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Disperse and Cationic Dyes from Aminophenyl-X-Azolo-Pyridines

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ABSTRACT

A series of monoazo dyes was obtained by coupling diazotized aminophenyl-X-azolo-pyridines to N,N-*diethylaniline. The dyes showed a great versatility towards different substrates such as polyamide, polyester, cellulose acetate and, after quaternization, polyacrylonitrile. In addition to the evaluation of parameters such as physical and spectroscopic constants, fastnesses on dyed fabrics, colour assessment and their correlation with structure, the dyes were also used in investigating the reactivity of the hetaryls.* ^{1}*H NMR was used to clarify the structure of the cationic dyes which, in the case of the imidazo-[4,5-c] isomers, proved to be imidazolium salts rather than the pyridinium salts previously observed for dyes containing an X-azolopyridine moiety.*

1 INTRODUCTION

Aminophenyl-X-azoles are well-known intermediates for the synthesis of heterocyclic dyes. The 'benzo' derivatives have been used for some time and their 'pyrido' analogues have recently been investigated by us with respect to their colouristic properties. Some derivatives of this type, mainly *ortho* isomers, have received attention within the pharmaceutical industry. The presence of a pyridine ring allows a wider application of the dyes which, by quaternization, are converted from disperse to cationic colourants.[1,2] This

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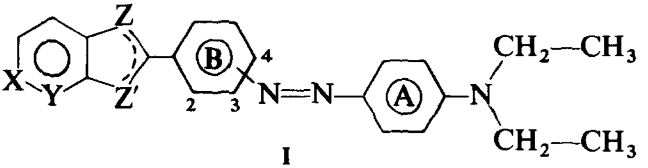
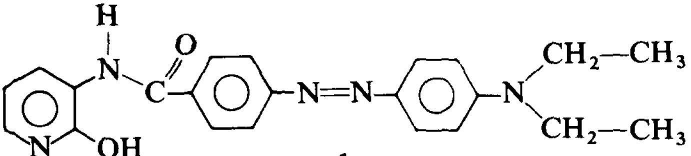
paper deals with the synthesis of dyes having the general formula **I**:



I

$X = CH, N, NH$
$Y = CH, N, {}^{+}N—CH_3$
$Z = N, NH$
$Z' = O, S, N, {}^{+}N—CH_3$

The synthesis of the intermediates and their physico-chemical and spectroscopic characterization are described and we have obtained some unusual results in the oxazole series due to the aptitude of the pentatomic ring to undergo cleavage. In this context, the ring 'opened' dyes **1**[3] and **2**[4] were prepared and shown to be suitable probes for checking the reactivity of oxazolopyridines.



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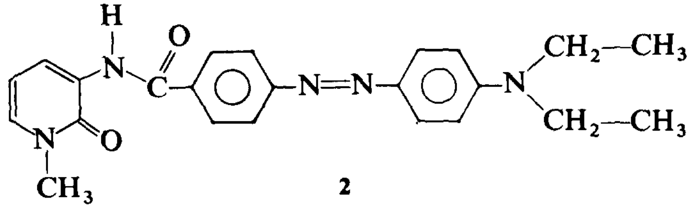

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2 EXPERIMENTAL

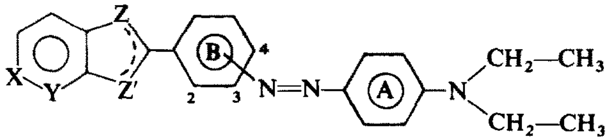
2.1 Dyes and intermediates

Amines used for the synthesis of dyes were prepared as described in Refs 3 and 4. The formulae of dyes **I** are depicted in Table 1.

