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Monoazo Dyes for Polyamide Derived from 2-(4-Alkylamido-2-hydroxyphenyl)benz-X-azoles

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SUMMARY

A series of 51 azo dyes derived from 2-(4-alkylamido-2-hydroxyphenyl)benz-X-azoles was prepared. The dyes were used as disperse dyes for polyamide fibres. Physical, chemical, spectroscopic and technical properties of the dyes are discussed. A 'spectroscopic constant' is introduced to account for the colour of dyes in solution and of dyed fabrics.

1. INTRODUCTION

The use of *p*-aminosalicylic acid (PAS; **I**) as starting material in the synthesis of ballasted monoazo dyes **III** for the disperse dyeing of polyamide has been reported in a previous paper.[1] The 4-alkylamido-2-hydroxybenzoic acids with a modular alkyl chain **II**, used as coupling

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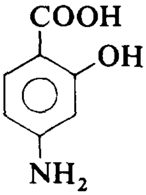
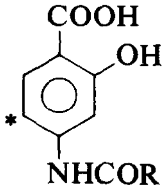
components in the synthesis of dyes **III**, were also investigated for micelle-forming ability.[2] In a recent study[3] we described a series of 2-(4-alkylamido-2-hydroxyphenyl)benz-X-azoles **IV**, similar to compounds **II** when the hetaryl residue replaces the carboxyl group; there is a close resemblance between the electronic effects of the carboxy and 2-benzothiazolyl substituents.[4,5] Compounds **IV** are interesting as complex-forming agents via the hydroxyl and the azole nitrogen and as couplers (at the starred position).



I



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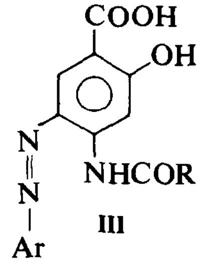
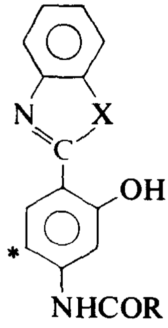
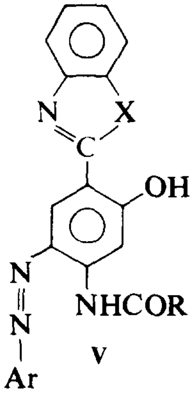


III



IV



V

$R = CH_3$, n-C_3H_7, n-C_7H_{15}, n-$C_{11}H_{23}$, n-$C_{15}H_{31}$; $X = O, S, NH$

The technical properties of dyes **V**, obtained from the couplers **IV** and from the aryldiazonium salts used in the synthesis of dyes **III**, were limited, in particular by the large size of long chain terms. However, the structure **V** is a good model to study changes in properties with respect to the nature of X and of the Ar groups and to the length of the hydrocarbon R chain. On this basis, a series of 51 selected dyes was prepared: usually the length of the hydrophobic chain was maintained constant (C_7), except for one case in which the range C_1–C_{15} was studied.

2. EXPERIMENTAL

2.1. Intermediates and dyes

2-(4-Alkylamido-2-hydroxyphenyl)benz-X-azoles **IV** were prepared as indicated in ref. 3.

The amines were diazotized by the usual procedures; coupling was carried out in 25 % aqueous pyridine. After coupling the mixture was kept overnight and acidified with acetic acid. The dye was collected and crystallized as indicated in Table 1. All the dyes gave correct elemental analyses.

2.2. Chromatography

R_f values were determined on RP-18 F_{254} TLC plates (Merck), using methanol as eluent.

2.3. Spectra

The electronic spectra of the dyes were determined on a Pye Unicam SP 8-100 spectrophotometer in 0·1 N ethanolic potassium hydroxide/dioxane (1/3 by volume).

2.4. Dyeings and fastness determinations

The baths were prepared by mixing an acetone solution of the dye with the dispersing agent (Disperlene T 333, A.I.C. SpA, Turin). After removing the solvent, distilled water was added to the required volume.

Dyeings on polyamide 6·6 were carried out on an Ahiba Texomat apparatus at 2% depth and 40:1 liquor ratio. The previously wetted pattern was entered into the dye dispersion at 60 °C and the temperature raised to boiling in 30 min and maintained for 45 min. The dyed fibre was then removed, rinsed and dried.

