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

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SUMMARY

Data on a series of 65 azo dyes derived from 4-alkylamido-2-hydroxybenzoic acids are reported The dyes are suitable for application to polyamide fibres

Many correlations between the nature of substituents and the physical, spectroscopic or tinctorial properties of dyes were established. Correlations between structure and colour of dyed fabrics were also found

1. INTRODUCTION

The field of dyes containing hydrophobic alkyl chains of modular length has been investigated for many technical purposes. In their classic work, Fierz-David and Kuster[1] studied the change of surface tension due to the change in chain length in azo dyes potentially usable as acid or direct dyes. Acid wool dyes of the 'Carbolan' series have been marketed by ICI,[2] besides the lightfastness inherent to the anthraquinone moiety, these show high fastness to repeated washings due to the presence of a C_{12} unit. The molecular areas and orientation at water surfaces of aromatic azo compounds containing long alkyl chains have been studied by Giles and Neustadter.[3] Many patents claim the use of weighted non-diffusing azo dyes in silver halide emulsions.[4] Several long alkyl chain azo dyes have been proposed for the dyeing of polypropylene fabrics.[5,6] Disazo dyes of this type also have been used to colour gasoline, fuel and diesel oils.[7] The effects of long chains on standard affinity, lightfastness, wetfastness and diffusion rate have been studied by several authors.[8-10]

In this paper a series of disperse monoazo dyes for polyamide fibres is described. Suitable aromatic amines were diazotized and coupled with acyl derivatives of 4-amino-2-hydroxybenzoic acid (**I**) containing alkyl chains in the range C_1–C_{15}. The effects of substituents and chains on chemical, physical and technical properties of the dyes (**III**) were investigated

2 EXPERIMENTAL

2.1. Dyes and intermediates

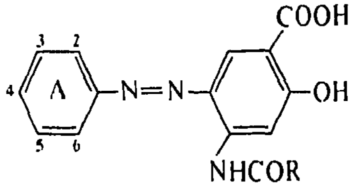
4-Alkylamido-2-hydroxybenzoic acids (**II**) were prepared as indicated in refs 11 and 12 and purified by repeated crystallization from ethanol.

The diazotization of the amines was performed following the usual procedures. Coupling was carried out in alkaline conditions, in water for $R = CH_3$, C_3H_7, in 25% aqueous ethanol for $R = C_7H_{15}$, $C_{11}H_{23}$ and in 50% aqueous ethanol (containing 10% pyridine) for $R = C_{15}H_{31}$. After coupling, the mixture was kept overnight and acidified with acetic acid. The dye was then collected and crystallized as indicated in Table 1. All the dyes gave correct elemental analyses.

2.2. Chromatography

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

TABLE 1
Characterization Data for Dyes **III**



Dye no	Structure 2	4	5	R	Crystallization[a] solvent	M.p (°C)	λ_{max}[b] (nm)	log ε[b]	R_f
1	—	—	—	CH_3	B	244–5			0·83
2	—	—	—	n-C_3H_7	B	227–8			0·84
3	—	—	—	n-C_7H_{15}	A	195–7	368	4·28	0·85
4	—	—	—	n-$C_{11}H_{23}$	A	178–9			0·86
5	—	—	—	n-$C_{15}H_{31}$	A	171–2			0·87
6	—	CH_3	—	CH_3	B	248–9			0·82
7	—	CH_3	—	n-C_3H_7	B	237–8			0·83
8	—	CH_3	—	n-C_7H_{15}	B	207–9	371	4·34	0·84
9	—	CH_3	—	n-$C_{11}H_{23}$	B	191–3			0·85
10	—	CH_3	—	n-$C_{15}H_{31}$	B	178–9			0·86
11	—	$COCH_3$	—	CH_3	B	261–2			0·74
12	—	$COCH_3$	—	n-C_3H_7	B	231–2			0·77
13	—	$COCH_3$	—	n-C_7H_{15}	B	185–7	387	4·34	0·79
14	—	$COCH_3$	—	n-$C_{11}H_{23}$	B	155–7			0·81
15	—	$COCH_3$	—	n-$C_{15}H_{31}$	B	129–30			0·82
16	—	NO_2	—	CH_3	B	283–4			0·75
17	—	NO_2	—	n-C_3H_7	B	268–9			0·76
18	—	NO_2	—	n-C_7H_{15}	A	237–8	396	4·30	0·77

TABLE 1—*contd.*

Dye no	*Structure*				*Crystallization*[a] *solvent*	*M p* (°C)	λ_{max}[b] (*nm*)	*log ε*[b]	R_f
	2	4	5	*R*					
19	—	NO_2	—	n-$C_{11}H_{23}$	A	209–11			0·79
20	—	NO_2	—	n-$C_{15}H_{31}$	A	195–7			0·80
21	—	OCH_3	—	CH_3	B	229–30			0·77
22	—	OCH_3	—	n-C_3H_7	B	219–21			0·78
23	—	OCH_3	—	n-C_7H_{15}	A	200–2	382	4·39	0·80
24	—	OCH_3	—	n-$C_{11}H_{23}$	A	166–7			0·81
25	—	OCH_3	—	n-$C_{15}H_{31}$	A	161–2			0·84
26	—	Cl	—	CH_3	B	250–1			0·82
27	—	Cl	—	n-C_3H_7	B	239–41			0·83
28	—	Cl	—	n-C_7H_{15}	A	221–2	376	4·33	0·85
29	—	Cl	—	n-$C_{11}H_{23}$	A	202–3			0·86
30	—	Cl	—	n-$C_{15}H_{31}$	A	189–91			0·87
31	—	CN	—	CH_3	E	260–2			0·76
32	—	CN	—	n-C_3H_7	A	251–3			0·80
33	—	CN	—	n-C_7H_{15}	A	244–6	404	4·32	0·82
34	—	CN	—	n-$C_{11}H_{23}$	A	241–3			0·84
35	—	CN	—	n-$C_{15}H_{31}$	A	237–9			0·86
36	—	$NHCOCH_3$	—	CH_3	A	261–3			0·75
37	—	$NHCOCH_3$	—	n-C_3H_7	A	246–8			0·76
38	—	$NHCOCH_3$	—	n-C_7H_{15}	A	220–2	390	4·45	0·79
39	—	$NHCOCH_3$	—	n-$C_{11}H_{23}$	A	193–5			0·80
40	—	$NHCOCH_3$	—	n-$C_{15}H_{31}$	E	191–3			0·82
41	—	BZT[c]	—	CH_3	C	288–90			0·77
42	—	BZT	—	n-C_3H_7	C	280–2			0·78