Dyes **3** and **4** were prepared by diazotization of amines with hydrochloric acid–isoamyl nitrite in ethanol as described in Ref. 3. Dye **1** was obtained by preparing the amine hydrochloride at high temperature before the diazotization, as indicated in Ref. 3. Dye **2** was prepared by refluxing dye **9** in concentrated hydrochloric acid, as reported in Ref. 4. Dye **5** was prepared by addition of concentrated hydrochloric acid (0·23 ml) and isoamyl nitrite (0·68 ml, 5×10^{-3} mol) to a solution of 0·57 g of the corresponding amine ($2{\cdot}5 \times 10^{-3}$ mol) in ethanol (15 ml) at 0°C with stirring. The solution of the

TABLE 1

Characterization Data of Dyes I



Dye no.	*Position in the B ring*	*X*	*Y*[a]	*Z*	*Z′*[a]	*Crystallization solvent*[b]	*Melting point (°C)*	λ_{max} *(nm)*	log ε	R_f
3	4	CH	N	N	O	A	195–197	479	4·64	0·91
4	3	CH	N	N	O	A	163–165	440	4·48	0·93
5	4	CH	N	N	S	B	206–208	484	4·60	0·94
6	3	CH	N	N	S	B	158–159	445	4·51	0·95
7	4	N	CH	NH	N	B	294–295	474	4·58	0·59
8	3	N	CH	NH	N	B	162–163	440	4·47	0·63
9	4	CH	$^+N—CH_3$	N	O	C	198–200	481	4·38	0·33
10	3	CH	$^+N—CH_3$	N	O	C	185–186	445	4·28	0·34
11	4	CH	$^+N—CH_3$	N	S	C	205–206	503	4·48	0·33
12	3	CH	$^+N—CH_3$	N	S	C	162–165	456	4·39	0·33
13	4	NH	CH	N	$^+N—CH_3$	C	278–281	464	4·72	0·35
14	3	NH	CH	N	$^+N—CH_3$	C	250–253	425	4·62	0·37

[a] The counterion of dyes **9**–**14** is iodide.

[b] A = methanol–water; B = ethanol–water; C = *tert*-butyl alcohol–ligroin.

diazonium salt thus obtained was added to *N*,*N*-diethylaniline (0·38 g, 2·5 × 10^{-3} mol) dissolved in acetic acid (5 ml) at 10–12°C with stirring. After 3 h, a saturated solution of sodium acetate was added and the crude dye was collected and washed with water. Characterization data are given in Table 1.

Dyes **6**–**8** were prepared by treating at 10–12°C a mixture of the corresponding amines (2·5 × 10^{-3} mol; 0·57 g, thiazole; 0·53 g, imidazoles) and concentrated hydrochloric acid (5 ml). A solution of sodium nitrite (0·18 g, 2·5 × 10^{-3} mol) in water (4 ml) was run in at 0°C. The solution of the diazonium salt thus obtained was worked up exactly as for dye **5**. Characterization data are given in Table 1.

Dyes **9**–**14** were prepared by refluxing 1 g of the corresponding disperse dye with a large excess of methyl iodide dissolved in *tert*-butyl alcohol (30 ml) for 20 h. After cooling, the crude cationic dyes were filtered. Characterization data are given in Table 1.

2.2 Chromatography

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

TABLE 2
Dyeing Procedure

Fabric	*Percentages based on the weight of textiles*					*Liquor to goods ratio*	*Entering temperature (°C)*	*Dyeing temperature*[b] *(°C)*	*Time of dyeing (min)*[c]
	Dye	*Sodium sulfate*	*Dispersogen A*	*Acetic acid*	*Lenol O*[a]				
Polyamide 6	0·5	0·25	0·5	—	40	40:1	50	100	45
Polyester	0·5	0·25	0·5	—	40	40:1	60	120	60
Cellulose acetate	1·0	0·5	1·0	—	20	20:1	40	90	90
Polyacrylonitrile	0·25	—	—	3·6	—	20:1	60	92 100 then	15 60

[a] Added as 1% aqueous solution.
[b] After entering the dyebath, the temperature was raised at 1°C/min.
[c] Acrylic fibre was then allowed to cool slowly to 60°C in the dyebath itself.

2.3 Spectra and colour measurements

The electronic spectra were determined on a Pye–Unicam SP 8-100 spectrophotometer using methanol as solvent.

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 D 65 source and barium sulphate as standard blank.