Fastness was assessed by standard procedures.[6] Lightfastness was determined on a Xenotest 150. The fastness to sublimation was evaluated after a treatment for 30 s at 150 °C.

2.5. Colour measurements

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

3. RESULTS AND DISCUSSION

3.1. Chemistry, structure and physical properties of the dyes

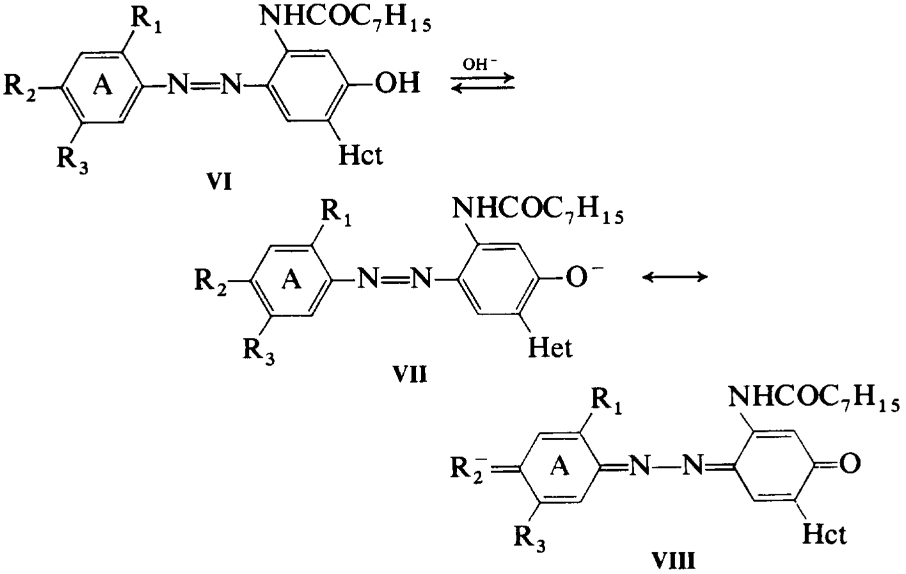
The formulae of dyes **V** and their physical and spectroscopic data are reported in Table 1.

The melting point of the dyes 1–15 depends on the chain length, lower values corresponding to larger sizes in agreement with the effect of bulky substituents on the formation of a crystalline lattice.[1,3] Moreover, the melting points of the benzimidazole derivatives are higher than those of the benzothiazole and benzoxazole counterparts, because of intermolecular hydrogen bonding in benzimidazoles already observed for other benz-X-azole series.[3,7,8] No evident correlation with the nature and the position of substituents in the A-ring is present, apart from the high values shown by the nitro derivatives.

3.2. Electronic absorption spectra

Dyes **III** are reported[1] to show satisfactory linear plots of the absorption maxima in alkaline solution versus Hammett's σ_p constants and the positive slope confirmed that the dyes existed solely in the azo form.[9]

The dyes herein described, which are regarded as resonance hybrids of the two extreme canonical forms **VII** and **VIII**, have the same

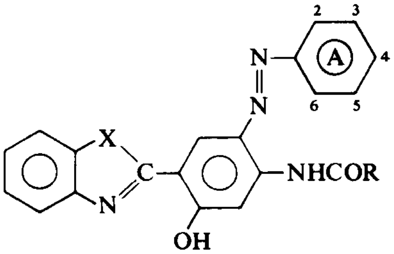


VI

VII

VIII

TABLE 1
Characterization Data on Dyes V



Dye no.	2	4	5	R	X	Crystallization solvent[a]	M.p. (°C)	λ_{max}[b] (nm)	log ε[b]	R_f[c]
1	CH_3	NO_2	—	CH_3	NH	D	>350			0·29
2	CH_3	NO_2	—	n-C_3H_7	NH	B	319–20			0·23
3	CH_3	NO_2	—	n-C_7H_{15}	NH	B	279–80	534	4·64	0·14
4	CH_3	NO_2	—	n-$C_{11}H_{23}$	NH	B	275–6			0·07
5	CH_3	NO_2	—	n-$C_{15}H_{31}$	NH	B	274–5			0·03
6	CH_3	NO_2	—	CH_3	O	B	304–6			0·28
7	CH_3	NO_2	—	n-C_3H_7	O	B	235–6			0·26
8	CH_3	NO_2	—	n-C_7H_{15}	O	C	197–8	518	4·68	0·16
9	CH_3	NO_2	—	n-$C_{11}H_{23}$	O	B	188–9			0·08
10	CH_3	NO_2	—	n-$C_{15}H_{31}$	O	C	182–3			0·04
11	CH_3	NO_2	—	CH_3	S	B	336–7			0·29

