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Heterocyclic Monoazo Dyes for Polyamide, Derived from 4-Alkylamido-2-hydroxybenzoic Acids*

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SUMMARY

Using 4-alkylamido-2-hydroxybenzoic acids containing alkyl chains in the range C_1–C_{15} as coupling components and diazotized aminophenyl-benzo(or pyrido)-X-azoles, a series of monoazo dyes was obtained. The dyes are suitable for application to polyamide fibres. Electronic absorption spectra of the amines and the dyes, dyeing properties and fastness data of the dyed fabrics, as well as their colour parameters, have been measured and discussed with respect to chemical structure and in comparison with previously described analogous compounds.

1 INTRODUCTION

Continuing our investigations on the synthesis of monoazo disperse dyes for polyamide fibres by using, as coupling components, acyl derivatives of 4-amino-2-hydroxybenzoic acid containing alkyl chains in the range C_1–C_{15} (**IV**),[1] we have obtained a series of heterocyclic dyes of general formula **V**. The reaction sequence used in the synthesis is shown in Scheme 1.

Considering the possibility of the amino group in **III** being present in three different positions in ring B, and also the variations used for X, Y and R, a

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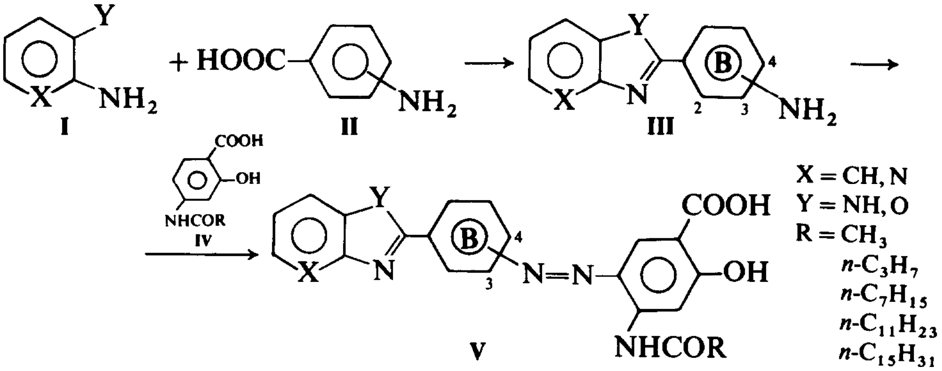


Scheme 1

total range of 60 dyes theoretically could have been synthesized. The number of dyes actually prepared was lower, i.e. 22, in view of the following factors:

(1) the difficulty of obtaining dyes from *ortho* isomers (for example, in the imidazo series, the diazonium salt led to a triazine);
(2) the length of the alkyl chain R was limited, for some series, to C_1 and C_{11}, these lengths being typically representative of short- and long-chain members respectively; moreover, this choice agrees with chemometric requirements (the related results will be presented in a separate paper).

2 EXPERIMENTAL

2.1 Dyes and intermediates

4-Alkylamido-2-hydroxybenzoic acids (**IV**) were prepared as described in refs 2 and 3, and purified by repeated crystallizations from ethanol.

Amines of formula **I**, namely 2-amino-3-hydroxypyridine, 2,3-diaminopyridine, *o*-aminophenol, 1,2-phenylenediamine and *o,m,p*-aminobenzoic acids (**II**), were commercial products.

Amines of formula **III** (nos **1**–**7** and **9**) were prepared as indicated in the references shown in Table 1. Amine **8** was obtained by condensing *m*-aminobenzoic acid (1 mol) with 2,3-diaminopyridine (1 mol) in polyphosphoric acid (85% phosphorus pentoxide). After stirring at 210°C for 6 h, the mixture was poured into water and ice, and the pH adjusted to 5 by addition of concentrated sodium hydroxide solution. The resultant grey solid was collected and then stirred into 10% sodium carbonate, filtered and crystallized from *N,N*-dimethylformamide/water.

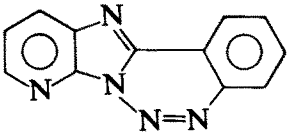
$C_{12}H_{10}N_4$ Calc.: C, 68·61; H, 4·71; N, 26·63%.
Found: C, 68·56; H, 4·79; N, 26·65%.