^{1}H NMR spectra were obtained with a Jeol GX 270 spectrometer in DMSO-d_6 solution (2%).

2.4 Dyeing and fastness determinations

Details of dyeing procedures are summarized in Table 2. Dispersogen A and Lenol O were purchased from Hoechst. The fastness was assessed by standard procedures.[5] Lightfastness was determined on a Xenotest 150.

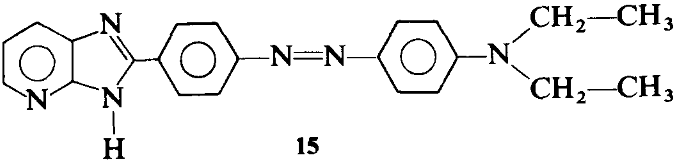
3 RESULTS AND DISCUSSION

3.1 Melting points and chromatographic data

As previously observed for compounds of this series,[2,3] melting points and R_fs (on silica gel) have opposite trends. Indeed, (1) in general, the *meta* isomers have lower melting points than the *para* isomers but they have higher R_f values, and (2) quaternary dyes are higher melting than their disperse counterparts and are more efficiently retained on the polar substrate. Unusual behaviour is shown by the family of dyes **7**, **8**, **13**, **14** (imidazoles, [4,5-c] isomers): the melting points of *para* isomers do not fall within the above-observed trends and the R_f values of the disperse dyes are surprisingly low (0·59, 0·63). We have also observed similar characteristics with the corresponding amines.

3.2 ^{1}H NMR spectra

In cases previously examined, we assigned the structures of *N*-methylpyridinium salts to the quaternary dyes.[1,2] In view of the close analogy of these with the dyes described in this paper, NMR analysis was restricted to selected dyes including the [4,5-c] isomers. Table 3 reports NMR data for dyes **5**, **7**, **8**, **11**, **13**, **14** (formulae in Table 1), **15**, **16** (formulae in the text, described in Ref. 2).



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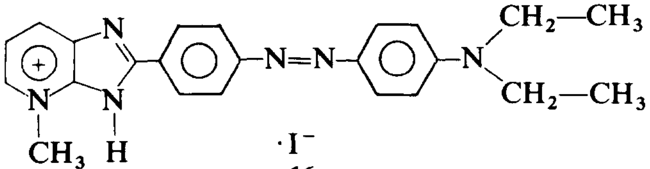

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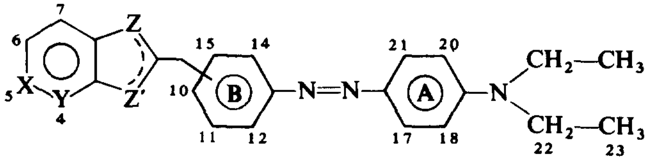
In ambiguous cases the assignments of the chemical shifts were made using selective decoupling techniques and comparison with simpler systems, i.e. dyes containing substituents other than hetaryls.

As a general rule, change of the heteroatom, presence of a formal positive charge and the position of the hetaryls (*meta* or *para* to the azo group) do not influence the chemical shifts of protons in ring A and at the diethylamino group: indeed, values for protons 17, 18, 22, 23 lie respectively in a very narrow range for the whole series of dyes. On the other hand, the hetaryls exert a marked deshielding effect on protons *ortho* to their linkage to the benzene ring and a similar effect is observed, but to a lesser extent, for protons *ortho* to the azo group. As far as the effect of quaternization is concerned, two distinct behaviours are evident. Dyes **11** and **16**, a thiazole and an imidazole derivative with [4,5-b] anellation, show the predictable structure of *N*-methylpyridinium salts, sustained by the marked downfield shift of pyridine protons in agreement with the usual pyridinium salts. On the other hand, a similar structure cannot be proposed for dyes **13** and **14**, which are *para* and *meta* imidazole derivatives with [4,5-c] anellation. In

TABLE 3

^{1}H NMR Spectra of Selected Dyes (chemical shifts, δ, ppm)