(continued)

TABLE 1—*contd.*

Dye no.	*2*	*4*	*5*	*R*	*X*	*Crystallization solvent*[a]	*M.p. (°C)*	λ_{max}[b] *(nm)*	*log* ε[b]	R_f^c
12	CH_3	NO_2	—	*n*-C_3H_7	S	B	314–5			0·24
13	CH_3	NO_2	—	*n*-C_7H_{15}	S	C	227–8	532	4·64	0·15
14	CH_3	NO_2	—	*n*-$C_{11}H_{23}$	S	C	201–2			0·06
15	CH_3	NO_2	—	*n*-$C_{15}H_{31}$	S	B	192–3			0·03
16	—	—	—	*n*-C_7H_{15}	NH	B	239–40	465	4·47	0·36
17	—	CH_3	—	*n*-C_7H_{15}	NH	B	223–4	465	4·44	0·30
18	—	$COCH_3$	—	*n*-C_7H_{15}	NH	B	239–40	504	4·57	0·26
19	—	NO_2	—	*n*-C_7H_{15}	NH	B	314–5	532	4·59	0·42
20	—	OCH_3	—	*n*-C_7H_{15}	NH	B	201–2	464	4·52	0·33
21	—	Cl	—	*n*-C_7H_{15}	NH	A	245–6	475	4·56	0·31
22	—	CN	—	*n*-C_7H_{15}	NH	A	271–2	509	4·62	0·28
23	—	$NHCOCH_3$	—	*n*-C_7H_{15}	NH	B	276–7	475	4·53	0·43
24	—	BZT[d]	—	*n*-C_7H_{15}	NH	B	278–9	507	4·61	0·00
25	Cl	NO_2	—	*n*-C_7H_{15}	NH	B	295–6	548	4·64	0·12
26	OCH_3	NO_2	—	*n*-C_7H_{15}	NH	B	283–4	492	4·58	0·14
27	OCH_3	—	NO_2	*n*-C_7H_{15}	NH	B	291–2	544	4·59	0·17
28	—	—	—	*n*-C_7H_{15}	O	C	197–8	452	4·52	0·17
29	—	CH_3	—	*n*-C_7H_{15}	O	B	171–2	454	4·48	0·11
30	—	$COCH_3$	—	*n*-C_7H_{15}	O	C	154–5	490	4·64	0·23
31	—	NO_2	—	*n*-C_7H_{15}	O	B	221–2	520	4·60	0·20
32	—	OCH_3	—	*n*-C_7H_{15}	O	B	129–30	460	4·48	0·17
33	—	Cl	—	*n*-C_7H_{15}	O	B	181–2	466	4·54	0·13
34	—	CN	—	*n*-C_7H_{15}	O	B	211–2	492	4·63	0·26

35	—	$NHCOCH_3$	—	n-C_7H_{15}	O	C	189–90	469	4·48	0·24
36	—	BZT[d]	—	n-C_7H_{15}	O	C	216–7	498	4·68	0·00
37	Cl	NO_2	—	n-C_7H_{15}	O	C	193–4	534	4·64	0·10
38	OCH_3	NO_2	—	n-C_7H_{15}	O	C	273–4	488	4·58	0·10
39	OCH_3	—	NO_2	n-C_7H_{15}	O	B	225–6	530	4·64	0·10
40	—	—	—	n-C_7H_{15}	S	A	202–3	467	4·47	0·17
41	—	CH_3	—	n-C_7H_{15}	S	C	208–9	466	4·44	0·12
42	—	$COCH_3$	—	n-C_7H_{15}	S	A	191–2	504	4·56	0·24
43	—	NO_2	—	n-C_7H_{15}	S	B	254–5	535	4·64	0·20
44	—	OCH_3	—	n-C_7H_{15}	S	A	185–6	468	4·50	0·16
45	—	Cl	—	n-C_7H_{15}	S	B	189–90	478	4·55	0·12
46	—	CN	—	n-C_7H_{15}	S	C	267–8	504	4·60	0·26
47	—	$NHCOCH_3$	—	n-C_7H_{15}	S	B	218–9	476	4·56	0·22
48	—	BZT[d]	—	n-C_7H_{15}	S	B	246–7	510	4·68	0·00
49	Cl	NO_2	—	n-C_7H_{15}	S	C	229–30	550	4·69	0·05
50	OCH_3	NO_2	—	n-C_7H_{15}	S	B	256–7	492	4·64	0·11
51	OCH_3	—	NO_2	n-C_7H_{15}	S	C	219–20	544	4·64	0·09