43	—	BZT	—	$n\text{-}C_7H_{15}$	C	256–8	409	4·51	0·80
44	—	BZT	—	$n\text{-}C_{11}H_{23}$	C	237–9			0·81
45	—	BZT	—	$n\text{-}C_{15}H_{31}$	C	227–9			0·83
46	Cl	NO_2	—	CH_3	A	285–7			0·77
47	Cl	NO_2	—	$n\text{-}C_3H_7$	A, D	269–71			0·79
48	Cl	NO_2	—	$n\text{-}C_7H_{15}$	A, D	236–8	422	4·30	0·82
49	Cl	NO_2	—	$n\text{-}C_{11}H_{23}$	A, D	222–4			0·85
50	Cl	NO_2	—	$n\text{-}C_{15}H_{31}$	A	220–2			0·87
51	CH_3	NO_2	—	CH_3	A	279–80			0·77
52	CH_3	NO_2	—	$n\text{-}C_3H_7$	A	276–7			0·79
53	CH_3	NO_2	—	$n\text{-}C_7H_{15}$	A	235–7	416	4·32	0·81
54	CH_3	NO_2	—	$n\text{-}C_{11}H_{23}$	A	228–9			0·83
55	CH_3	NO_2	—	$n\text{-}C_{15}H_{31}$	A	206–8			0·85
56	OCH_3	NO_2	—	CH_3	F	282–3			0·77
57	OCH_3	NO_2	—	$n\text{-}C_3H_7$	A	275–7			0·80
58	OCH_3	NO_2	—	$n\text{-}C_7H_{15}$	A	238–9	433	4·36	0·82
59	OCH_3	NO_2	—	$n\text{-}C_{11}H_{23}$	A	226–7			0·83
60	OCH_3	NO_2	—	$n\text{-}C_{15}H_{11}$	A	206–8			0·85
61	OCH_3	—	NO_2	CH_3	G	287–9			0·67
62	OCH_3	—	NO_2	$n\text{-}C_3H_7$	G	265–7			0·71
63	OCH_3	—	NO_2	$n\text{-}C_7H_{15}$	G	251–3	402	4·30	0·74
64	OCH_3	—	NO_2	$n\text{-}C_{11}H_{23}$	A	213–5			0·75
65	OCH_3	—	NO_2	$n\text{-}C_{15}H_{31}$	A	208–10			0·77

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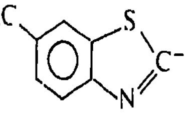
[a] A = ethanol, B = ethanol/water, C = dioxane, D = dioxane/water, E = acetic acid, F = pyridine, G = dimethylformamide/acetone, A, D = first crystallization from ethanol followed by a second from dioxane/water

[b] One value for a given substitution in the A ring, being the same independent of the chain length.

[c] BZT, 6-methyl-2-benzothiazolyl



2.3. Spectra

The electronic spectra of the dyes were determined on a Pye Unicam SP 8-100 spectrophotometer in ethanol (data in Table 1) and in ethanolic 0·1M-potassium hydroxide (data in Fig. 5).

Nuclear magnetic resonance spectra were obtained with a Varian T-60 spectrometer in DMSO-d_6 solution (6%) using TMS as internal standard.

2.4. Dyeings and fastness determinations

The baths were prepared by dissolving the dyes into a small amount of acetone, adding Disperlene T 333 (A.I.C S.p A , Turin) as dispersing agent and gently removing the solvent Distilled water was added to the final required volume.

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

The fastness was assessed by standard procedures.[13] Lightfastness was determined on a Xenotest 150. The fastness to sublimation was evaluated after treatment for 30 s at 150 °C.

2.5. Colour measurements

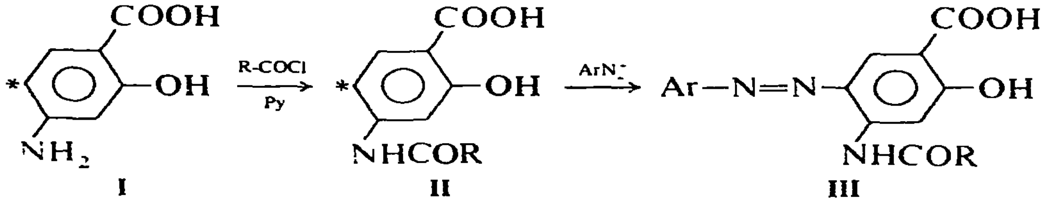
The colour of dyed fabrics was determined on an IBM 7841 mod. 2 colour analyser using the D source and barium sulphate as standard white

3 RESULTS AND DISCUSSION

3.1. Chemistry, structure and physical properties of the dyes

The starting material for the synthesis of dyes was *p*-aminosalicylic acid (**I**), an intermediate easily available at low cost and well known for pharmaceutical purposes. It can be employed not only as a coupling component at the starred position, but also as a diazo component in the synthesis of azo dyes.[14] By reaction with acyl halides (Schotten–Baumann) the amino group may be acylated (R in the range C_1–C_{15}) and the resulting coupling agents (**II**), reacting with the diazonium salts of suitable aromatic amines, give monoazo dyes of general structure **III**. The micellar properties of some compounds **II** have recently been investigated.[15]

In Table 1 the formulae of dyes **III** and their physical and spectroscopic data are reported.



In Figs 1 and 2 the outlined NMR pattern of dyes 26 and 10 are shown, as an example. The related attributions confirm the structure of the dyes.

