant wavelength. The excitation purity ($P\%$) of dyed fabrics was greater when $X = CH_3$ than when $X = NO_2$. Other structure features affected the lightness of colour. Higher lightness of colour was obtained for the smaller dye molecule (**7a**), whereas the larger molecule of dye **7j** had the lowest lightness. Substituents with electron-donating or electron-withdrawing character did not have much influence on the lightness of colour, but the effect of substituents X was in the sequence $H > NO_2 > CH_3$, whereas the substituents in R gave the sequence $H > CH_2CH_2OH > CH_2CH_2N(CH_3)_2 > CH_3 > C_{12}H_{25}$. Figure 1 shows the CIELAB colour coordinates of dyes **7a**–**7o** on polyester fabrics. The positions of the colours are distributed in the yellow–green area with hue angle h^*_{ab} 98–119° and longer radial chroma C^*_{ab}[3] of length 78·96–99·19, with the exception of dyes **7d**, **7i** and **7n**. Figure 2 shows the position of the deviations of hue angle and radial chroma of dyes, in comparison with those of dye **7a** as model compound. The colour of the dyed fabrics showed a

TABLE 1

IR, ^{1}H-NMR and Electronic Spectra Data of Dyes **7a**–**7h**

Dye no.	IR: ν^{KBr} (cm^{-1})	^{1}H-NMR: δ (ppm) (Solvent)	Electronic spectrum in DMSO	
			λ_{max}(nm)	Log ε
7a	3 580–3 290 [ν(—NH)] 2 220 [ν(—C≡N)] 1690 [ν(—C=O)]	2·76 (s, 3H, CH_3 on heterocyclic) 7·55 (m. 5H, on arylazo) (DMSO)	432	4·565
7b	2220 [ν(—C≡N)] 1 680 [ν(—C=O)] 1 632	2·61 (s, 3H, CH_3 on heterocylic) 3·35 (s, 3H, $CH_3N—CH_3$) 7·24–7·49 (m, 5H, on arylazo) ($CDCl_3$)	434·5	4·609
7c	2 225 [ν(—C≡N)] 1 671 [ν(—C=O)] 1 626	2·62 (s, 3H, CH_3 on heterocyclic) 3·86–3·89 (t, 2H, N—CH_2—) 4·21–4·25 (t, 2H, —CH_2—O—) 7·24–7·47 (m, 5H, arylazo) ($CDCl_3$)	434	4·56
7d	2 941–2 805 [ν(—CH— on aliphatic)] 2 227 [ν(—C≡N)] 1 682 [ν(—C=O)] 1 629	2·55 (s, 3H, CH_3 on heterocyclic) 2·82 (s, 6H, —$N(CH_3)_2$) 4·07 (t, 2H, N—CH_2—) 4·20 (t, 2H, —CH_2—N—) 7·29–7·73 (m, 5H, arylazo) (DMSO)	434	4·51

7e	2 954–2 848 [ν(—CH— on aliphatic)] 2 227 [ν(—C≡N)] 1 678 [ν(—C=O)] 1 627	0·83–0·87 (t, 3H, CH_3 on aliphatic) 1·23–1·59 (m, 2OH, —$(CH_2)_{10}$—) 2·60 (s, 3H, CH_3 on heterocyclic) 3·91–3·96 (t, 2H, N—CH_2—) 7·24–7·46 (m, 5H, arylazo) ($CDCl_3$)	431	4·55
7f	3 500–3 280 [ν(—NH)] 2 226 [ν(—C≡N)] 1 660 [ν(—C=O)]	2·36 (s, 3H, CH_3 on arylazo) 2·46 (s, 3H, CH_3 on heterocyclic) 7·22–7·30 (d, 2H, 3,5-position on arylazo) 7·50–7·58 (d, 2H, 2,6-position on arylazo) (DMSO)	443	4·45
7g	2 224 [ν(—C≡N)] 1 674 [ν(—C=O)] 1 630	2·37 (s, 3H, CH_3 on arylazo) 2·60 (s, 3H, CH_3 on heterocyclic) 3·34 (s, 3H, N—CH_3) 7·24–7·25 (d, 2H, 3,5-position on arylazo) 7·35–7·38 (d, 2H, 2,6-position on arylazo) ($CDCl_3$)	443	4·59
7h	2 222 [ν(—C≡N)] 1 665 [ν(—C=O)] 1 624	2·38 (s, 3H, CH_3 on arylazo) 2·61 (s, 3H, CH_3 on heterocyclic) 3·85–3·89 (t, 2H, N—CH_2—) 4·21–4·25 (t, 2H, —CH_2—O—) 7·24–7·25 (d, 2H, 3,5-position on arylazo) 7·35–7·38 (d, 2H, 2,6-position on arylazo) ($CDCl_3$)	444	4·64