Dye no.	***7***	***13***	***8***	***14***	***5***	***11***	***15***	***16***
Hetaryl position	10	10	11	11	10	10	10	10
X =	N	NH	N	NH	CH	CH	CH	CH
Y =	CH	CH	CH	CH	N	$^+$N—CH$_3$	N	$^+$N—CH$_3$
Z =	NH	N	NH	N	N	N	NH	NH
Z' =	N	$^+$N—CH$_3$	N	$^+$N—CH$_3$	S	S	N	N
4	9·17	8·93	9·20	8·95	—	—	—	—
5	—	—	—	—	8·66	9·21	8·43	8·82
6	8·44	8·05	8·46	8·06	7·66	8·29	7·37	7·79
7	7·83	7·75	7·87	7·77	8·50	9·21	8·16	8·68
10	—	—	8·34	8·43	—	—	—	—
11	8·43	8·52	—	—	8·29	8·39	8·42	8·46
12	7·96	7·88	8·66	8·77	7·96	8·01	7·95	8·01
14	7·96	7·88	7·95	7·86	7·96	8·01	7·95	8·01
15	8·43	8·52	7·77	7·64	8·29	8·39	8·42	8·46
17	7·83	7·82	7·86	7·86	7·85	7·85	7·83	7·84
18	6·83	6·83	6·85	6·85	6·86	6·87	6·84	6·85
22	3·48	3·48	3·50	3·49	3·51	3·52	3·49	3·51
23	1·17	1·18	1·18	1·18	1·19	1·19	1·17	1·19
$^+$N—CH$_3$	—	4·24	—	4·25	—	4·64	—	4·51

such dyes the pyridine protons (4, 6, 7) are found systematically upfield to their disperse counterparts (dyes **7** and **8**), clearly indicating that the reaction of methyliodide did not involve the pyridine ring. The presence of a mole of methyliodide is confirmed by elemental analysis and since the protons of the **B** ring are deshielded by the proximity of a positive charge, the structure of *N*-methylimidazolium iodides proves to be the most suitable for dyes **13** and **14**. Furthermore, the chemical shifts of $^+$N—CH$_3$ protons (4·24, 4·25 ppm) do not agree with the usual position of *N*-methylpyridinium salts, such as 4·64 and 4·51 ppm observed for dyes **11** and **16**.

The data currently available seem to indicate a probable quinonoid structure for the pyridine ring arising by tautomeric phenomena, as observed for simpler imidazopyridines.[6,7] Such a structure could also explain the shielding of pyridine protons in dyes **13** and **14** and other apparent irregularities of physical and spectroscopic features (see Section 3.3). Further studies are in progress to clarify these observations.

3.3 Electronic absorption spectra

The positions of the absorption maxima are consistent with the assignment of the dyes as donor–acceptor substituted azobenzenes.

Para isomers show well-defined shifts to longer wavelengths compared with the *meta* isomers, and the change from 'hetaryl' to 'hetarylium' also causes an analogous shift. Again, the [4,5-c] isomers show unexpected behaviour, in that the absorption of the cationic dyes is hypsochromic (10–15 nm) with respect to the corresponding disperse dyes (absorptions in a relatively short wavelength region were also observed for the starting amines). These data further support our interest in investigating other 'c' derivatives.

3.4 Dyeing properties

Versatility is the first technical property of the present dyes to be emphasized. Table 4 gives data on four different substrates, viz. polyester, polyamide-6, cellulose acetate and polyacrylonitrile. Satisfactory colour yields, compared with commercial dyes applied under similar conditions, were obtained at 0·25–1% depths, and excellent levelling and exhaustion of dye liquors were also achieved. Furthermore, as shown in Table 2, the cationic dyes gave excellent uniformity of colouration of acrylic fabrics without the use of a retarding agent.

The use of a star for indicating the maximum score ('5') in Table 4 makes the overall data self evident and the principal deviations from such a rating are immediately apparent. The following generalizations can be drawn:

(a) the substrate greatly influences the fastnesses of each dye,
(b) excellent behaviour is shown in the fastnesses to washing at 40°C, to perspiration, to acetic acid and to sodium carbonate,
(c) washing under more severe conditions mainly affects the dyeings on polyamide and cellulose acetate (although on the latter substrate these tests are not usually performed),
(d) data on polyester are excellent with the exception of lightfastness which, on average, is higher on polyamide and on cellulose acetate.