The melting points of individual dyes are plotted against chain length in Fig. 3. In general these molecules have quite high melting points and this could be a significant property in connection with technical finishing. There can be seen a general trend whereby melting points decrease as the

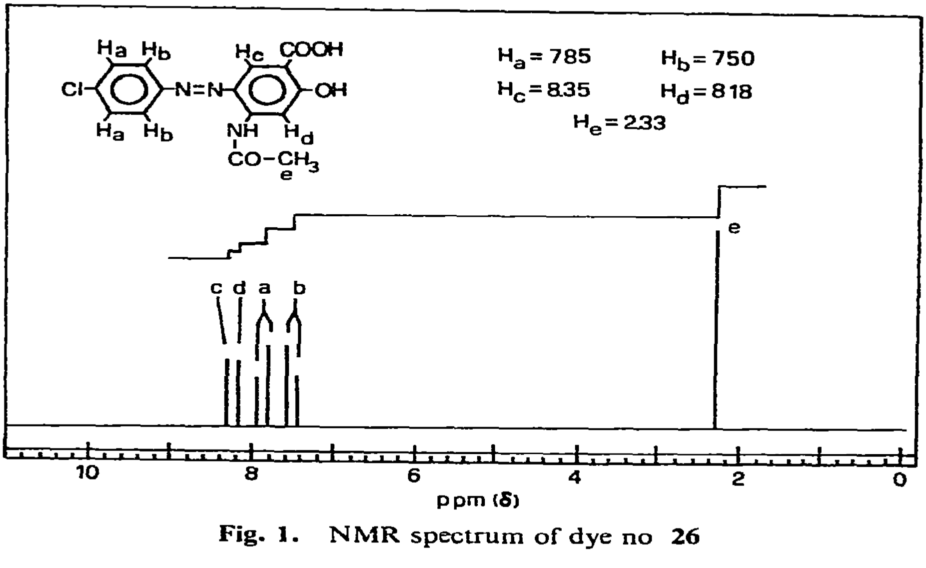


Fig. 1. NMR spectrum of dye no 26

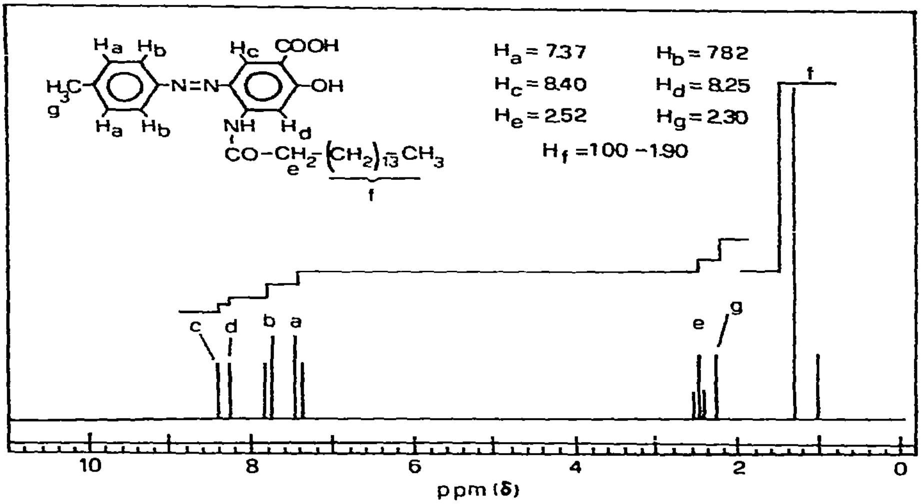


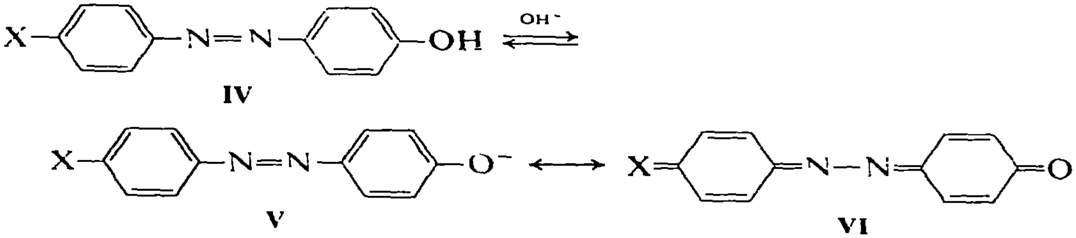
Fig. 2. NMR spectrum of dye no **10**

chain length increases This is not unexpected, taking into consideration the negative effect of weighted hydrophobic structures on accommodation into a crystalline lattice.

An opposite effect is shown if R_f data are considered (Fig. 4). In this case the chain lengthening causes a loss of interaction with the polar substrate. The apparently low R_f values for the 2-OCH_3,5-NO_2 series can be explained in terms of polarity at the A ring moiety. The donor (OCH_3) and acceptor (NO_2) groups are in the *para* position, while in the other nitro bisubstituted series the *meta* position is occupied

3.2. Electronic absorption spectra

In the case of the monosubstituted dyes falling within the general structure of donor–acceptor substituted azobenzenes (**IV**), the λ_{max} of the