TABLE 2
IR, ^{1}H-NMR and Electronic Spectra Data of Dyes **7i**–**7o**

Dye no.	*IR: ν^{KBr} (cm^{-1})*	*^{1}H-NMR: δ (ppm) (Solvent)*	*Electronic spectrum in DMSO*	
			λ_{max} (nm)	*Log ε*
7i	2 982–2 814 [ν(—CH$_2$— on aliphatic)] 2 218 [ν(—C≡N)] 1 676 [ν(—C═O)] 1 630	2·33 (s, 3H, CH$_3$ on arylazo) 2·54 (s, 3H, CH$_3$ on heterocyclic) 2·82 (s, 6H, —N(CH$_3$)$_2$) 4·05–4·09 (t, 2H, —N—CH$_2$—) 4·19–4·21 (t, 2H, —CH$_2$—N—) 7·29–7·32 (d, 2H, 3,5-position on arylazo) 7·60–7·63 (d, 2H, 2,6-position on arylazo) (DMSO)	444	4·49
7j	2 994–2 805 [ν(—CH$_2$— on aliphatic)] 2 226 [ν(—C≡N)] 1 679 [ν(—C═O)] 1 627	0·83–0·87 (t, 3H, CH$_3$ on aliphatic) 1·23–1·57 (m, 2OH, —(CH$_2$)$_{10}$—) 2·59 (s, 3H, CH$_3$ on heterocyclic) 3·91–3·96 (t, 2H, N—CH$_2$—) 7·22–7·24 (d, 2H, 3,5-position on arylazo) 7·35–7·38 (d, 2H, 2,6-position on arylazo) (CF$_3$COOD)	445	4·62
7k	3 574–3 303 [ν(—NH)] 2 233 [ν(—C≡N)] 1 679 [ν(—C═O)] 1 514, 1 339 [ν(—NO$_2$)]	2·76 (s, 3H, CH$_3$ on heterocyclic) 7·78–7·87 (d, 2H, 3,5-position on arylazo) 8·22–8·31 (d, 2H, 2,6-position on arylazo) (DMSO)	441	4·71