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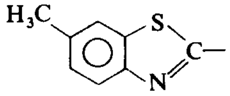
[a] A = ethanol/water, B = dioxane/water, C = acetic acid/water, D = dimethyl sulphoxide/water.

[b] For dyes 1–15 one value for a given X heteroatom is reported. The observed shifts in the positions of the absorption maxima of the dyes, differing only in chain length, are in the range 3–4 nm. This can be considered as the uncertainty in the position of the maxima due to the broad shape of the absorptions.

[c] The dye number and, in parentheses, the R_f on silica gel, eluent BAW (buthanol:acetic acid:water, 4:1:5), are indicated: 4 (0·93), 5 (0·94), 9 (0·94), 10 (0·97), 14 (0·94), 15 (0·98), 24 (0·88), 36 (0·87), 48 (0·87), 49 (0·90), 51 (0·90).

[d] BZT =



(6-methyl-2-benzothiazolyl).

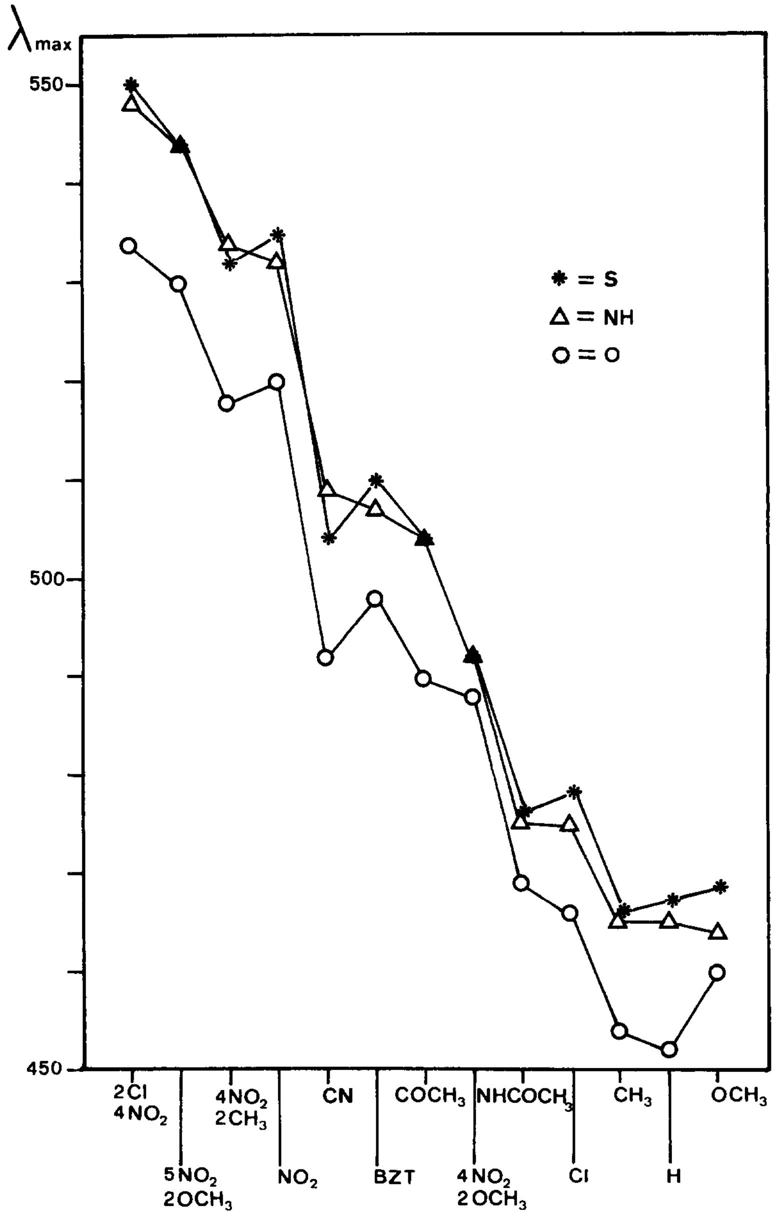


Fig. 1. Absorption maxima of dyes V according to the substitution in the A-ring. BZT, 6-methyl-2-benzothiazolyl.