IV

V

VI

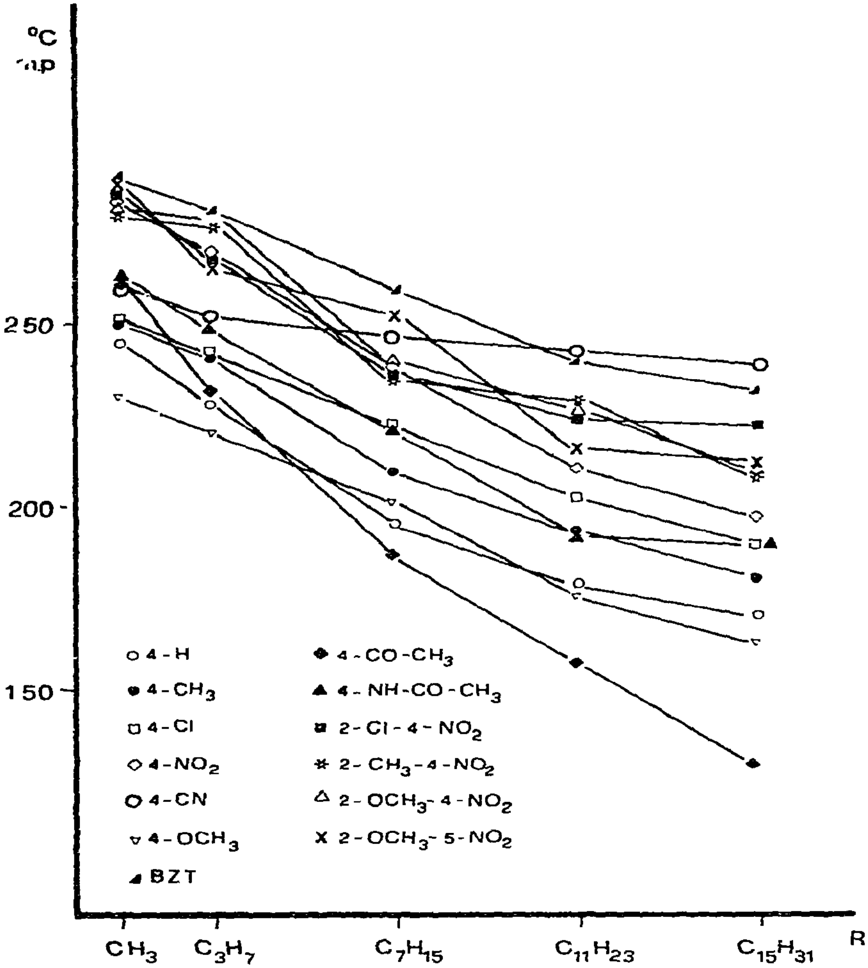


Fig. 3. Correlation between melting points and structure of dyes

long wavelength bands have been plotted against Hammett's σ_p constants (Fig 5) and a good relationship observed. The λ_{max} values were taken in alkaline solution, in which the conjugated system could be regarded as a resonance hybrid of the two extreme canonical forms **V** and **VI**, in order to enhance the slope of the regression. No effect of the chain on the wavelength of absorption was observed. The σ_p value here assigned to the hetaryl substituent, 6-methyl-2-benzothiazolyl, is $+0{\cdot}64$ as previously obtained for 2-benzothiazolyl.[16] The bathochromic shifts associated with

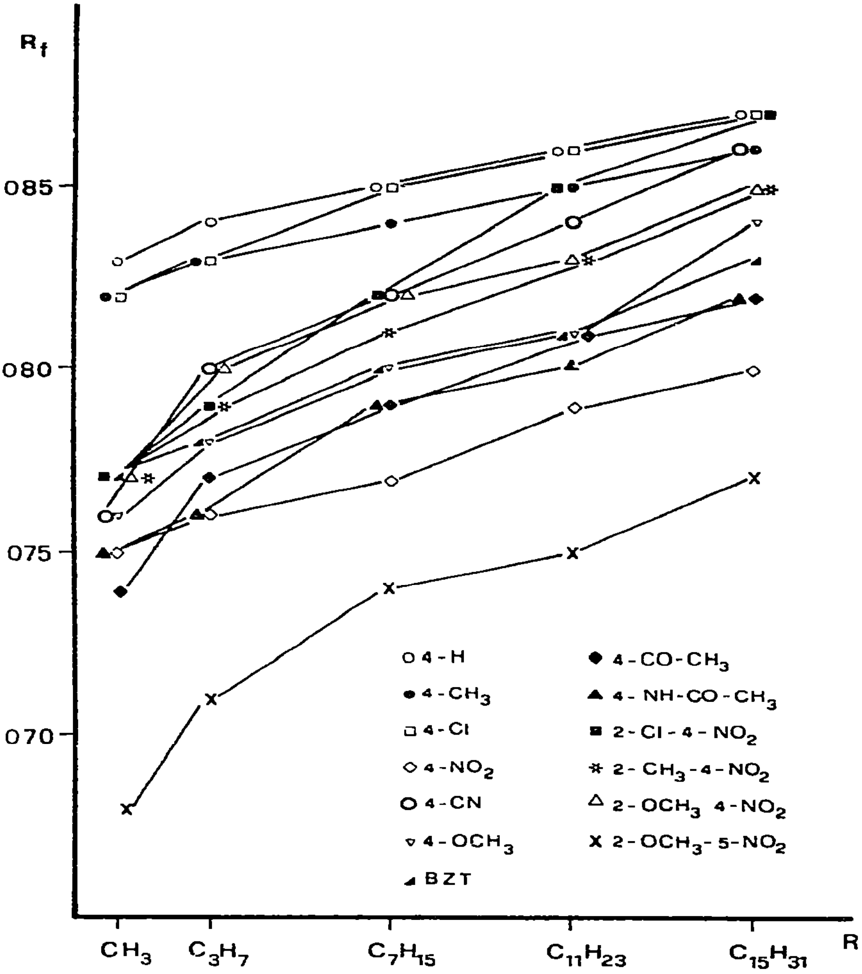


Fig. 4. Correlation between R_f and structure of dyes

the electron withdrawing power of substituents (also observed in neutral media) indicate that these dyes, as with the majority of arylazophenols, exist solely in the azo and not in the hydrazone form.[17]

3.3. Dyeing properties

All the dyes were particularly suitable for use as disperse dyes in the dyeing of polyamide 6 6 fabrics. Attempts at application to polyester were

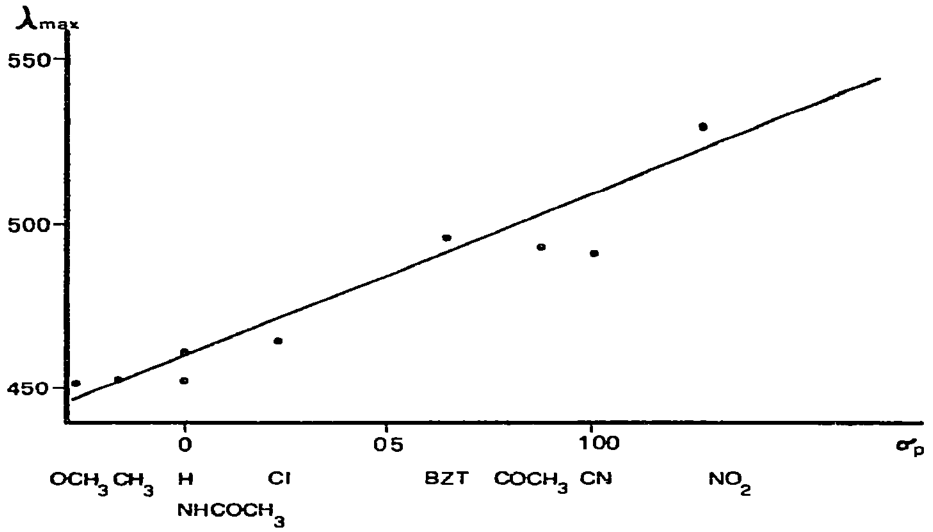


Fig. 5. Correlation between λ_{max} of dyes and Hammett's σ_p constants The equation for the regression is

$$\lambda_{max} = 49\ 33\sigma_p + 460\ 75$$

and $r = 0\ 977$. The CN series is excluded from the regression, if included, $r = 0\ 959$

unsatisfactory, mainly due to the long chain substituents. Exhaustion of dye liquors, levelling and colour yield (compared with commercial dyes in similar conditions) were good. A slight tendency to exhibit phototropic changes was however observed for most dyes in the series.