3.5 Colour assessment

The colour of the dyed fabrics was assessed by tristimulus colorimetry. The results are shown in Table 5. A first systematic effect, predictable by the

TABLE 4
Fastness Properties of Dyes I

Dye no.[a]	Washing[b]															Perspiration[b]						Acid	Alkali	Tetra-chloro-ethylene[b]			Rubbing		Light
	CO1 40°C			CO2 50°C			CO3 60°C			CO4 95°C			CO5 95°C + steel balls			pH 5			pH 8								Dry	Wet	
3	*	*	*	*	4	*	*	3–4	*	3	2–3	4	2–3	2	3	*	*	*	*	*	*	*	*	*	4	*	*	*	3–4
4	*	*	*	*	4–5	*	4–5	4–5	4–5	2	3	4–5	1	2	4–5	*	*	*	*	*	*	*	*	*	4	*	*	*	3–4
5	*	*	*	*	4–5	*	*	4	4	2–3	3	3–4	2	2–3	3	*	*	*	*	*	*	*	*	*	4	*	*	*	2
6	*	*	*	*	4–5	*	*	4–5	4	2–3	2–3	*	2–3	1–2	*	*	*	*	*	*	*	*	*	*	3–4	*	*	*	4
7	*	*	*	*	3–4	*	*	3–4	4–5	3	2–3	2	2	2	2	*	*	*	*	*	*	*	*	*	4–5	*	*	*	4
8	*	*	*	*	4	*	*	3–4	4	2–3	2–3	*	2–3	1–2	*	*	*	*	*	*	*	*	*	*	4–5	*	*	*	4–5
3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2
4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4
5	*	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2
6	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4
7	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	2
8	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2
3	*	*	*	*	*	*	*	4–5	4	2	2	4	1	2	4	*	*	4–5	*	*	*	*	*	*	*	*	3	2–3	3–4
4	*	*	*	*	*	*	*	*	4–5	3	3	*	1	3	*	*	*	*	*	*	*	*	*	*	*	*	3	3	4–5
5	*	*	*	*	*	*	*	*	4–5	2	4	4–5	1	3	4–5	*	*	*	*	*	*	*	*	*	*	*	3	2–3	1–2
6	*	*	*	*	*	*	*	*	4–5	2	4	*	1	3–4	*	*	*	*	*	*	*	*	*	*	*	*	3	3	4
7	*	*	*	*	*	*	*	*	4	2	3	3–4	1	2	3–4	*	*	*	*	*	*	*	*	*	*	*	3	2–3	4–5
8	*	*	*	*	*	*	*	*	4	2–3	3	*	1	2	*	*	4–5	*	*	*	*	*	*	*	*	*	4	4	5
9	*	*	*	*	*	*	*	*	*	*	*	*	3	*	*	*	4–5	*	*	4–5	*	*	*	*	*	*	4–5	4–5	3
10	*	*	*	*	*	*	*	*	*	*	*	*	3–4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	[c]
11	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
12	*	*	*	*	*	*	*	*	*	*	*	*	3–4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	[c]
13	*	*	*	*	*	*	*	*	*	4–5	*	*	3	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	3
14	*	*	*	*	*	*	*	*	*	4	*	*	2–3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2

[a] Structures in Table 1. The first set of data refers to polyamide, the second to polyester, the third to cellulose acetate, and the fourth to polyacrylonitrile.

[b] Values in the first column refer to the change of colour, in the second column to the staining of the proper fibre (indicated in Ref. 5), and in the third column to the staining of the same kind of fibre as the specimen.

[c] Under irradiation the colour of the specimen is deeply impaired.

