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Pyridyl-substituted Azobenzene Disperse Dyes

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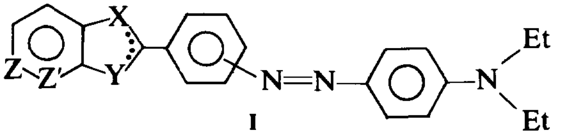
ABSTRACT

N,N-*Disubstituted aminoazobenzene dyes containing a 2-pyridyl substituent were prepared and used for the dyeing, as disperse dyes, of polyamide, polyester and cellulose acetate. The dyeings and the fastness tests gave very satisfactory results. Correlations of physico-chemical constants and spectroscopic parameters, as well as of colour parameters of dyed fabrics, with the structure of the present set of dyes and of previous ones were found. A detailed* ^1H *and* ^{13}C *nuclear magnetic resonance (NMR) analysis of dyes, including correlation techniques, was performed.*

INTRODUCTION

An extensive series of azobenzene disperse dyes containing heterocyclic substituents has been previously described.[1-5]

The general formula I represents this series, where the heterocyclic substituents are X-azolo-pyridines. Some members of the series contained usual organic substituents. The dyes showed, as a whole, great versatility



I

Z = CH, N
Z′ = N, CH
Y = N, NH, O, NCH_3
X = O, S, NH, N, NCH_3

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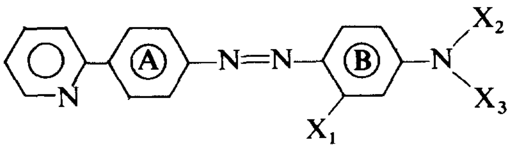
towards different fibres (such as polyamide, polyester and cellulose acetate), excellent dyeing uniformity, dye bath exhaustion and fastness of resultant dyeings.

This paper deals with the synthesis and properties of new heterocyclic azo dyes depicted by the general formula **II**. A simple hetaryl is present, i.e. 2-pyridyl.



$X_1 = H, CH_3, NHCOCH_3$
$X_2 = CH_3, C_2H_5, C_2H_5OH, C_2H_5CN, C_2H_5OCOCH_3$
$X_3 = H, CH_3, C_2H_5, C_2H_5OH, C_2H_5CN, C_2H_5OCOCH_3$

II

EXPERIMENTAL

Dyes and intermediates

Commercial pyridine, 4-nitroaniline, *N*-methylaniline, *N*,*N*-dimethylaniline, *N*,*N*-dimethyl-*m*-toluidine, *N*,*N*-diethylaniline, *N*,*N*-diethyl-*m*-toluidine, *N*-(2-hydroxyethyl)aniline, *N*-ethyl-*N*-(2-hydroxyethyl)aniline, *N*,*N*-bis-(2-hydroxyethyl)aniline and *N*,*N*-bis(2-cyanoethyl)aniline were employed for the synthesis of dyes.

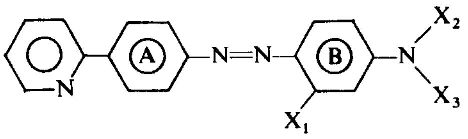
The following intermediates were prepared according to literature procedures: 4-(2-pyridyl)aniline,[6] *N*-methyl,*N*-ethyl-aniline,[7] *m*-diethylaminoacetanilide,[8] *N*,*N*-bis(2-hydroxyethyl)-*m*-toluidine,[9] *N*,*N*-bis(2-cyanoethyl)-*m*-toluidine,[10] *N*-ethyl-*N*-(2-acetoxyethyl)aniline[11] and *N*,*N*-bis-(2-acetoxyethyl)aniline.[12]

The diazotization of the heterocyclic amine and the coupling reaction were carried out as indicated in Ref. 13, where the synthesis of dyes **9**, **10**, **11** and **12** was reported. By crystallization the dyes attained a high level of purity, as indicated by the occurrence of a single spot in chromatographic tests. Characterization data are reported in Table 1.

Chromatography

R_f values were determined on Silica Gel 60 F-254 thin-layer chromatography (TLC) plates (Merck), using butanol–acetic acid–water (BAW) (4:1:5 by volume) as eluant.