Fastness data of the dyeings are reported in Table 2. The following comments can be made:

(a) Fastness to solvents and to sublimation are very good or excellent in the whole series (data not reported in Table 2). Fastness to rubbing is very good for monosubstituted classes (except for the hetaryl substituent, BZT) but generally lower for the bisubstituted ones.

(b) While the behaviour of individual dyes in the specific tests has to be evaluated, it was nevertheless interesting to work out some generalizations in view of the large amount of available data. Plotting the total wetfastness (Table 2) versus substitution, the curve in Fig. 6 is obtained. The worst effect is due to 2-Cl,4-NO_2 substitution, whereas the best is due to 2-OCH_3,5-NO_2. No correlation between lightfastness (total light, Table 2) and wetfastness is found. The graphs are helpful if a compromise

TABLE 2

Fastness Properties of Dyes **III**

Dye[a] no	*Wetfastness*						*Total[c] wetfastness*		*Rubbing*		*Lightfastness*	*Total[d] lightfastness*
	Washing at 60°C, W^b			*Perspiration, P^b*								
	Colour change	*Polyamide staining*	*Wool staining*	*Colour change*	*Polyamide staining*	*Wool staining*	$W+P$	$\Sigma(W+P)$	*Dry*	*Wet*		
1	3	3-4	3-4	3-4	2	3	18 5		5	5	2-3	
2	2-3	3-4	3-4	3-4	2	3	17 5		5	5	2-3	
3	3	3-4	4	3-4	3	3-4	20 5	110	5	5	2-3	12 5
4	4	5	4-5	3-4	3-4	4 5	25 0		5	5	2-3	
5	4	5	5	4-5	5	5	28 5		5	5	2-3	
6	4	4-5	4	4	3-4	4	24 0		5	5	2-3	
7	4	3-4	3	3-4	2	2-3	18 5		5	5	2-3	
8	4-5	4-5	4	3-4	3	3-4	23 0	120 5	5	5	2-3	12 5
9	4-5	5	5	4	4	4	26 5		5	5	2-3	
10	4-5	4-5	5	4-5	5	5	28 5		5	5	2-3	
11	4-5	5	5	4	2-3	3-4	24 5		5	4-5	3-4	
12	4	4	4	4	2-3	3	21 5		5	4-5	4	
13	4-5	4-5	4-5	4-5	3-4	4	25 5	128 5	5	4-5	3-4	18 0
14	4-5	5	4-5	4-5	4	4-5	27 0		5	4-5	3-4	
15	5	5	5	5	5	5	30 0		5	5	3-4	
16	3-4	3	3	4	1-2	2-3	17 5		5	5	4-5	
17	3-4	3	3	4	2-3	3	19 0		5	5	4-5	
18	4	1-2	2-3	4	3	3-4	19 0	108	5	5	4-5	20 5
19	4-5	3-4	4	4-5	3-4	4	24 0		5	5	3-4	
20	4	5	5	4-5	5	5	28 5		5	5	3-4	
21	4-5	4-5	4-5	3	1-2	2-3	20 5		5	4-5	2-3	

22	4	4	4–5	3–4	2–3	3–4	22 0		5	4–5	2–3	
23	4	4–5	4	4	3–4	4	24 0	121	5	5	2–3	12·5
24	4–5	4–5	5	4	3–4	4–5	26 0		5	5	2–3	
25	4–5	5	4–5	4–5	5	5	28 5		5	5	2–3	
26	4	3–4	3–4	3–4	2	3–4	20 0		5	5	2–3	
27	4	4	4	3–4	2–3	3–4	21 5		5	5	2–3	
28	4–5	4–5	4–5	4	3	4	24 5	124	5	5	2–3	12·5
29	4–5	5	5	4–5	4–5	5	28 5		5	5	2–3	
30	5	5	5	4–5	5	5	29 5		5	5	2–3	
31	4	4–5	4–5	3–4	1–2	2	20 0		5	5	4–5	
32	4	4–5	4–5	3–4	3	3	22 5		5	5	4–5	
33.	4–5	3–4	4–5	3–4	3	3–4	22 5	119 5	3–4	4–5	4–5	21 5
34	4–5	4–5	5	4	2–3	5	25 5		5	5	4–5	
35	4–5	5	5	4–5	5	5	29 0		5	5	3–4	
36	5	4–5	4–5	3	3	4–5	24 5		5	4	1–2	
37	4–5	4–5	4–5	2	2	4	21 5		5	4–5	1–2	
38	4–5	4	4–5	2–3	1–2	3	20 0	118 5	5	4–5	1–2	8·0
39	4–5	4–5	5	3	2–3	4–5	24 0		5	5	1–2	
40	5	5	5	3–4	5	5	28 5		5	5	2	
41	4	3–4	4	2–3	2–3	3–4	20 0		2	3	4	
42	4	2–3	4	2–3	3	4	20 0		2	2–3	4–5	
43	4–5	4–5	5	3–4	4–5	5	27 0	123 0	4–5	4–5	3	18 0
44	4–5	5	5	3	5	5	27 5		3–4	4–5	3	
45	5	5	5	3–4	5	5	28 5		4–5	4–5	3–4	
46	3–4	2–3	3	1–2	1–2	1–2	13·5		2	3	4–5	
47	3–4	2–3	2–3	1–2	2	3	15 0		3–4	4	4–5	
48	3–4	3–4	4–5	2–3	4	4–5	22 5	100 5	3	4–5	4–5	21 5
49	4	4–5	5	2	3–4	4–5	13 5		2–3	4–5	4–5	
50	4–5	5	5	2–3	4–5	4–5	26 0		3	4–5	3–4	
51	4	4	4–5	3	3	3–4	22 0		2	4	4–5	
52	4	3–4	4	3	2–3	2–3	19·5		3	3	4–5	