behaviour. A plot of $\lambda_{\max}$· values versus the substituents of the A-ring (Fig. 1) in the arbitrary sequence of decreasing values of the benzimidazole series shows no clear correlation but indicates the hypsochromic shift of the benzoxazole derivatives. If the monosubstituted dyes only are considered, correlations of $\lambda_{\max}$ versus σ_p (figures not reported) result in regression equations for benzimidazoles (1), benzoxazoles (2) and benzothiazoles (3) with correlation factors which are not satisfactory.

$$X = NH \quad \lambda_{\max} = 44{\cdot}97\sigma_p + 471{\cdot}43 \quad r = 0{\cdot}975 \tag{1}$$

$$X = O \quad \lambda_{\max} = 41{\cdot}54\sigma_p + 462{\cdot}78 \quad r = 0{\cdot}944 \tag{2}$$

$$X = S \quad \lambda_{\max} = 44{\cdot}83\sigma_p + 473{\cdot}60 \quad r = 0{\cdot}969 \tag{3}$$

Since the correlations between reaction parameters, like Hammett's constants, and non-reaction data, like $\lambda_{\max}$ values, are not consistent, we have used a 'spectroscopic constant' of the substituent, defined as the difference between the absorption maximum of a substituted dye and the absorption maximum of the parent unsubstituted dye, arbitrarily choosing a given series (i.e. benzimidazole dyes). The obtained values using

$$\Delta\lambda = \lambda_{R_2 \neq H} - \lambda_{R_2 = H} \quad X = NH \tag{4}$$

eqn (4) are collected in Table 2. The plot of the $\lambda_{\max}$ values of other series versus $\Delta\lambda$ give rise to satisfactory plots (Fig. 2 and Table 2). The improvement in correlation factors is observed not only in the benzoxazole and in the benzothiazole series, but also in the series of dyes **III** (with the CN substituent, previously excluded to improve the Hammett plot[1]). The susceptibilities to the effects of the substituents are essentially not different and this may be explained by considering the low contribution of the hetaryls and of the carboxyl to the conjugation of the main chromogen.

3.3. Dyeing properties

The dyes were tested as disperse in the dyeing of polyamide 6·6 fabrics. Application to other substrates was unsatisfactory.

The best dye–fibre interaction was found with the benzimidazole derivatives: for example, only the benzimidazole compounds gave acceptable dyeings among the dyes with long alkyl chains (C_{11} and C_{15}). This effect can be related to the greater polarity and to the ability of the benzimidazole ring to form hydrogen bonds. It is not surprising that the compounds 24, 36 and 48, because of their large shape and highly hydrophobic character, showed very poor dyeing properties.

Fastness data of the dyeings are reported in Table 3. Fastness to solvents or to acids and lightfastness are not reported, as the individual values are very similar. The fastness to solvents was excellent (level 5), whereas the remaining tests gave poor results (level 2 in the proper scale).

TABLE 2

Spectroscopic Constants ($\Delta\lambda$) and $\lambda_{max}/\Delta\lambda$ Correlations

Substituent	$\Delta\lambda$ (*nm*)
OCH_3	−1
H	0
CH_3	0
Cl	10
$NHCOCH_3$	10
$COCH_3$	39
BZT	42
CN	44
NO_2	67

$$\lambda_{max} = a\Delta\lambda + b$$

Series	*a*	*b*	*r*
Benzothiazoles	0·97	466·99	0·994
Benzoxazoles	0·92	456·31	0·989
Dyes (III)	1·08	452·11	0·992

(The scale for most tests is 1 to 5; the lightfastness scale is 1 to 8. A given score must be related to the proper scale, e.g. a score of 5 is excellent for washing, but good for light.) In typical wet tests, such as washing and perspiration, the change of colour (degradation) was sometimes dramatic, probably owing to the sensitivity of the dyes to the pH of the standard solutions, while the staining on reference fibres was practically nil, indicating the good efficiency of the dye–substrate linkages. The fastness to rubbing, to bases and to sublimation gave, on the whole, acceptable results, depending on the nature of individual dyes.