TABLE 1
Characterization Data of Dyes



Dye number	Structure			Crystal-lization solvent[a]	M.p. (°C)	λ_{max} (nm)	log ε	R_f
	X_1	X_2	X_3					
1	H	CH_3	CH_3	A	221–224	430	4·52	0·89
2	CH_3	CH_3	CH_3	A	145–146	435	4·52	0·82
3	H	CH_2CH_3	CH_3	B	177–180	438	4·57	0·84
4	H	CH_2CH_3	CH_2CH_3	B	173–175	449	4·52	0·91
5	CH_3	CH_2CH_3	CH_2CH_3	A	115–118	450	4·57	0·90
6	$NHCOCH_3$	CH_2CH_3	CH_2CH_3	A	142–143	477	4·62	0·79
7	H	CH_2CH_2OH	H	A	218–220	418	4·53	0·82
8	H	CH_2CH_2OH	CH_2CH_3	B	150–152	438	4·56	0·84
9	H	CH_2CH_2OH	CH_2CH_2OH	A	168–169	432	4·51	0·81
10	CH_3	CH_2CH_2OH	CH_2CH_2OH	A	131–132	438	4·56	0·81
11	H	CH_2CH_2CN	CH_2CH_2CN	A	201–202	408	4·43	0·81
12	CH_3	CH_2CH_2CN	CH_2CH_2CN	A	152–154	414	4·49	0·84
13	H	$CH_2CH_2OCOCH_3$	CH_2CH_3	B	125–126	431	4·59	0·80
14	H	$CH_2CH_2OCOCH_3$	$CH_2CH_2OCOCH_3$	B	108–109	422	4·58	0·77

[a] A, Chlorobenzene; B, ethanol.

Spectra and colour measurements

The electronic spectra were determined on a Pye–Unicam SP 8-100 spectrophotometer in methanol (molarity of the dye was 1×10^{-5}). In view of the phototropic *trans–cis* isomerization of 4-aminoazobenzene and its derivatives,[14] the neutral solutions were retained in cells in the spectrophotometer until maximum values were reached.

The colour parameters of the dyed fabrics were determined on a Cary 210 spectrophotometer equipped with an integrating sphere and connected to an Apple II computer, using the D_{65} source and barium sulphate as standard blank.

^1H nuclear magnetic resonance (NMR) spectra were obtained with a Jeol EX 400 spectrometer in DMSO-d_6 solution (2%). The two-dimensional homonuclear proton COSY experiment was performed with a spectral width of 3300 Hz over 2000 data points. The acquisition involved four scans for 256 experiments and the data were collected and transformed using a sine bell squared function. The two-dimensional ^{13}C–^1H COSY spectrum was recorded with spectral windows of 18 000 and 3400 Hz in the F_2 and F_1 dimensions, respectively. The acquisition involved 320 scans for 256 experiments. The data were collected and transformed using a sine bell squared function.

Dyeing and fastness determinations

The baths for the dyeing of polyamide 6-6 (Lilion, Snia Fibre, Italy), polyester (Terital, Montefibre, Italy) and cellulose acetate (Silene, Novaceta, Italy) were prepared by milling the dye with sodium sulphate and Dispersogen-A (Hoechst Italia Spa, Turin) and diluting with an aqueous (1%) solution of Lenol O (Hoechst Italia Spa, Turin) to the final liquor ratio. The patterns, previously wetted, were introduced into the dispersion and

TABLE 2
Dyeing Procedure

Fabric	*Percentages based on the weight of textiles*			*Liquor to goods ratio*	*Entering temperature (°C)*	*Dying temperature*[a] *(°C)*	*Time of dyeing (min)*
	Dye	*Sodium sulphate*	*Dispersogen A*				
Polyamide 6-6	0·5	0·25	0·5	40:1	50	100	45
Polyester	0·5	0·25	0·5	40:1	60	120	60
Cellulose acetate	1·0	0·50	1·0	20:1	40	80	90

[a] After entering the dyebath, the temperature was raised at 1°C/min.

dyed at appropriate temperature. The dyed fabrics were removed, well rinsed and dried in hot air. Details are reported in Table 2.