7l	2 227 [ν(—C≡N)] 1 682 [ν(—C=O)] 1 641 1 509, 1 336 [ν(—NO_2)]	2·76 (s, 3H, CH_3 on heterocyclic) 3·48 (s, 3H, N—CH_3) 7·82–7·85 (d, 2H, 3,5-position on arylazo) 8·43–8·46 (d, 2H, 2,6-position on arylazo) (DMSO)	440	4·73
7m	2 227 [ν(—C≡N)] 1 675 [ν(—C=O)] 1 630 1 511, 1334 [ν(—NO_2)]	2·54 (s, 3H, CH_3 on heterocyclic) 3·52–3·56 (t, 2H, N—CH_2—) 3·91–3·95 (t, 2H, —CH_2—O—) 7·89–7·92 (d, 2H, 3,5-position on arylazo) 8·28–8·31 (d, 2H, 2,6-position on arylazo) (DMSO)	440	4·72
7n	2 951–2 825 [ν(—CH_2— on aliphatic)] 2 226 [ν(—C≡N)] 1 691 [ν(—C=O)] 1 642 1 511, 1 341 [ν(—NO_2)]	2·57 (s, 3H, CH_3 on heterocyclic) 2·82 (s, 6H, —$N(CH_3)_2$) 4·07 (t, 2H, —N—CH_2—) 4·19 (t, 2H, —CH_2—N—) 7·93–7·96 (d, 2H, 3,5-position on arylazo) 8·31–8·34 (d, 2H, 2,6-position on arylazo) (DMSO)	441	4·54
7o	2 954–2 848 [ν(—CH_2— on aliphatic)] 2 227 [ν(—C≡N)] 1 678 [ν(—C=O)] 1 634 1 509, 1 339 [ν(—NO_2)]	0·83–0·86 (t, 3H, CH_3 on aliphatic) 1·23–1·61 (m, 20H, —$(CH_2)_{10}$—) 2·61 (s, 3H, CH_3 on heterocyclic) 3·92–3·95 (t, 2H, N—CH_2—) 7·53–7·56 (d, 2H, 3,5-position on arylazo) 8·30–8·33 (d, 2H, 2,6-position on arylazo) (DMSO)	442	4·61

TABLE 3
Colour data of Dyes **7a**–**7o** on Polyester[a]

Dye no.	*Chromaticity*		*Helmholtz coordinates*			*CIELAB*		
	x	*y*	*Dominant wavelength* λ_D *(nm)*	*Luminance factor* *Y (%)*	*Purity* *P (%)*	*L**	*a**	*b**
7a	0·409	0·480	570	80·89	67·1	97·72	−27·86	84·57
7b	0·427	0·487	572	76·37	74·7	97·12	−24·97	95·97
7c	0·410	0·476	571	85·99	66·0	97·61	−28·52	84·67
7d	0·341	0·384	561	86·28	17·6	97·38	−17·97	34·68
7e	0·419	0·482	572	79·19	70·7	97·02	−29·03	87·81
7f	0·428	0·473	573	77·82	70·8	96·81	−20·86	88·15
7g	0·452	0·489	575	68·21	82·4	95·15	−14·57	96·08
7h	0·439	0·484	574	73·85	77·2	96·16	−21·12	91·73
7i	0·362	0·405	568	78·27	30·0	96·04	−16·90	41·55
7j	0·401	0·464	572	78·72	62·3	88·68	−22·63	73·12
7k	0·411	0·467	572	80·81	63·6	97·47	−27·15	82·40
7l	0·413	0·474	571	78·86	66·3	96·98	−29·67	77·75
7m	0·415	0·476	572	84·33	67·7	97·23	−29·02	83·80
7n	0·340	0·386	560	79·94	22·2	97·14	−18·08	32·14
7o	0·396	0·466	569	78·64	65·4	96·94	−29·48	73·25

[a] Dye concentration 1·0% owf.