TABLE 1
Characterization Data for Amines **III**

Compound number	*Position in the B ring*	*X*	*Y*	λ_{max} *in ethanol (nm)*	*log ε*	R_f	*Reference*
1	3	CH	O	296	4·36	0·87	4
2	4	CH	O	326	4·50	0·88	4
3	3	CH	NH	296	4·35	0·74	5
4	4	CH	NH	318	4·54	0·76	5
5	3	N	O	303	4·38	0·79	6
6	4	N	O	347	4·51	0·83	6
7	2	N	NH	306, 360	4·20, 4·08	0·80	7
8	3	N	NH	308	4·40	0·70	—
9	4	N	NH	336	4·38	0·75	8

Diazotization of the amines **III** and coupling to the phenols **IV** were carried out as described in ref. 1. The resulting dyes gave correct elemental analyses and relevant data are shown in Table 2.

All attempts at coupling with the diazonium salt from amine **7** (i.e. the *ortho* isomer) gave the triazine (**VI**), a result similar to that previously reported[9] in similar reactions.



(**VI**)

2.2 Chromatography

R_f values were determined on silica gel 60 F-254 TLC plates, using *n*-butanol:acetic acid: water (4:1:5), BAW as eluent.

2.3 Spectra

The electronic spectra were determined on a Pye–Unicam SP 8-100 spectrophotometer using ethanol, dimethylformamide and ethanolic 0·1M potassium hydroxide as solvents. Relevant data are shown in Tables 1–3.

2.4 Dyeing and fastness determinations

The dyebaths were prepared by dissolving the dyes in a small amount of acetone, adding Disperlene T 333 (Hoechst Italia SpA, Turin) as a dispersing

TABLE 2
Characterization Data of Dyes V

Dye number	*Position in the B ring*	*X*	*Y*	*R*	*Crystallization solvent*	*Melting point*	λ_{max}[a]	*log ε*	R_f
10	4	N	NH	CH_3	DMSO	324–325	466	4·35	0·59
11	4	N	NH	C_3H_7	DMSO	311–312			0·64
12	4	N	NH	C_7H_{15}	DMSO	297–298			0·67
13	4	N	NH	$C_{11}H_{23}$	DMSO	285–286			0·71
14	4	N	NH	$C_{15}H_{31}$	DMSO	253–255			0·74
15	4	N	O	CH_3	Pyridine	258–260	477	4·48	0·58
16	4	N	O	C_3H_7	DMSO–dioxane	268–269			0·63
17	4	N	O	C_7H_{15}	DMSO	258–259			0·68
18	4	N	O	$C_{11}H_{23}$	DMSO	247–248			0·70
19	4	N	O	$C_{15}H_{31}$	DMSO	223–224			0·73
20	3	N	NH	C_3H_7	DMSO	283–284	419	4·22	0·70
21	3	N	NH	$C_{11}H_{23}$	DMSO	278–279			0·78
22	3	N	O	C_3H_7	DMSO	273–274	437	4·32	0·66
23	3	N	O	$C_{11}H_{23}$	DMSO	243–244			0·71
24	4	CH	NH	C_3H_7	DMSO	289–290	463	4·48	0·75
25	4	CH	NH	$C_{11}H_{23}$	DMSO	265–266			0·80
26	4	CH	O	C_3H_7	DMSO–EtOH	267–268	471	4·51	0·77
27	4	CH	O	$C_{11}H_{23}$	DMSO–EtOH	244–246			0·80
28	3	CH	NH	C_3H_7	DMSO–EtOH	279–280	417	4·36	0·79
29	3	CH	NH	$C_{11}H_{23}$	DMSO–EtOH	267–268			0·82
30	3	CH	O	C_3H_7	DMSO–EtOH	242–244	438	4·31	0·80
31	3	CH	O	$C_{11}H_{23}$	DMSO–EtOH	193–194			0·83

[a] One value reported, since the value for all dyes is the same, irrespective of chain length.

agent (1:1 with respect to the dye) and gently removing the solvent. Distilled water was added to give the final required volume.