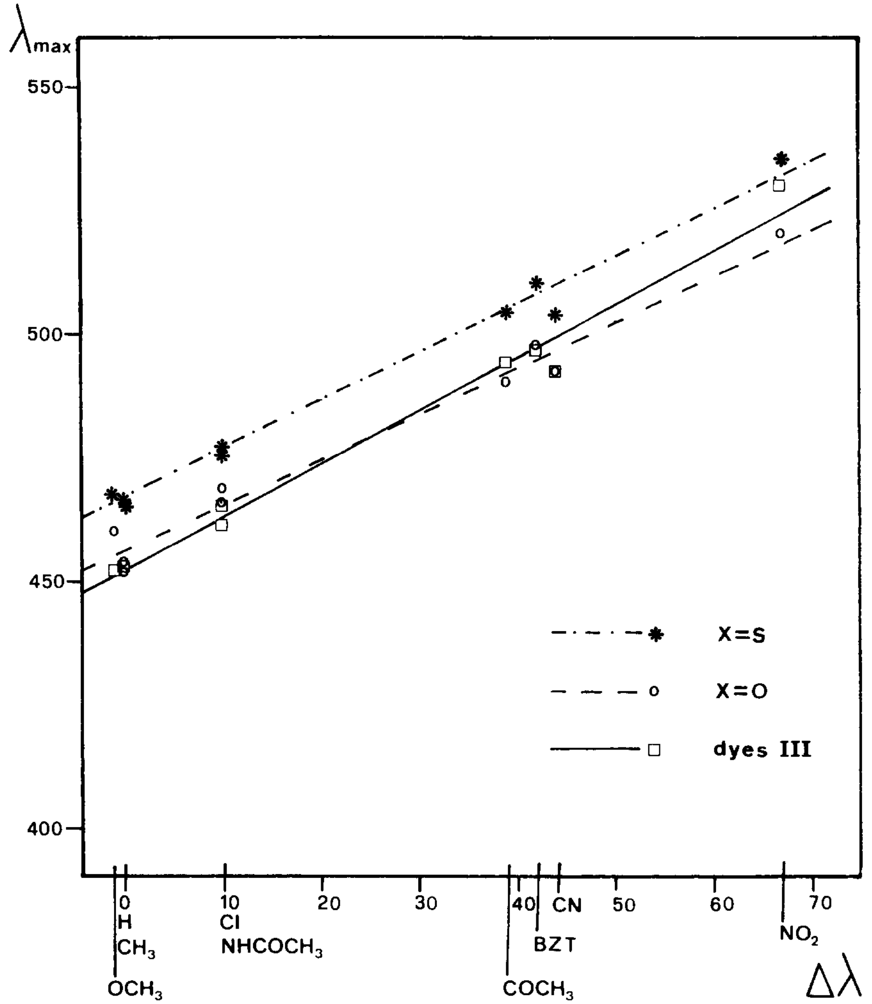


Fig. 2. Plots of absorption maxima of dyes III and V versus spectroscopic constants (Δλ). BZT, 6-methyl-2-benzothiazolyl.

3.4. Colour assessment

An analysis of the colour of dyed fibres was made in terms of tristimulus colorimetry. The related data are reported in Table 4.

The compounds fall into two different luminosity (Y %) ranges; to one (higher luminosity values, $Y = 55$–81 %) belong dyes with donor or moderately acceptor substituents, to the other (lower luminosity values,