All the dyeings were carried out on a Linitest (Hanau, Germany) apparatus. The fastness properties were assessed by standard procedures.[15] Lightfastness was determined on a Xenotest 150.

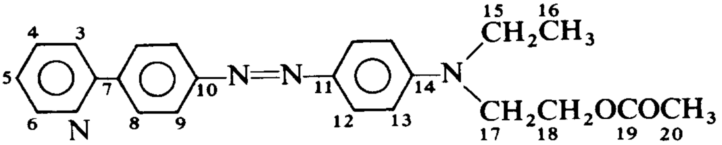
RESULTS AND DISCUSSION

Melting points and chromatographic data

By comparison of data reported in Table 1 (and previously reported data) some general melting point–structure relationships appear: (i) the presence of hetaryls on the azobenzene parent structure enhances the melting points, following the sequence x-azolo-pyridine[1–3,5] > benzothiazole[4] > pyridine, i.e. the dyes of the present series tend to be low-melting, and thus are useful for purposes which demand this parameter; (ii) the substitution at X_1 with methyl or acetamido groups causes a decrease of melting point (compare dyes from couples **1–2**, **9–10**, **11–12**, and **4–5–6**); (iii) when $X_1 = H$ and $X_2 = X_3$ (dyes **1**, **4**, **9**, **11** and **14**) the melting points decrease in the sequence $X_2 = X_3$: $CH_3 > CH_2CH_2CN > CH_2CH_3 > CH_2CH_2OH > CH_2CH_2$-$OCOCH_3$ (the two geminal bulky substituents give rise to the lowest-melting dye). In general, the dyes show very high R_f values, as a result of their hydrophobicity, which allows a slight interaction with the polar substrate.

NMR spectra

For the assignment of dye structures, although a complete ^1H and ^{13}C NMR analysis may appear unnecessary, the availability of spectroscopic data is justified in view of future general correlations. Furthermore, in the light of the continuing overlap between physical organic chemistry and the chemistry of dyes, the dissemination of updated spectroscopic data in the area of colour chemistry is essential. In Fig. 1 the spectra of dye **13** are reported as an example. The assignment of aliphatic protons is made by simple inspection. The methylene and methyl groups appear as a quartet and triplet at 3·52 and 1·18 ppm, respectively, as observed for similar heterocyclic