Dyeings on polyamide-6 (Snia Viscosa) were carried out on a Linitest apparatus to 2% depth and at a liquor ratio of 40:1. The previously wetted patterns were introduced into the dye dispersion at 60°C and the temperature raised to boiling over 30 min and maintained for 45 min. The dyed fibre was then removed, rinsed and dried in hot air.

The fastness was assessed by standard procedures.[10] Lightfastness was determined on a Xenotest 150.

2.5 Colour measurements

The colour parameters of the dyed fabrics were determined on a Cary 210 spectrophotometer equipped with integrating sphere and connected to an Apple II computer, using the D65 source and barium sulphate as standard blank.

3 RESULTS AND DISCUSSION

3.1 Melting points and chromatographic data

From the data in Table 1 the following general effects can be noted.

(i) R_f values decrease in the order *ortho* isomer > *para* isomer > *meta* isomer.
(ii) The pyrido and imidazole derivatives have lower R_f values than the benzo and oxazole derivatives.

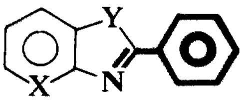
The data in Table 2 show the following general effects.

(1) On increasing the number of methylene groups in the alkyl chain, the melting point decreases, whereas the R_f value increases.
(2) The *meta* isomers have lower melting points than the *para* isomers but they have higher R_f values.
(3) The pyrido derivatives have higher melting points but lower R_f values than the benzo analogues.
(4) The imidazole series have higher values of both melting point and R_f compared with the oxazole derivatives.

3.2 Electronic absorption spectra

Some data on the electronic spectra of aminophenyl-X-azoles has been previously reported[6] and the additional results in Table 1 enable further comparisons to be made. Figure 1 shows examples of typical spectra. Three principal effects are apparent in the long-wavelength band of the benzylideneimino chromogen represented by structure **VII**, namely:

(1) The *para* isomers absorb at wavelengths 22 nm (cf. dyes **3** and **4**) to 44 nm (cf. dyes **5** and **6**) longer than the corresponding *meta* isomers.
(2) The presence of the pyridine ring results in a bathochromic shift with respect to the carbocyclic analogues and the shift is more pronounced for the *para* isomers (18 to 21 nm, comparing dyes **4**/**9** and **2**/**6** respectively) than for the *meta* isomers (7 to 12 nm, comparing dyes **1**/**5** and **3**/**8** respectively). This can be attributed to the participation of the pyridine nitrogen atom to the conjugation of the main chromogen.
(3) Comparing the oxazole and imidazole derivatives, much lower differences are apparent.



(VII)