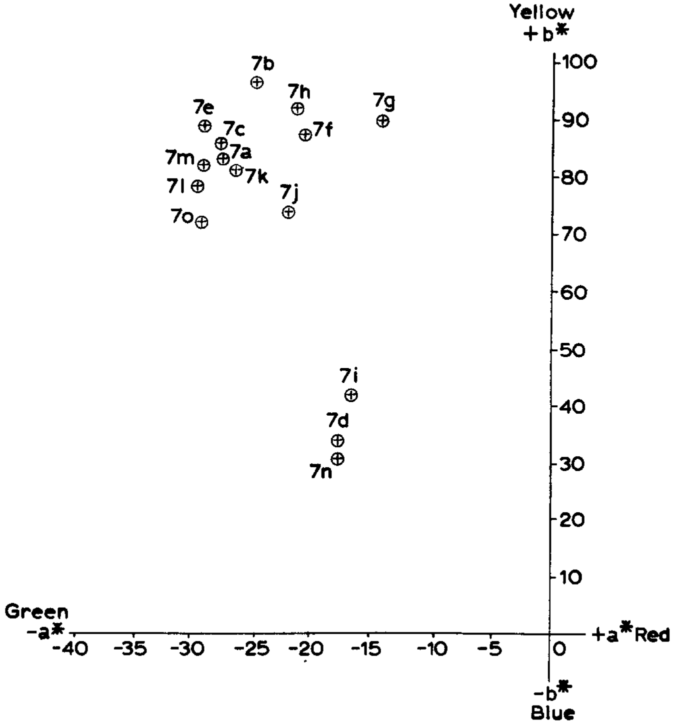


Fig. 1. CIELAB 1976 colour coordinates (L^*, a^* and b^*) of dyes **7a**–**7o** on polyester fabrics (using D_{65} as reference source).

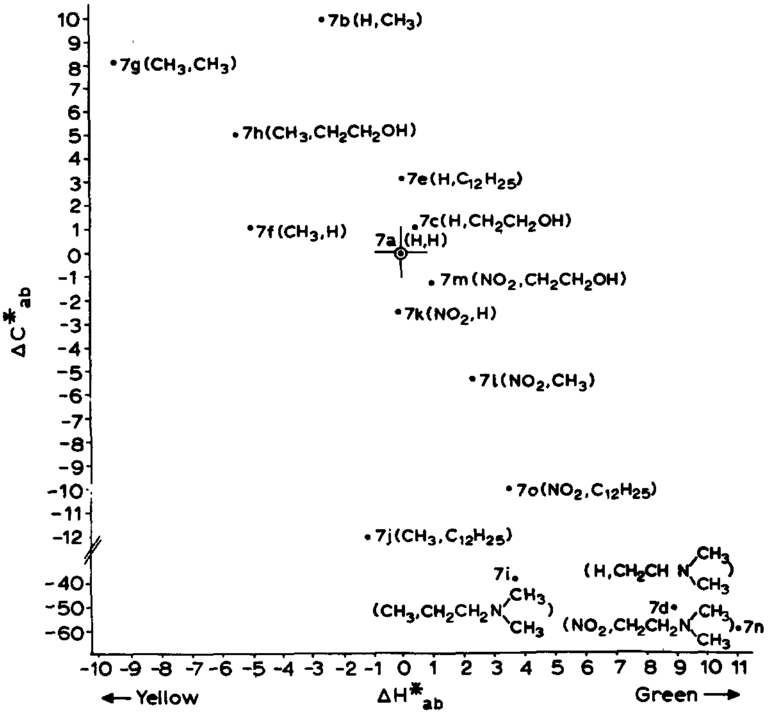


Fig. 2. Diagram of ΔC^*_{ab} plot of ΔH^*_{ab} (dye **7a** as model compound).

TABLE 4
Deviation of Hue Angle and Radial Chroma

Dye no.	H^*_{ab} *(degrees)*	ΔH^*_{ab} *(degrees)*	C^*_{ab}	ΔC^*_{ab}
7a	108·24	0	89·05	0
7b	104·62	−3·62	99·19	10·14
7c	108·44	0·20	90·12	1·07
7d	117·41	9·17	40·10	−48·95
7e	108·30	0·06	92·48	3·43
7f	103·32	−4·92	90·55	1·50
7g	98·62	−9·62	97·17	8·12
7h	102·96	−5·28	94·13	5·08
7i	112·13	3·89	44·85	−44·20
7j	107·19	−1·05	76·54	−12·51
7k	108·23	−0·01	86·75	−2·30
7l	110·88	2·64	83·21	−5·84
7m	109·10	0·86	88·60	−0·45
7n	119·35	11·11	36·87	−52·18
7o	111·92	3·68	78·96	−10·09

greener hue and a shorter radial chroma than dye **7a**, for those dyes where X = NO_2 or R = *N,N*-dimethylethylene, i.e. **7m**, **7l**, **7o**, **7n**, **7i** and **7d**. On the other hand, with dyes **7b**, **7f**, **7g** and **7h**, where X, R = CH_3, the colours were yellower and showed a longer radial chroma (Table 4). These dyes were suitable for the dyeing of polyester and give yellow or greenish-yellow hues.[4-6]