13

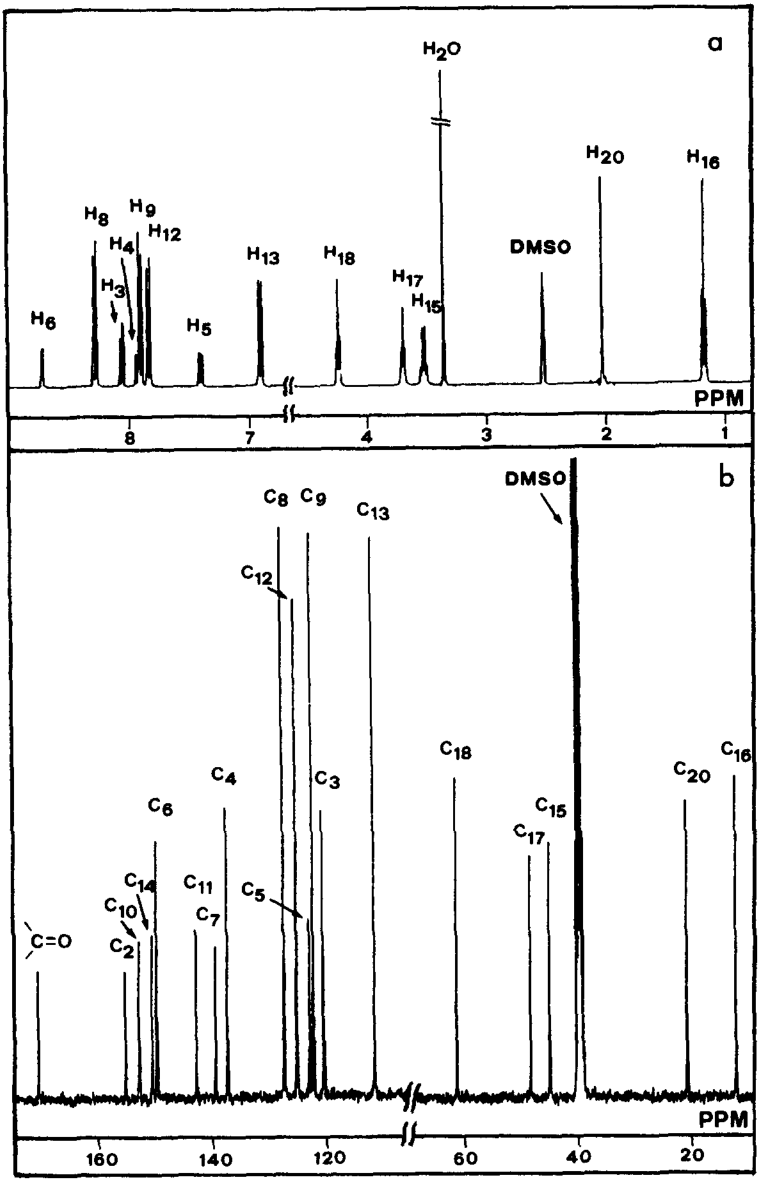


Fig. 1. NMR data of dye **13**: (a) ^1H NMR spectrum; (b) ^{13}C NMR spectrum with proton decoupling.

azo dyes.[3,5] The singlet at 2·02 ppm is due to the methyl of the acetate ester. The remaining methylene groups show two distinct signals at 4·24 and 3·69 ppm related to H_{17} and H_{18}, respectively, in agreement with the electronic effects of neighbouring groups.

The assignment of aromatic protons was made easier by a proton 2-D NMR COSY experiment. An expansion of the 6·6–9·2-ppm region in the H–H correlation spectrum is shown in Fig. 2. This experiment offers a means of determining the correlations of pairs of J-coupled nuclei in a molecule by allowing the observations of cross-peaks (Ref. 16, Chapter 8). Data from analogous heterocyclic azo dyes[3,5] allow us to assign the doublet at 6·90 ppm to H_{13}. A cross-peak connects it to the doublet at 7·83 ppm which is related to H_{12}. Another cross-peak is evident between the doublets at 7·90 and 8·28 ppm caused by H_9 and H_8, respectively. H_6 (pyridine ring) displays a signal at low field (doublet at 8·72 ppm), owing to the effect of the pyridine nitrogen. The signal shows a marked cross-peak with the multiplet at 7·39 ppm, which is therefore related to H_5. The remaining signals (doublet at

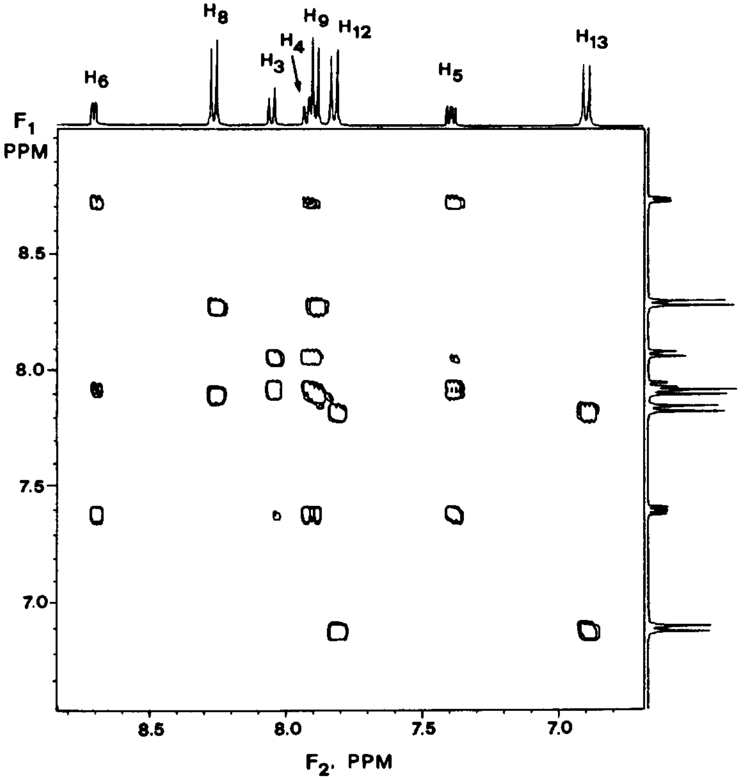


Fig. 2. Aromatic region of H–H COSY spectrum of dye 13.