TABLE 2—*contd*

Dye[a] *no*	*Wetfastness*						*Total*[c] *wetfastness*		*Rubbing*		*Lightfastness*	*Total*[d] *lightfastness*
	Washing at 60°C, W[b]			*Perspiration, P*[b]			*W + P*	*Σ(W + P)*	*Dry*	*Wet*		
	Colour change	*Polyamide staining*	*Wool staining*	*Colour change*	*Polyamide staining*	*Wool staining*						
53	4–5	4	4	4	3	4	23·5	119·5	4–5	5	4–5	23·0
54	4–5	5	5	3-4	4	5	27·0		4–5	4–5	4–5	
55	4–5	5	5	3	5	5	27·5		5	4–5	5	
56	4–5	4	4–5	3-4	3	4–5	24·0		5	4–5	3–4	
57	4	3-4	3-4	2-3	2	2	17·5		3	3	5	
58	4–5	3-4	3-4	3	3	4	21·5	112·0	3	3–4	4–5	21·5
59	4	4	4–5	2-3	3	3-4	21·5		2-3	4–5	4–5	
60	5	5	4–5	3	5	5	27·5		4–5	4–5	4	
61	5	4–5	4–5	4	3–4	5	26·5		5	4–5	1–2	
62	4–5	4	4–5	3-4	3–4	5	25·0		4–5	4–5	3	
63	5	4–5	5	4	4	5	27·5	137·0	5	5	2	12·0
64	5	5	5	4–5	5	5	29·5		4–5	5	3	
65	5	5	5	3-4	5	5	28·5		5	4	2–3	

[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

[c] Values in the first column are the sums of all wetfastness values (washing at 60 °C + perspiration), the total sum of these values for a given substitution in the A ring appears in the second column

[d] Sum of lightfastness values for a given substitution in the A ring

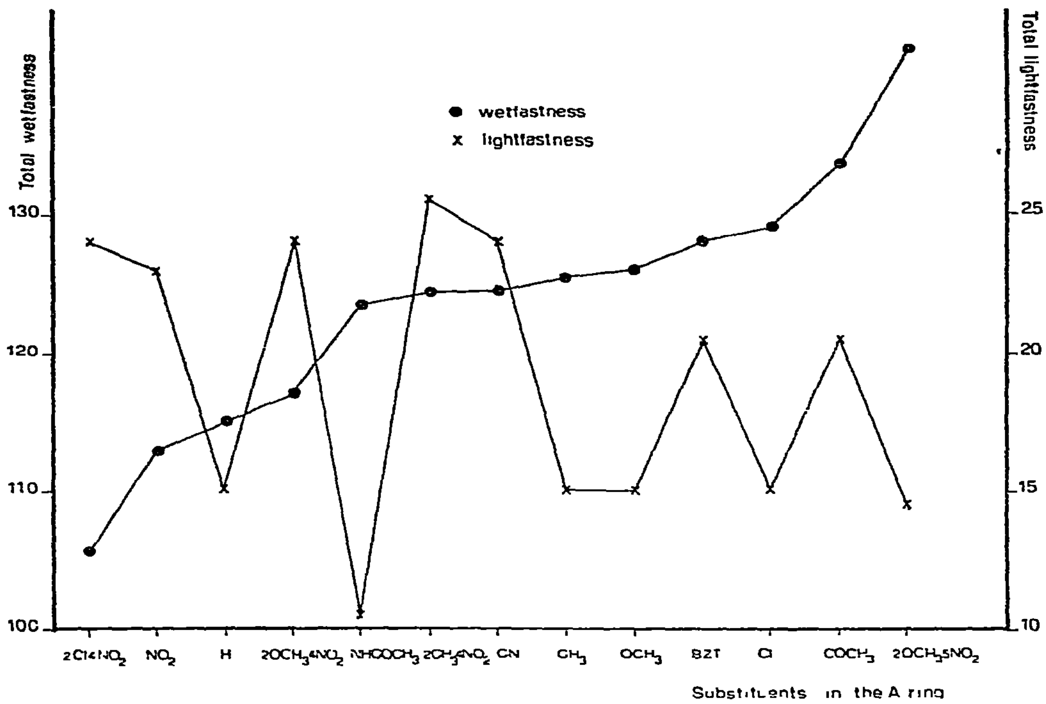


Fig. 6. Wetfastness and lightfastness properties of dyeings according to the substitution

is sought. The 2-OCH_3,4-NO_2 and 4-CN series, besides having the highest lightfastness, display a satisfactory fastness to wet treatments and the 4-BZT and 4-$COCH_3$ series associate high wetfastness with an appreciable fastness to light. Substitution, however, plays an important role and this becomes evident considering the very poor results for the unsubstituted series.

(c) In order to weigh the effect of chain extension on wetfastness (lightfastness is not particularly affected), in Fig. 7 total wetfastness values (Table 2) are plotted against the number of carbon atoms in the chain. The general trend is consistent with an increase of fastness with chain lengthening. A tendency towards a 'levelling out' effect towards longer chain lengths is evidenced by the shape of the area included within the dotted lines (the spread of values changes from 13 ($R = CH_3$) to 4 ($R = C_{15}H_{31}$)). In some cases the transition $C_1 \rightarrow C_3$ is accompanied by a falling-off of fastness.