3 EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a JASCO Hc-12 FT/IR-3 (Fourier Transform Infrared Spectrophotometer) using the KBr technique. Absorption spectra in DMSO were recorded on a Shimadzu UV–VIS 240 recording spectrophotometer. The ^{1}H-NMR spectra were determined with a JUM-FX-100 (JEOL) FT–NMR spectrometer using TMS as internal standard. The mass spectra were determined on a JMS-D-300 (JEOL) mass spectrometer.

3.1 Dyeing and colour measurement

The dye baths were prepared from the dye (1·0% weight of fibre) with an amphoteric dispersol–levelling agent (1 g litre^{-1}) to a final liquor ratio of 30:1, w/w. The pH value of the bath was adjusted to 4–5 with acetic acid (10%). The polyester fabrics, previously wetted, were placed into the dye liquor at 25–30°C. The temperature was raised 2°C min^{-1} to 130°C, and dyeing continued for 60 min. After cooling, the dyed fabrics were reduction-cleared in sodium hydroxide (6 g litre^{-1}), soap (1 g litre^{-1}) and hydrosulphite (2 g litre^{-1}) at 75°C and then washed and dried. The colour parameters of the dyed fabrics were determined on a Multi Channel Photo Detector (MCPD-110A) connected to an NEC PC-9801 computer using the D_{65} source.

3.2 2-Hydroxy-4-methyl-5-cyano-6-pyridone (4a)

A mixture of ethyl acetoacetate (65·07 g, 0·5 mol), ethyl cyanoacetate 56·56 g, 0·5 mol), ethanol (50 ml), piperidine (15 ml) and ammonia 70 ml, 0·5 mol) was stirred and refluxed until the reaction was completed (about 7–8 h). During the reaction, the white product precipitated. The crude product was filtered, dried and recrystallised from ethanol to give white crystals (91%), m.p. 303·1°C (P^+ at *m/e* 150). Calculated for $C_7H_6N_2O_2$: C, 56·0; H, 4·0; N, 18·7. Found: C, 56·0; H, 4·1; N, 18·6%.

3.3 1-Methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4b)

The pyridone **4b** was prepared in a manner similar to **4a**, and after completion of the reaction, the alcohol was removed on a rotatory evaporator and the viscous residue poured slowly into ice-cold 10% aqueous hydrochloric acid (600 ml) to precipitate the product. The crude product was recrystallised from ethanol as white crystals (86%), m.p. 296·5°C (P^+ at *m/e* 164). Calculated for $C_8H_8N_2O_2$: C, 58·5; H, 4·9; N, 17·1. Found: C, 58·2; H, 4·9; N, 17·1%.

3.4 1-Hydroxyethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4c)

Compound **4c** was prepared in a similar manner to that described above for **4b**, and was recrystallised from ethanol as white crystals (90%), m.p. 175·1°C (P^+ at *m/e* 194). Calculated for $C_9H_{10}N_2O_3$: C, 55·7; H, 5·15; N, 14·4. Found: C, 55·7; H, 5·15; N, 14·1%.

3.5 1-(*N*,*N*-Dimethylaminoethyl)-2-hydroxy-4-methyl-5-cyano-6-pyridone (4d)

Compound **4d** was prepared in a similar manner to that described above for **4a**. It was recrystallised from ethanol as white crystals (85%), m.p. 162·3°C (P^+ at *m/e* 221). Calculated for $C_{11}H_{15}N_3O_2$: C, 59·7; H, 6·8; N, 19·0. Found: C, 58·0; H, 6·9; N, 19·3%.