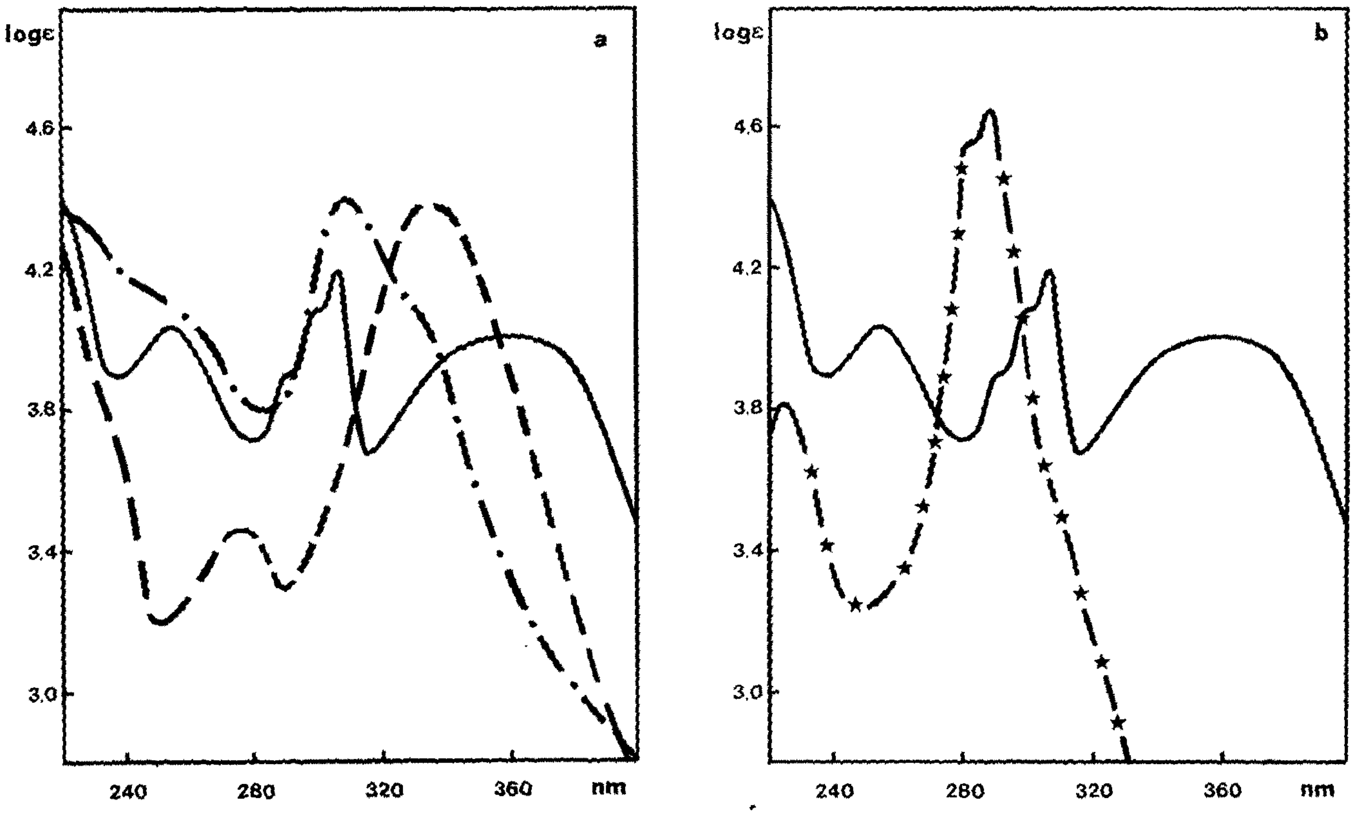


Fig. 1. Electronic absorption spectra. (a) ——, Compound 7; —·—, compound 8; — — —, compound 9. (b) ——, Compound 7; —★— cyclic compound of formula VI.

TABLE 3
Spectral Data of Dyes V

Dye number[a]	*λ_{max} in 95% EtOH*[b]	*λ_{max}(nm) in DMF*	*log ε*	*λ_{max}(nm) in 0·1 M-KOH–95% EtOH*	*log ε*	*$\Delta\lambda_{max}$ (nm)*[c]
10–14	410	466	4·35	479	4·64	69
15–19	404	477	4·48	505	4·51	101
20, 21	379	419	4·22	454	4·34	75
22, 23	382	437	4·32	464	4·48	82
24, 25	406	463	4·48	479	4·62	73
26, 27	404	471	4·51	500	4·45	96
28, 29	377	417	4·36	453	4·45	76
30, 31	378	438	4·31	466	4·48	88

[a] Structure given in Table 2.
[b] Due to the low solubility in 95% EtOH, only qualitative data are reported.
[c] $\Delta\lambda_{max} = \lambda_{max}$ in 0·1M KOH–95% EtOH $- \lambda_{max}$ in 95% EtOH.

As previously observed for the azole analogue,[6] the *ortho* isomer **7** shows an additional band in the range 300–320 nm which could be due to the appearance of benzenoid bands connected to the formation of N_{azole}---H—N hydrogen bonds.[11,12] In Fig. 1b the spectra of amine **7** and of the cyclic compound (VI) are compared.The marked difference in the spectral patterns shows the difference in the chromophoric system, which changes from a donor–acceptor system with charge-transfer character for amine **7** to a system characteristic of polycondensed heterocyclic compounds.

Table 3 summarizes spectral data for the dyes, recorded in ethanol, dimethylformamide and ethanolic 0·1M potassium hydroxide. Sets of five or two dyes were assembled (see Table 2), these being indicative of the differences imparted by chains of different length, within experimental error. The following conclusions can be drawn.