8·06 ppm and multiplet about 7·92 ppm), connected by another marked cross-peak, are finally related to H_3 and H_4, respectively.

A 2-D heteronuclear carbon–proton COSY experiment (H–C COSY) was used for the assignments of ^{13}C spectra (see Fig. 1(b)). In Fig. 3 the C–H correlation spectrum of dye **13** is reported. Contour spots occur at the intersection of the shift positions of directly bonded C–H pairs, allowing an unambiguous assignment of carbons bonded to protons (Ref. 16, Chapter 9). The resonance at 170·39 ppm is assignable to the carbonyl group for the high chemical shift value. The ^{13}C data of a large series of substituted azobenzene dyes[17] suggest the assignment of the signal at 150·53 ppm to C_{14}. By comparison with ^{13}C NMR data for 2-phenylpyridine[18] and adding to the chemical shift values of phenyl carbon atoms the empirical increment of a phenylazo group,[19] signals at 155·22 and 152·76 ppm are assigned to C_2 and C_{10}, respectively. The assignment of signals at 139·40 and 142·77 ppm, which are ambiguous between C_{11} and C_7, was made by comparison of coupled and selectively decoupled ^{13}C spectra. In Fig. 4(a) an expansion of the 138·60–143·40-ppm region is reported with the coupled signals, showing the long-range couplings. Figure 4(b) shows the same region after irradiation at 6·90 ppm (H_{13}). The multiplet at 142·77 ppm is simplified to a singlet, thus

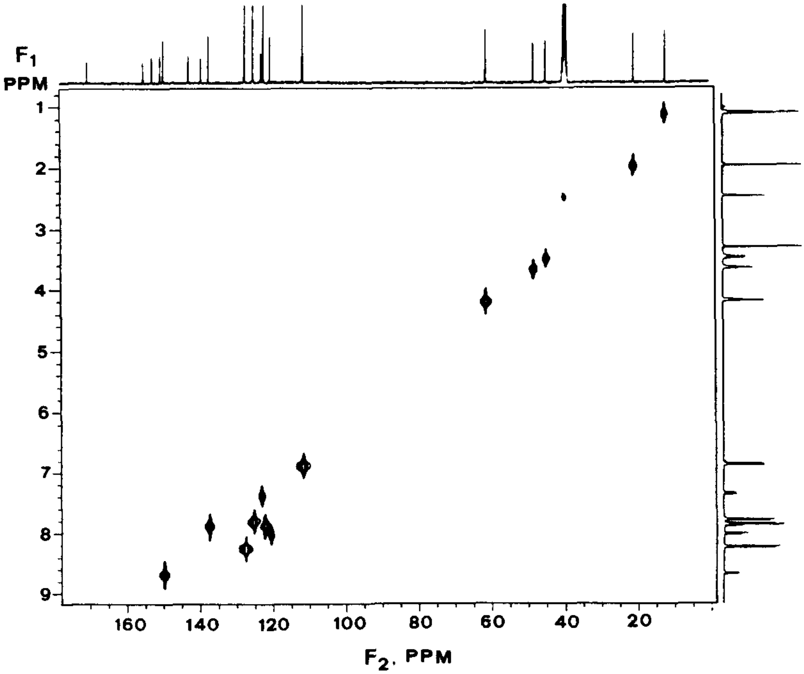


Fig. 3. H–C COSY spectrum of dye **13**.