3.6 1-Dodecyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4e)

Compound **4e** was prepared in a similar manner to that described above for **4b**. It was recrystallised from ethanol as white crystals (88%), m.p. 95·1°C (P^+ at *m/e* 318). Calculated for $C_{19}H_{30}N_2O_2$: C, 71·7; H, 9·4; N, 8·8. Found: C, 71·6; H, 9·5; N, 8·5%.

3.7 3-Phenylazo-2-hydroxy-4-methyl-5-cyano-6-pyridone (7a)

Aniline (9·3 ml, 0·1 mol) was dissolved in aqueous hydrochloric acid (26·7 ml, 0·3 mol), the solution was cooled with stirring to 0–5°C and sodium nitrite (7·04 g, 0·102 mol) was added to it. The mixture was stirred for 40–45 min at 0–5°C and excess nitrous acid was destroyed by the addition sulphamic acid. The clear diazonium salt solution was slowly poured into a solution of 2-hydroxy-4-methyl-5-cyano-6-pyridone (15 g, 0·1 mol) in water–acetone (1:1, 300 ml), keeping the pH at 3–4, and the liquor was stirred for 4–5 h at 0–5°C. The yellow dye was filtered off, washed with water, dried and recrystallised from acetone to yield yellow crystals (84%), m.p. 288·1°C (P^+ at *m/e* 254). Calculated for $C_{13}H_{10}N_4O_2$: C, 61·4; H, 3·9; N, 22·0. Found: C, 61·5; H, 3·8; N, 22·1%.

The other dyes **7b–7e**, **7f–7j** and **7k–7o** were prepared in a similar manner to that described above for **7a**. Absorption spectra, IR, ^{1}H-NMR and MS spectra are summarised in Tables 1 and 2.

3.8 3-Phenylazo-1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7b)

Recrystallised from acetone as orange crystals (75%), m.p. 264·8°C (P^+ at *m/e* 268). Calculated for $C_{14}H_{12}N_4O_2$: C, 62·6; H, 4·5; N, 20·9. Found: C, 62·6; H, 4·2; N, 20·9%.

3.9 3-Phenylazo-1-hydroxyethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7c)

Recrystallised from acetone as orange crystals (88%), m.p. 237·0°C (P^+ at *m/e* 298). Calculated for $C_{15}H_{14}N_4O_3$: C, 60·4; H, 4·5; N, 18·8. Found: C, 60·5; H, 4·7; N, 18·6%.

3.10 3-Phenylazo-1-(*N*,*N*-dimethylaminoethyl)-2-hydroxy-4-methyl-5-cyano-6-pyridone (7d)

Recrystallised from acetone as orange crystals (76%), m.p. 218·5°C (P^+ at *m/e* 325). Calculated for $C_{17}H_{19}N_5O_2$: C, 62·7; H, 5·8; N, 21·5. Found: C, 62·1; H, 5·8; N, 21·5%.

3.11 3-Phenylazo-1-dodecyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7e)

Recrystallised from acetone as yellow crystals (65%), m.p. 157·0°C (P^+ at *m/e* 422). Calculated for $C_{25}H_{34}N_4O_2$: C, 71·1; H, 8·0; N, 13·3. Found: C, 71·3; H, 8·05; N, 13·0%.

3.12 3-(*p*-Methylphenyl)azo-2-hydroxy-4-methyl-5-cyano-6-pyridone (7f)

Recrystallised from acetone as orange crystals (90%), m.p. 284·4°C (P^+ at *m/e* 268). Calculated for $C_{14}H_{12}N_4O_2$: C, 62·6; H, 4·5; N, 20·9. Found: C, 62·55; H, 4·6; N, 20·9.

3.13 3-(*p*-Methylphenyl)azo-1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7g)

Recrystallised from acetone as orange crystals (82%), m.p. 256·2°C (P^+ at *m/e* 282). Calculated for $C_{15}H_{14}N_4O_2$: C, 63·8; H, 5·0; N, 19·8. Found: C, 63·8; H, 4·85; N, 19·8%.