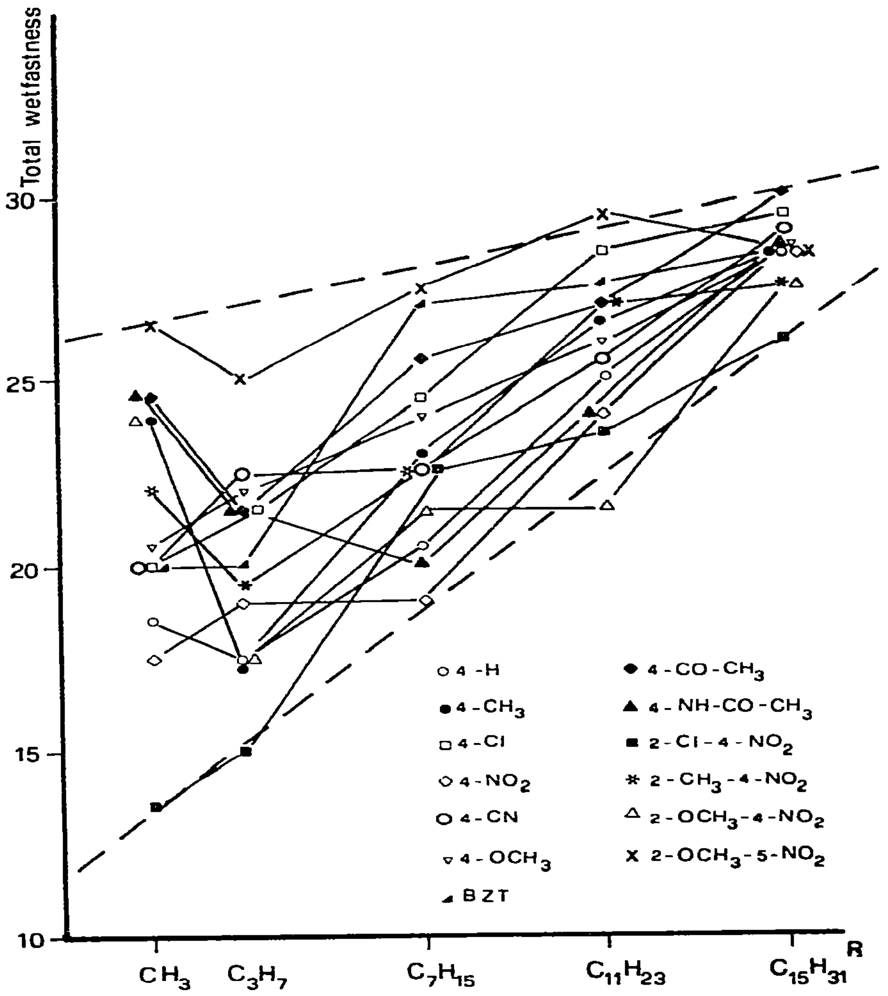


Fig. 7. Effect of chain lengthening on wetfastness

3.4. Colour assessment

The colour of dyed fabrics was assessed by tristimulus colorimetry. The observed colour on the fibre, as well as the chromaticity values, are reported in Table 3. Some general remarks can be made:

(a) For a given substitution, the highest luminance is shown by dyes with R $= C_{15}H_{31}$ whereas the percentage purity with these dyes

TABLE 3
Colour of Dyed Fibres

Dye[a] no	Colour on fibre	Chromaticity coordinates		Luminance factors		Helmholtz coordinates			
						Dominant wavelengths		Purity	
		x	y	Y (%)	$\bar{Y}$ (%)[b]	λ_D (nm)	$\bar{\lambda}_D$[b]	P (%)	$\bar{P}$ (%)[b]
1	Y	0 47	0 47	55 20		579		77 3	
2	Y	0 48	0 47	55 30		580		87 5	
3	Y	0·47	0 47	58 78	59 07	579	579	77 3	80·5
4	Y	0 46	0 47	63 74		578		81 4	
5	Y	0 45	0 47	65 33		577		79 1	
6	Y	0 46	0 47	56 15		578		81 4	
7	Y	0 48	0 48	57·28		579		90 6	
8	Y	0 47	0 48	59 47	60 49	578	578	87·6	84 6
9	Y	0 46	0 48	63 20		577		84·5	
10	Y	0 45	0 47	66 36		577		79 1	
11	Y O	0 52	0 44	29 93		586		90 2	
12	Y O	0 52	0 44	35 00		586		90 2	
13	Y O	0 52	0 45	40 10	40 39	585	585	92 4	89 5
14	Y O	0 52	0 45	44 55		585		92 4	
15	Y.O	0 49	0 45	52 35		583		82 2	
16	R O	0 58	0 38	18 22		596		91 3	
17	R O	0 58	0 38	17 54		596		91·3	
18	R O	0 58	0 38	20 23	20 64	596	595	91 3	90 6
19	R.O	0 58	0 38	19 62		596		91 3	
20	R O	0 55	0 40	27 61		593		88 0	
21	Y	0 47	0 47	51 39		579		77 3	
22	Y	0 47	0 48	54 27		578		87 6	
23	Y	0 47	0 48	60 45	59 45	578	577	87 6	83 2

TABLE 3—*contd*

Dye[a] *no*	*Colour on fibre*	*Chromaticity coordinates*		*Luminance factors*		*Helmholtz coordinates*			
						Dominant wavelengths		*Purity*	
		x	y	Y (%)	$\bar{Y}$ (%)[b]	λ_D (*nm*)	$\bar{\lambda}_D^b$	P (%)	$\bar{P}$ (%)[b]
24	Y	0 46	0 48	63 41		577		84·5	
25	Y	0 44	0 48	67 75		575		79 2	
26	Y	0 49	0 47	48 16		580		90 7	
27	Y	0 48	0 47	53 96		580		87 5	
28	Y	0 49	0 47	56 57	55 82	580	580	90 7	84 7
29	Y	0 47	0 47	60 21		579		77 3	
30	Y	0 47	0 47	60 19		579		77 3	
31	Y O.	0 52	0·44	41 14		585		89 1	
32	Y O	0·50	0·45	43 32		583		86 3	
33	Y O	0 51	0·45	44 92	47 12	583	582	89·3	82·4
34	Y O.	0 51	0 45	44 98		583		89 3	
35	Y O.	0 42	0 43	61 23		578		58 0	
36	Y	0 48	0 48	47 98		578		89 2	
37	Y	0 49	0 47	39 19		580		89 2	
38	Y	0 49	0 47	46 09	49 81	580	578	89 2	86 4
39	Y	0 48	0 48	53·57		578		89 2	
40	G Y	0 44	0 47	62 21		575		75·2	
41	Y O.	0 53	0 44	37 90		586		92 0	
42	Y O	0 53	0 44	39 63		586		92 0	
43	Y.O	0·52	0 44	45·12	45 73	585	584	89 1	81 3