(1) Irrespective of the solvent, the *para* isomers absorb at longer wavelength (22 to 47 nm) than corresponding *meta* isomers.
(2) The solvents exert a bathochromic effect following the order ethanol < dimethylformamide < KOH–ethanol.
(3) Because of the enhanced electron-releasing power of the phenoxide ion in donor–acceptor substituted azobenzenes, the shifts towards longer wavelengths on changing from ethanol to KOH–ethanol is very marked (69 to 101 nm) and is more apparent with the oxazole derivatives than the imidazole analogues, the former heterocyclic system being a more effective electron-withdrawer.

3.3 Dyeing properties

The dyes were found to be suitable as disperse dyes for the coloration of polyamide-6 fabrics. Exhaustion of the dye liquors, levelling and colour yield (compared with commercial dyes applied under similar conditions) were satisfactory. A slight tendency to exhibit phototropic changes was, however, observed for most dyes in the series.

Fastness data are reported in Tables 4 and 5. Details are not given for the fastnesses to tetrachloroethylene, to rubbing (dry and wet) and to spotting with acetic acid since the fastness of the dyes in these tests was generally excellent, almost all dyes having maximum fastness.

As previously noted for an analogous series of azo dyes,[1] chain lengthening is associated with an increase in fastness to wet treatments such as washing (at 40, 60 and 95°C), perspiration (acid and basic) and spotting

TABLE 4
Fastness Properties of Dyes V

Dye number[a]	*Washing*[b]									*Perspiration*[b]						*Spotting*[c] *with* *Na_2CO_3*	*Light*
	At 40°C			*At 60°C*			*At 95°C*			*Acid*			*Basic*				
10	5	5	4/5	5	4/5	2/3	2	1	2	5	5	5	5	4/5	4	5	4/5
11	5	5	3/4	5	4/5	1/2	2/3	1	1	5	5	5	5	4/5	4	5	4/5
12	5	5	3/4	5	4/5	1/2	3	2/3	1	5	5	5	5	5	4/5	4	4/5
13	5	5	5	5	5	4/5	4	4/5	1/2	5	5	5	5	5	5	5	4/5
14	5	5	5	5	5	5	4/5	5	2/3	5	5	5	5	5	5	5	4/5
15	4/5	5	4	4	4	2	1/2	4	1/2	5	4/5	3	5	4	2/3	3/4	4
16	5	5	3/4	5	4	1/2	2	1/2	1	5	4/5	3	5	4	3	4	4
17	5	5	3/4	5	4/5	2/3	3	3/4	1/2	5	5	5	5	5	5	2/3	3/4
18	5	5	5	5	5	5	4	4/5	1/2	5	5	5	5	5	5	2	3/4
19	5	5	5	5	5	4/5	4/5	5	3/4	5	5	5	5	5	5	4/5	3/4
20	5	5	4/5	5	4/5	2	3/4	2/3	1/2	5	5	5	5	5	4	4/5	3/4
21	5	5	5	5	5	4/5	4/5	4/5	2	5	5	5	5	5	5	4/5	3/4
22	5	5	5	5	5	4	3	4/5	2/3	5	5	5	5	5	4/5	4/5	1/2
23	5	5	5	5	5	5	3/4	5	2/3	5	5	5	5	5	5	4	2/3
24	5	5	2	5	4	1	3/4	2	1	5	5	4/5	5	4/5	3	4/5	4
25	5	5	3/4	5	4/5	2	4	4/5	1	5	5	5	5	5	5	4/5	3/4
26	5	5	3	5	4	1/2	4/5	2/3	1	5	5	4/5	5	4/5	3/4	3/4	3/4
27	5	5	5	5	5	5	4	5	2	5	5	5	5	5	5	3/4	3/4
28	5	5	3	5	4	1	4/5	4	1	5	5	4/5	5	4/5	3/4	4	2/3
29	5	5	5	5	5	4	4	5	1/2	5	5	5	5	5	5	4/5	2/3
30	5	5	4/5	5	4/5	1/2	4/5	4/5	1	5	5	5	5	5	4	5	3/4
31	5	5	5	5	5	5	5	5	2/3	5	5	5	5	5	5	5	3/4

[a] Structure given in Table 2.