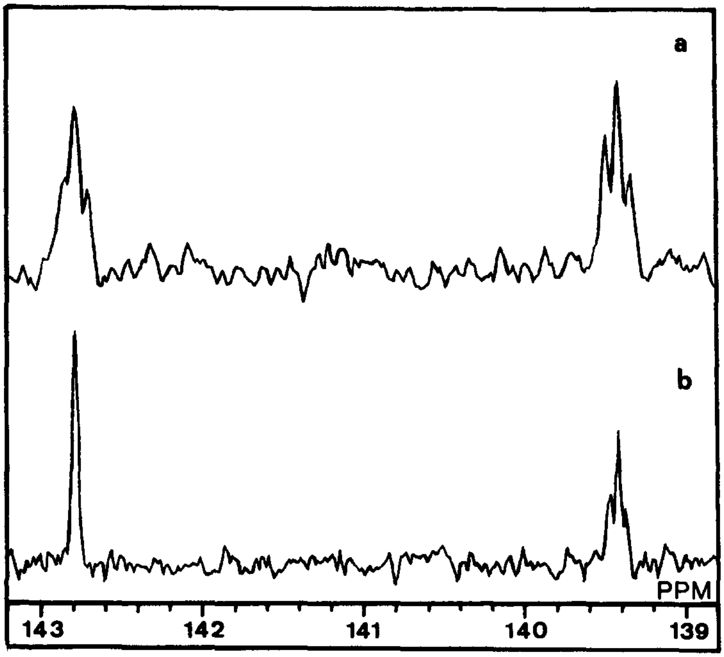


Fig. 4. Expansion of 138–144-ppm region of coupled ^{13}C spectrum of dye **13**: (a) without decoupling; (b) irradiated at 6·90 ppm.

confirming the assignment to C_{11}. The remaining signal at 139·40 ppm is consequently assigned to C_7.

Electronic absorption spectra

In the current literature,[20] the concept of comparing hetaryl moieties with more usual substituents has been widely accepted. Therefore, the present series can be considered as a donor–acceptor substituted azobenzene.[21] Spectroscopic data for analogous heterocyclic azobenzene dyes confirm this point of view.[1–5] By comparison of spectral data for dyes **1–14** with those for reference compounds (i.e. not having the hetaryl on the A ring[4]), a general batho-hyperchromic effect arises ($\Delta\lambda_{max} = 33–22$ nm, $\Delta \log \varepsilon = 0·04–0·14$), thus indicating that the 2-pyridyl substituent behaves as a moderate acceptor whose strength is similar to that of *N*-methylimidazo[4,5-c]-pyridine.[3] As far as substitution in the B ring is concerned, the following observations can be made: (i) substituents in the X_1 position promote a batho-hyperchromic effect ($\Delta\lambda_{max} = 1–28$ nm, $\Delta \log \varepsilon = 0·00–0·10$); (ii) if $X_1 = H$ and $X_2 = X_3$, the following order of absorption maxima is observed:

$$CH_2CH_3 > CH_2CH_2OH = CH_3 > CH_2CH_2OCOCH_3 > CH_2CH_2CN$$

TABLE 3
Fastness Properties of Dyes II (* indicates score 5)

Dye no.[a]	*Washing*[b]															*Perspiration*[b]						*Acid–alkali*		*Tetrachloroethylene*[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*	
1	*	*	*	*	*	4/5	*	*	4	2	*	3	1	4	3/4	*	4/5	3/4	*	4/5	4	*	*	*	*	*	*	*	3/4
2	*	*	4/5	*	*	4	4/5	*	4	2/3	*	3	2/3	*	2	*	*	4	*	*	4/5	*	*	*	*	*	*	*	3/4
3	*	*	4/5	4/5	*	4	*	*	4	3	*	2	2	*	2	*	*	4/5	*	*	4	*	*	*	*	*	*	*	4
4	*	*	*	*	*	*	*	*	*	1	*	4	1	*	3/4	*	*	4/5	*	*	4/5	*	*	*	*	*	*	*	3/4
5	*	*	*	*	*	*	*	*	*	2	*	3	1	*	3	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
6	*	*	*	*	*	*	4	*	4/5	2	*	2	2	*	2	*	4/5	*	*	*	*	*	*	*	*	4/5	*	*	3/4
7	*	*	*	*	*	4	*	3/4	*	2	*	3	1	*	3/4	*	4	3	*	4	3/4	*	*	*	4	4	*	*	3/4
8	*	*	*	*	*	4/5	*	*	*	1	*	4	1	*	3/4	*	3/4	3	*	*	4	*	*	*	*	*	*	*	3
9	*	*	*	*	*	2/3	4/5	*	2/3	2	2	*	2	2	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
10	*	*	*	*	3/4	*	4/5	3	*	2	*	2	2	*	2	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
11	*	*	*	*	*	4/5	4	*	4/5	1/2	*	3/4	1	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
12	*	*	*	*	*	4	4/5	*	4/5	2	*	2/3	1/2	*	2/3	*	*	*	*	*	*	*	*	*	*	*	*	*	5/6
13	*	*	*	*	*	*	4	*	*	1/2	*	3/4	1	*	3	*	*	*	*	*	4	*	*	*	*	*	*	*	4
14	*	*	*	*	*	*	4	*	*	2	*	3/4	2	*	3	*	*	*	*	*	4/5	*	*	*	*	*	*	*	3/4
1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
2	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
5	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3