44	Y O.	0·49	0·43	46·96		584		77·8	
45	Y O	0·42	0·42	59·04		579		55·4	
46	R O	0·59	0·36	12·97		602		85·5	
47	R.O	0·59	0·35	10·46		605		85·2	
48	R.O.	0·58	0·36	9·40	11·89	602	601	82·9	83·3
49	R.O.	0·58	0·36	11·81		602		82·9	
50	R.O.	0·55	0·38	14·78		596		80·0	
51	O	0·57	0·39	20·93		595		89·0	
52	O	0·57	0·39	20·11		595		89·0	
53	R O	0·59	0·37	16·39	20·71	600	595	88·9	88·4
54	O	0·57	0·39	20·37		595		89·0	
55	O	0·55	0·40	25·76		592		86·1	
56	R O	0·58	0·38	20·18		597		88·9	
57	R O	0·58	0·37	15·56		600		86·2	
58	R.O.	0·59	0·36	13·58	17·44	602	599	86·1	86·0
59	R O.	0·59	0·36	14·91		602		86·1	
60	O	0·55	0·39	22·95		594		82·9	
61	Y	0·47	0·48	59·91		578		86·8	
62	Y	0·48	0·48	59·82		578		89·2	
63	Y	0·48	0·47	56·47	59·21	579	578	86·4	81·0
64	Y	0·47	0·47	56·39		578		83·5	
65	G.Y.	0·41	0·44	63·46		575		58·9	

[a] Structures given in Table 1

[b] Mean values for a given substitution in the A ring

Abbreviations: Y, *yellow*; Y O, yellow-orange, R O, red-orange, G Y, green-yellow

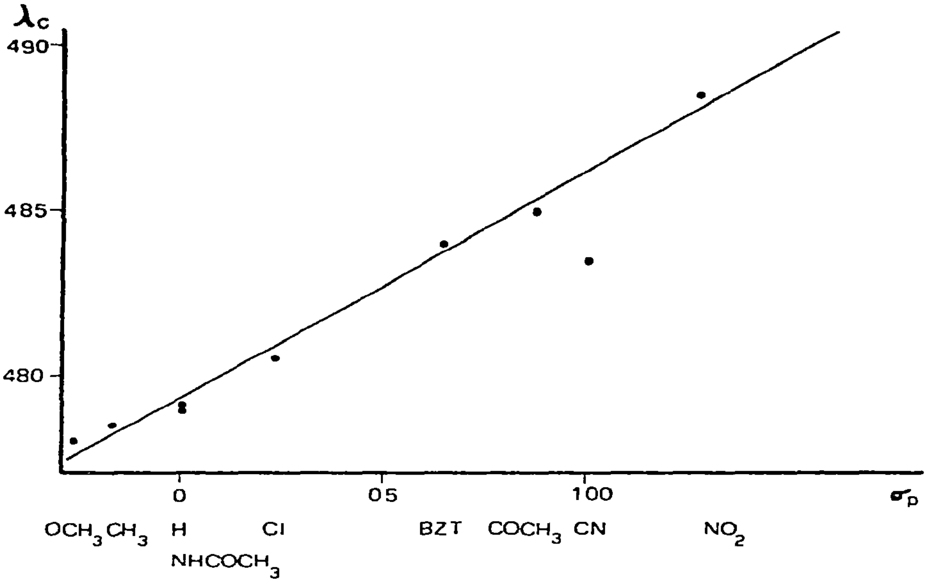


Fig. 8. Correlation between λ_C of dyed fabrics and Hammett's σ_p constants The equation for the regression is

$$\lambda_C = 6\ 92\sigma_p + 479\ 34$$

and $r = 0\ 994$ The CN series is excluded from the regression, if included, $r = 0\ 967$

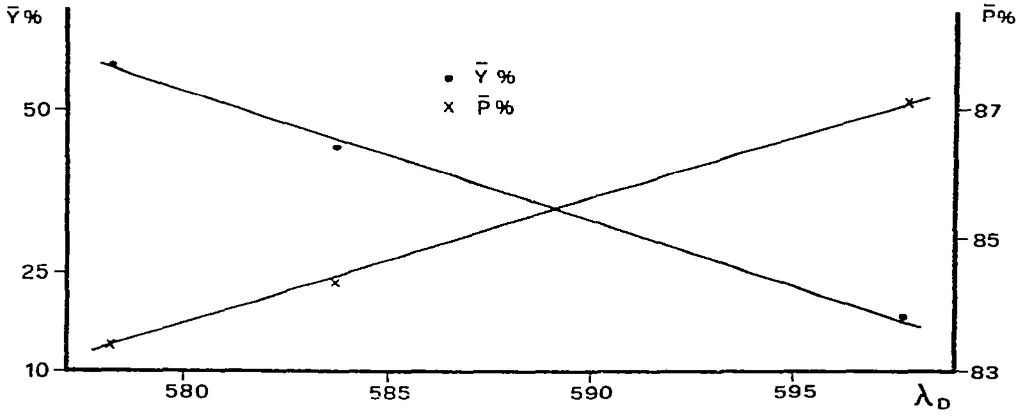


Fig. 9. General correlation between λ_D, $\bar{Y}$ and $\bar{P}$

has the lowest or low values. This behaviour could be due to the dyeing method which employs a fixed depth of shade (2 % based on the weight of fibre) with no allowance for the effect of molecular weight on the consequent molar concentration. Aggregation in the absorbed state provides another possible explanation of lower percentage purity with dyes carrying $C_{15}H_{31}$ side chains.

(b) Figure 8 shows the linear correlation between λ_c values and Hammett's σ_p constants of substituents. This correlation is not unexpected if two facts are taken into consideration: the previously reported plot of the absorption maxima of dyes in solution against Hammett constants and the general connection between λ_c values and the absorbed portion of the incident radiation.

(c) Collecting the dyes into three groups according to the hue of the dyeings (yellow $\bar{\lambda}_D$ 578, yellow–orange $\bar{\lambda}_D$ 584, red–orange $\bar{\lambda}_D$ 598) a general correlation between $\bar{\lambda}_D$, $\bar{Y}$ and $\bar{P}$ is found. The results in a typical group are shown in Fig. 9 which shows that, as shade becomes deeper the higher is the purity percentage and the lower the luminance

4. CONCLUSIONS

The versatility of 4-amino-2-hydroxybenzoic acid (PAS) has been exploited in the synthesis of variously substituted monoazo disperse dyes. The substitution has involved traditional (and hetaryl) substituents and hydrophobic chains of modular length. The dyes gave good dyeings on polyamide 6.6 fabrics and their fastness is sufficient, in many cases, for practical applications.

Owing to the large amount of available data, many interesting correlations have been found These correlations involved on one hand the nature and the position of substituents and the length of hydrophobic chains and, on the other, physical (melting points and R_f values), spectroscopic (electronic absorption maxima), technical (fastness data) and colour (dominant wavelength, complementary dominant wavelength, luminance and purity) properties

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