3.14 3-(*p*-Methylphenyl)azo-1-hydroxyethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7h)

Recrystallised from acetone as orange crystals (74%), m.p. 235·2°C (P^+ at *m/e* 312). Calculated for $C_{16}H_{16}N_4O_3$: C, 61·5; H, 5·1; N, 17·9. Found: C, 61·4; H, 5·1; N, 18·0%.

3.15 3-(*p*-Methylphenyl)azo-1-(*N*,*N*-dimethylaminoethyl)-2-hydroxy-4-methyl-5-cyano-6-pyridone (7i)

Recrystallised from acetone as orange crystals (89%), m.p. 239·4°C (P^+ at *m/e* 339). Calculated for $C_{18}H_{21}N_5O_2$: C, 63·7; H, 6·2; N, 20·6. Found: C, 63·7; H, 6·2; N, 20·3%.

3.16 3-(*p*-Methylphenyl)azo-1-dodecyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7j)

Recrystallised from acetone as yellow crystals (70%), m.p. 138·6°C (P^+ at *m/e* 436). Calculated for $C_{26}H_{36}N_4O_2$: C, 71·5; H, 8·25; N, 12·8. Found: C, 71·5; H, 8·15; N, 12·9%.

3.17 3-(*p*-Nitrophenyl)azo-2-hydroxy-4-methyl-5-cyano-6-pyridone (7k)

Recrystallised from acetone as yellow crystals (91%), m.p. 324·0°C (P^+ at *m/e* 299). Calculated for $C_{13}H_9N_5O_4$: C, 52·15; H, 3·0; N, 23·4. Found: C, 52·2; H, 3·1; N, 23·4%.

3.18 3-(*p*-Nitrophenyl)azo-1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7l)

Recrystallised from acetone as yellow crystals (79%), m.p. 319·6°C (P^+ at *m/e* 313). Calculated for $C_{14}H_{11}N_5O_4$: C, 53·65; H, 3·5; N, 22·35. Found: C, 53·55; H, 3·5; N, 22·4%.

3.19 3-(*p*-Nitrophenyl)azo-1-hydroxyethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7m)

Recrystallised from acetone as yellow crystals (83%), m.p. 288·6°C (P^+ at *m/e* 343). Calculated for $C_{15}H_{13}N_5O_5$: C, 53·5; H, 3·8; N, 20·4. Found: C, 52·5; H, 3·7; N, 20·8%.

3.20 3-(*p*-Nitrophenyl)azo-1-(*N,N*-dimethylaminoethyl)-2-hydroxy-4-methyl-5-cyano-6-pyridone (7n)

Recrystallised from acetone as orange crystals (70%), m.p. 235·5°C (P^+ at *m/e* 370). Calculated for $C_{17}H_{18}N_6O_4$: C, 55·1; H, 4·9; N, 22·7. Found: C, 55·1; H, 5·0; N, 22·5%.

3.21 3-(*p*-Nitrophenyl)azo-1-dodecyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (7o)

Recrystallised from acetone as yellow crystals (68%), m.p. 186·8°C (P^+ at *m/e* 467). Calculated for $C_{25}H_{33}N_5O_4$: C, 64·25; H, 7·1; N, 15·0. Found: C, 64·0; H, 7·1; N, 15·0%.

REFERENCES

1. Hunt, R. W. G., *Color Res. Appl.*, **2** (1977) 55.
2. Agoston, G. A., *Color Theory and Its Application in Art and Design*, ed. J. M. Enoch & D. L. Mac-Adam. Springer-Verlag, New York, Berlin, Heidelberg, 1979, pp. 54–81.
3. Richter, K., *Color Res. Appl.*, **5** (1980) 25.
4. Kelly, K. L., *J. Opt. Soc. Am.*, **33** (1943) 627.
5. Mclaren, K. & Taylor, P. F., *Color Res. Appl.*, **6** (1981) 75.
6. Huntsman, J. R., *Color Res. Appl.*, **14** (1989) 240.