TABLE 3
Fastness Properties of Dyes V

Dye[a] no.	*Washing, 60°C[b]*			*Perspiration[b]*			*Rubbing*		*Alkali*	*Sublimation*
							Dry	*Wet*		
1	3–4	5	4–5	1	5	4	4–5	4	4	3–4
2	1–2	5	5	1–2	5	4–5	4	3	4	5
3	2	4–5	4–5	1	5	4–5	3	3	2–3	3–4
4	2–3	5	4–5	1–2	5	4–5	4	4–5	3	4
5	3	5	5	1–2	5	5	4	3–4	3–4	4–5
6	2–3	4	4	1	5	4–5	3–4	3–4	3–4	4–5
7	2–3	5	4–5	1	5	4–5	3–4	4	3–4	4–5
8	4	5	5	1	5	4–5	4	3–4	3–4	4–5
11	3	3–4	4	1	5	4–5	4–5	4–5	3	4–5
12	3–4	5	5	1	5	5	4–5	4–5	4	4–5
13	3–4	5	5	1	5	5	5	4–5	3–4	5
16	4	5	5	2–3	5	5	5	4–5	4	4–5
17	4	5	5	4	5	5	4–5	4	4	5
18	2	5	5	1	5	4–5	5	4–5	1–2	3–4
19	3–4	5	4–5	1	5	5	5	3–4	3	4
20	4	5	5	2–3	5	5	5	5	3–4	4
21	4	5	5	1–2	5	5	5	4–5	3	3–4
22	2–3	5	5	1	5	5	5	5	2	3
23	3	4–5	4–5	1–2	5	4–5	5	5	4	4
25	3	3–4	4–5	1	4–5	4–5	2	3	4	3
26	4	4–5	4–5	1–2	4–5	4–5	4–5	3–4	2–3	3–4
27	4	4–5	4–5	1	5	4–5	4–5	4–5	1–2	4
28	4–5	5	5	4	5	5	5	4–5	4–5	5
29	4	5	5	1–2	5	5	5	4	4–5	5
30	3–4	5	5	1	5	5	5	4–5	3	4–5
31	3–4	5	5	1	5	5	5	4	3–4	4–5
32	4	5	5	3–4	5	5	5	5	4	5
33	4	5	5	2	5	5	5	4–5	4–5	5
34	4	5	4–5	2	5	5	4–5	4–5	3–4	4–5
35	4–5	5	5	2–3	5	4–5	4–5	4–5	4–5	5
37	3–4	5	5	1	5	5	4–5	4–5	4	4–5
38	4	5	5	2	5	5	4–5	4	4	5
39	3	5	5	1	5	4–5	4	4–5	3–4	4–5
40	3–4	5	5	1	5	5	4–5	4–5	2–3	4–5
41	3	5	5	1	5	5	4–5	4–5	1–2	5
42	2–3	4–5	4–5	1	4–5	4–5	5	4–5	2–3	5
43	4	5	5	1–2	5	5	5	4–5	5	4–5
44	3	5	5	1	5	5	4–5	4	2	5
45	4–5	5	5	1–2	5	5	5	4–5	2–3	4–5
46	4	5	5	1–2	5	5	5	5	4	5
47	3	4–5	4–5	1	5	4–5	5	4–5	3–4	4–5
49	3–4	5	5	1–2	5	5	2–3	4–5	4–5	4–5
50	3–4	5	5	1	5	5	5	4	3	5
51	4	5	5	1	5	5	5	3–4	3	4–5

[a] Structures given in Table 1.

[b] Values in the first column refer to the change of colour, in the second column to the staining of the same kind of fibre as the specimen, and in the third column to the staining of wool.