TABLE 5
Colour of Dyed Fibres

Dye no.[a]	*Luminance factor Y (%)*	*CIELAB co-ordinates*			*Hunter L, a, b co-ordinates*			*Helmoholtz co-ordinates*			*λ*$_{max}$ *(nm)*
		*L**	*a**	*b**	*L*	*a*	*b*	*Dominant wavelength* λ_D *(nm)*	*Complementary dominant wavelength* λ_C *(nm)*	*Purity P (%)*	
3	35·00	65·74	45·91	55·08	59·16	45·18	30·68	594	489	73·73	479
4	65·93	84·86	1·52	69·52	81·20	1·47	42·62	577	478	70·02	440
5	34·59	65·43	41·85	48·78	58·82	40·67	28·46	594	488	67·87	484
6	65·25	84·61	11·28	88·62	80·78	11·12	47·79	579	481	83·60	445
7	42·40	71·15	43·02	72·06	65·12	43·05	37·48	591	487	82·68	474
8	64·29	84·11	11·40	90·51	80·18	11·22	47·94	579	481	84·88	440
3	45·91	73·49	35·28	67·75	67·76	34·99	37·39	588	486	77·93	479
4	71·46	87·71	1·93	76·72	84·53	1·89	46·10	577	478	73·92	440
5	34·36	65·25	45·92	59·27	58·62	45·08	31·73	594	488	77·42	484
6	66·05	85·02	7·92	85·48	81·27	7·77	47·26	578	480	81·40	445
7	51·71	77·11	29·92	63·94	71·91	29·77	37·68	586	486	72·59	474
8	74·05	88·95	−1·41	66·85	86·05	−1·38	43·20	576	477	65·56	440
3	38·14	68·12	45·73	54·80	61·76	45·47	31·08	594	488	71·15	479
4	64·45	84·20	9·41	83·11	80·28	9·22	46·27	579	480	80·49	440
5	45·88	73·47	30·16	39·78	67·74	29·53	26·83	590	487	52·68	484
6	65·87	84·93	8·38	79·35	81·16	8·22	45·62	579	480	77·64	445
7	34·22	65·14	45·44	71·12	58·50	44·54	34·54	592	488	85·62	474
8	56·75	80·04	21·94	100·64	75·33	21·71	47·43	582	483	91·74	440
9	21·80	53·81	46·22	19·02	46·69	42·97	12·61	619	492	41·31	481
10	55·52	79·34	19·55	51·12	74·51	19·17	33·60	584	484	59·30	445
11	22·99	55·06	40·36	7·07	47·95	37·08	5·25	—	495	28·54	503
12	46·85	74·09	30·29	56·74	68·44	29·75	34·13	587	486	68·47	456
13	22·73	54·79	51·42	27·31	47·68	48·83	17·00	611	491	52·76	464
14	32·47	63·73	46·10	58·10	56·99	44·98	30·83	594	488	77·47	425

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[a] Structures in Table 1. The first set of data refers to polyamide, the second to polyester, the third to cellulose acetate, and the fourth to polyacrylonitrile.

absorption values of the dyes in solution (Table 1) relates to *meta–para* isomerism and in this context

(1) λ_D and λ_C values are higher for the *para* isomers,
(2) this trend is consistent with a higher contribution of redness (*a* and *a**) and a lower contribution of yellowness (*b* and *b**),
(3) luminous reflectance parameters (Y, L, L^*) are higher for the *meta* isomers.

A second effect relates to the nature of the substrate and here, in particular,

(1) for a given dye λ_D and λ_C values are lower on polyester, higher on polyacrylonitrile and intermediate on polyamide and cellulose acetate,
(2) luminosity (Y, L, L^*) on polyamide, polyester and cellulose acetate are most dissimilar and higher than those on polyacrylonitrile,
(3) attempts to correlate the colour in solution with the colour on fabrics, i.e. λ_D or λ_C vs λ_{max}, gave acceptable results for polyamide (r of linear plot λ_D/λ_{max}0·96, λ_C/λ_{max}0·95), poor for polyester (λ_Ds plot, 0·92; λ_Cs, 0·93) and worthless (r_{max}0·88) for polyacrylonitrile and cellulose acetate.

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