[b] Values in the first column refer to the change of colour; in the second column to the staining of wool or cotton; in the third column to the staining of the same kind of fibre.

[c] The dyed fibres showed a colour change towards red.

with sodium carbonate, whereas no correlation occurs between chain length and lightfastness, this feature being more susceptible to variations in the nature and in the position of the hetaryl moieties.

Some general trends in the fastness to light, to washing and to alkaline spotting were evident, viz. lightfastness was enhanced by the presence of the imidazole and pyrido ring, and by *para* substitution; fastness to washing was highest for dyes containing the oxazole or benzo ring, and by *meta* substitution; and the fastness to alkaline spotting was highest with the imidazole derivatives and by *meta* substitution. Fastness to perspiration is excellent for the whole series with the exception of a few cases (with a minimum score 2–3) randomly distributed. Dyes **14**, **19** and **31**, in particular, had excellent overall properties.

The heterocyclic dyes described in the present paper show, as a rule, better

TABLE 5
Colour of Dyed Fibres

Dye number[a]	*Structure*[b]	*Colour*[c]	L^*	Y	L	a^*	b^*
29	BN*m*	Y	85·66	66·32	81·43	−5·49	79·70
21	PN*m*	Y	86·58	69·17	83·17	−1·67	80·75
31	BO*m*	Y	86·12	68·23	82·60	−0·09	86·00
23	PO*m*	Y	80·70	57·94	76·12	11·38	76·54
13	PN*p*	YO	80·09	56·84	75·39	15·27	87·63
25	BN*p*	YO	75·30	56·33	75·06	22·04	95·45
27	BO*p*	YO	72·89	45·00	72·89	32·21	84·00
18	PO*p*	YO	63·74	40·64	63·74	37·06	77·54

	a	b	λ_D	λ_C	λ_{max} (*nm*)			P (%)
					EtOH	*EtOH* OH^-	*DMF*	
29	−5·22	45·82	574	475	377	453	417	76·8
21	−1·62	46·78	576	477	379	454	419	77·0
31	−0·09	48·08	576	477	378	466	438	81·0
23	11·02	42·93	580	481	382	464	437	78·2
13	14·88	45·23	581	482	410	479	466	85·5
25	21·80	46·51	583	483	406	479	463	89·7
27	31·61	40·79	586	486	404	500	471	88·0
18	36·31	38·09	589	487	404	505	477	86·3

[a] Structures given in Table 2.

[b] B indicates benzo series; P, pyrido series; N, imidazo series; O, oxazo series; *m*, *meta* isomers; *p*, *para* isomers.

[c] Colour on fibre: Y, yellow; YO, yellow–orange.

fastness properties than their non-heterocyclic analogues with the same coupling moiety (i.e. the previously reported alkylamidosalycylic acids).[1]

3.4 Colour assessment

The colour of the dyed fabrics was assessed by tristimulus colorimetry. Typical results are shown in Table 5, which gives the values obtained for dyes having a C_{11} chain length, as illustrative of the general results.

The *meta* isomers have a yellow hue, lower values of λ_D (574–580 nm), of λ_C (475–481 nm) and of percentage purity (76·8–81·0%) than analogous *para* isomers, which are yellow–orange and have higher values of λ_D (581–589 nm), of λ_C (482–487 nm) and of percentage purity (85·5–89·7%). Progressing down Table 5 (i.e. from dye **29** to dye **18**), the values of a^*, a, λ_D, λ_C, λ_{max}(EtOH) and λ_{max}(DMF) increase, whilst values of L^*, L and Y decrease (with minor exceptions). It is of interest to note that, in other colour systems (Cielab, Hunter), the hue of the samples is better described than in the CIE space: variations of λ_D and λ_C lie in a narrow range, whereas a^* and a are widely spread, thus indicating that the overall colour variations are mainly due to redness variations (b^* and b, yellowness changes, are markedly more restrained).

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