TABLE 4
Chromaticity Values of Dyed Fibres

Dye[a] *no.*	x[b]	y[b]	$Y(\%)$[c]	λ_D[d] (*nm*)	λ_c[e] (*nm*)	$P(\%)$[f]
1	0·51	0·37	28·90	—	504	23·81
2	0·50	0·38	44·62	647	503	21·05
3	0·53	0·38	23·07	608	499	40·91
4	0·51	0·38	32·04	616	501	27·45
5	0·49	0·38	41·81	—	505	16·53
6	0·53	0·39	35·86	600	497	47·37
7	0·54	0·38	39·00	605	499	47·62
8	0·53	0·37	29·94	620	501	35·18
11	0·49	0·36	16·44	—	514	24·07
12	0·46	0·35	19·32	—	560	23·30
13	0·47	0·37	25·52	—	530	17·31
16	0·51	0·44	74·76	585	485	65·22
17	0·49	0·43	76·03	585	485	47·83
18	0·59	0·37	34·74	604	498	75·00
19	0·53	0·36	22·25	—	504	30·95
20	0·53	0·44	71·41	586	487	79·17
21	0·54	0·43	65·74	588	490	80·00
22	0·56	0·38	41·23	602	498	61·54
23	0·55	0·43	58·13	589	491	84·62
25	0·50	0·36	9·45	—	510	26·67
26	0·56	0·40	54·91	595	495	73·44
27	0·51	0·37	19·99	—	504	23·81
28	0·47	0·43	75·84	581	472	33·33
29	0·49	0·43	77·65	585	485	47·83
30	0·56	0·40	52·56	595	495	73·44
31	0·53	0·38	32·41	608	499	40·91
32	0·50	0·44	78·46	584	483	59·10
33	0·49	0·43	80·91	585	485	47·83
34	0·58	0·38	33·63	600	497	73·68
35	0·52	0·44	68·81	586	487	73·91
37	0·52	0·37	34·36	648	503	27·97
38	0·50	0·42	67·70	588	490	68·00
39	0·54	0·38	35·37	605	499	47·62
40	0·52	0·42	63·57	590	491	58·49
41	0·52	0·42	68·94	590	491	58·49
42	0·56	0·36	26·70	620	502	46·73
43	0·46	0·34	17·60	—	562	34·45
44	0·52	0·43	66·96	588	490	66·67
45	0·54	0·40	59·07	595	495	60·94
46	0·54	0·36	37·60	687	503	33·87
47	0·55	0·41	51·85	593	494	72·41
49	0·44	0·34	8·67	—	570	22·81
50	0·53	0·39	56·11	600	497	47·37
51	0·45	0·37	21·68	—	564	14·29

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[a] Structures given in Table 1.

[b] Chromaticity coordinates.

[c] Luminance factor.

[d] Helmholtz coordinate 'dominant wavelength'.

[e] Helmholtz coordinate 'complementary dominant wavelength'.

[f] Helmholtz coordinate 'purity'.

$Y = 10\text{–}53\,\%$), dyes with typical electron withdrawing constituents. The benzoxazole derivatives exhibit higher values compared with the other heterocyclic counterparts.

The correlation between λ_c values and Hammett's σ_p constants, observed for dyes **III**,[1] holds also for the series **V** (eqns (5)–(7)). If $\Delta\lambda$ values obtained for dyes in solution are used, eqns (8)–(10) can be calculated: their correlation factors show slight but significative improvement.

$$X = \mathrm{NH} \qquad \lambda_c = 11{\cdot}34\sigma_p + 488{\cdot}10 \qquad r = 0{\cdot}958 \tag{5}$$

$$X = \mathrm{O} \qquad \lambda_c = 12{\cdot}48\sigma_p + 483{\cdot}30 \qquad r = 0{\cdot}833 \tag{6}$$

$$X = \mathrm{S} \qquad \lambda_c = 10{\cdot}46\sigma_p + 492{\cdot}66 \qquad r = 0{\cdot}986 \tag{7}$$

$$X = \mathrm{NH} \qquad \lambda_c = 0{\cdot}27\Delta\lambda + 486{\cdot}55 \qquad r = 0{\cdot}985 \tag{8}$$

$$X = \mathrm{O} \qquad \lambda_c = 0{\cdot}30\Delta\lambda + 481{\cdot}45 \qquad r = 0{\cdot}877 \tag{9}$$

$$X = \mathrm{S} \qquad \lambda_c = 0{\cdot}28\Delta\lambda + 491{\cdot}08 \qquad r = 0{\cdot}994 \tag{10}$$

4. CONCLUSIONS

The present work concludes an investigation based on the possibility of obtaining dye intermediates and dyes from *p*-aminosalicylic acid (PAS), a starting material more popular in the pharmaceutical industry. Reported in this present work are coupling components derived by acylation of the amino group with modular chains and the 'replacement' of the carboxyl with hetaryls. The resulting dyes were studied with respect to their physical, chemical, spectroscopic and technical properties. The introduction of a 'spectroscopic constant' enabled satisfactory relationships to be made on the colour of dyes in solution and on fabrics.

Many of the dyes described here and in ref. 1 are under investigation concerning kinetic and thermodynamic aspects of their interaction with fibres, their behaviour in various media including surface-active agents and vescicles, and a chemiometric approach to their technical data.

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