6	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
7	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
8	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2/3
9	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
10	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2
11	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
12	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
13	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
14	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3/4
1	*	*	*	*	*	*	*	*	*	1	*	4	1	*	4	*	4/5	4/5	*	*	*	*	*	*	*	*	4/5	*	4
2	*	*	*	*	*	*	*	*	*	2/3	4/5	2	2	4	2	*	*	*	*	*	*	*	*	*	*	*	*	*	4/5
3	*	*	*	*	*	*	*	*	*	1/2	*	3	1/2	*	3	*	*	*	*	*	*	*	*	*	*	*	4	4	4
4	*	*	*	*	*	*	*	*	*	2	*	4/5	1	*	4/5	*	4/5	4/5	*	*	*	*	*	*	*	*	4/5	5	4/5
5	*	*	*	*	*	*	*	*	*	3	*	3	1	4/5	3	*	*	*	*	*	*	*	*	*	*	*	*	*	5
6	*	*	*	*	*	*	*	*	*	2	4	3	1/2	4	2	*	4/5	4	*	4/5	*	*	*	*	*	*	4/5	*	4
7	*	*	*	*	*	*	*	*	*	1	4	*	1	*	4	*	4	2/3	*	*	*	*	*	*	*	*	*	4/5	4
8	*	*	*	*	*	*	*	*	*	2/3	*	4	1	*	4/5	*	4	4	*	3	2/3	*	*	*	*	*	*	4	3/4
9	*	*	*	*	*	*	*	*	*	2	3	3/4	1	*	4	*	*	*	*	*	*	*	*	*	*	*	*	4/5	3/4
10	*	*	*	*	*	*	*	*	*	2/3	*	3/4	1	4	3	*	*	*	*	*	*	*	*	*	*	*	*	*	4
11	*	*	*	*	*	*	*	*	*	4/5	*	3	1	*	*	*	*	*	*	*	*	*	*	*	*	*	4/5	4	6
12	*	*	*	*	*	*	*	*	*	3/4	4	3/4	1	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	6
13	*	*	*	*	*	*	*	*	*	3	*	3	2	4	2	*	*	4/5	*	*	*	*	*	*	*	*	*	*	6/7
14	*	*	*	*	*	*	*	*	*	3/4	*	4	3	3	2	*	*	4	*	*	*	*	*	*	*	*	*	*	6

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

[b] Values in Col. 1 refer to the change of colour, in Col. 2 to the staining of the fibre (indicated in Ref. 15) and in Col. 3 to the staining of the same kind of fibre as the specimen.

TABLE 4
Colour of Dyed Fibres[b]

Dye number[a]	*Luminance factor, Y* (%)	*CIELAB coordinates*			*Helmholtz coordinates*		λ_{max} (*nm*)
		*L**	*a**	*b**	*Dominant wavelength,* λ_D (*nm*)	*Purity, P* (%)	
1	60·55	82·14	15·94	84·34	584	79·55	430
2	43·98	72·22	20·52	65·72	583	75·96	435
3	50·73	76·51	15·73	78·51	581	82·09	438
4	56·48	79·89	21·98	86·60	583	85·39	449
5	49·08	75·50	49·08	72·90	584	79·55	450
6	49·93	76·03	29·77	61·90	587	71·58	477
7	54·81	78·93	13·10	81·61	580	82·55	418
8	53·26	78·03	26·85	87·31	584	86·90	438
9	53·20	78·00	22·50	85·07	583	85·53	432
10	45·84	73·44	35·32	82·24	587	86·93	438
11	74·23	89·03	−8·03	64·22	573	62·71	408
12	63·84	83·88	3·78	78·57	577	77·35	414
13	64·37	84·16	3·88	74·25	577	74·19	431
14	58·61	81·08	−4·39	51·95	574	56·13	422
1	59·81	81·71	15·95	91·38	581	86·68	430
2	54·43	78·72	20·26	81·35	582	82·92	435
3	62·13	82·95	9·16	81·63	579	80·20	438
4	54·48	78·74	22·89	90·65	583	88·04	449
5	46·84	74·09	25·03	76·76	584	82·89	450
6	47·67	74·62	29·63	54·17	587	65·85	477
7	67·31	85·66	4·96	85·36	578	80·83	418
8	62·05	82·94	14·15	88·76	580	84·65	438
9	54·95	84·12	2·95	71·75	577	72·30	432
10	61·08	82·42	9·96	65·74	579	69·20	438
11	65·58	84·78	−6·04	66·28	574	66·82	408
12	57·16	80·27	14·40	85·25	580	84·06	414
13	60·21	81·95	0·35	65·32	576	68·19	431
14	66·97	85·49	−1·67	71·69	576	71·12	422
1	68·68	81·74	15·95	91·38	578	75·62	430
2	43·98	91·89	−5·97	0·02	585	89·60	435
3	53·26	78·09	11·84	80·80	580	82·46	438
4	61·42	78·74	22·88	90·65	581	83·57	449
5	40·15	69·57	37·74	83·44	588	89·56	450
6	39·52	69·13	42·37	81·42	590	88·97	477
7	67·85	85·66	4·96	85·36	578	85·36	418
8	58·17	82·94	14·15	46·95	582	88·28	438
9	54·95	79·01	19·49	93·07	582	88·92	432
10	43·77	72·08	36·95	89·37	588	91·04	438
11	69·56	86·78	−2·66	82·03	575	77·68	408
12	55·60	79·39	18·83	95·83	582	89·97	414
13	51·85	77·19	10·94	74·72	580	78·89	431
14	52·36	77·49	18·93	94·51	582	90·24	422

[a] Structure in Table 1.

[b] The first set of data refers to polyamide, the second to polyester and the third to cellulose acetate.

Dyeing properties

In Table 3 the fastness data for the dyeings are reported, and because of the wide occurrence of the maximum rating ('5'), a star (*) has been used to indicate the maximum rating; lightfastness is excluded, being measured on a 1–8 scale. The present series of disperse azobenzene dyes showed great versatility, giving good dyeings on three different substrates, viz. polyamide 6-6, polyester and cellulose acetate. Satisfactory exhaustion of dye liquors, dyeing uniformity and colour yields were obtained. If the demand of fastness to wet treatments, solvents and rubbing is the required parameter, dyeings on polyester are preferred, whereas lightfastness is at its highest on cellulose acetate.

Colour assessment

In Table 4 colour parameters assessed by tristimulus colorimetry are reported. The percentage purity ($P\%$) follows, as a general trend, the order cellulose acetate > polyester > polyamide. The parameters more representative of the colour on the fibre (λ_D, a^* and b^*) show an increase of redness and a decrease of yellowness if a substituent is present at X_1 (dyes **2**, **5**, **6**, **10** and **12**). The same substitution causes a decrease of the lightness parameters ($Y\%$ and L). Compared with the present series, dyes with benzothiazoles[4] or X-azolopyridines[1-3,5] as hetaryl substituents showed lower yellowness (lower b^* values) and, consequently, lower lightness (lower $Y\%$ and L^* values).

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