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Technical Properties and Photofading of Disperse Heterocyclic Azo Dyes

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ABSTRACT

A series of heterocyclic azo dyes derived from aminophenyl-benzothiazoles and substituted dialkylanilines was prepared and tested on polyamide and polyester. The overall properties were satisfactory and compared favourably with related dyes previously described.

Several correlations between structure and physical, spectroscopic (VIS and NMR) and fastness properties were found. An investigation of the photofading of the dyes on substrates as a function of time, checked with colourimetric techniques, proved a close time-dependent feature for colour parameters.

1 INTRODUCTION

Aminophenyl-benzothiazoles are well-known heterocyclic intermediates for the synthesis of dyes[1–3] and substituted dialkylanilines have been widely used as coupling components in the preparation of disperse azo dyes.[4,5] The present paper deals with the synthesis of a series of dyes of general formula **I**, which have been tested successfully as disperse dyes for polyamide and polyester fabrics. In addition to characterization of the dyes, an evaluation

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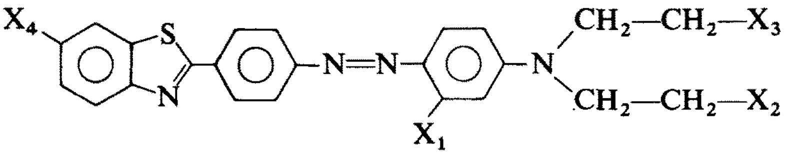


I

(X_1, $X_4 = H, CH_3$; X_2, $X_3 = CN, OH$)

of their technical properties and a colour assessment, a comparison was also made with similar heterocyclic dyes having pyrido-X-azole moieties and which have been recently investigated.[6,7]

The dyes were also studied with respect to their photofading on substrates as a function of time, following the process by colourimetric procedures. The overall results encourage an extension of this approach to other dye series in order to achieve some general rules in the complex field of the photodegradation of organic dyes.

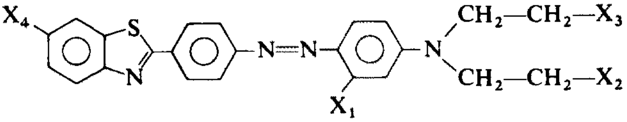
2 EXPERIMENTAL

2.1 Dyes and intermediates

The following intermediates were purchased commercially: 6-methyl-2-(*p*-aminophenyl)benzothiazole, *N*,*N*-diethylaniline, *N*,*N*-bis(hydroxyethyl)aniline.

TABLE 1

Characterization Data for Dyes



Dye no.	X_1	X_2	X_3	X_4	*M.p.*[a] (°C)	λ_{max} (nm)	$\log \varepsilon$	R_f
1	H	H	H	CH_3	222–223	472	4·64	0·98
2	CH_3	H	H	CH_3	163–165	482	4·63	0·98
3	H	CN	CN	CH_3	225–226	425	4·51	0·91
4	CH_3	CN	CN	CH_3	228–230	430	4·52	0·92
5	H	OH	OH	CH_3	200–202	456	4·63	0·94
6	CH_3	OH	OH	CH_3	199–200	459	4·61	0·91
7	H	H	H	H	185–187	470	4·54	0·97
8	CH_3	H	H	H	114–116	481	4·51	0·97
9	CH_3	CN	CN	H	194–196	428	4·52	0·91
10	H	OH	OH	H	210–211	454	4·60	0·90
11	CH_3	OH	OH	H	186–188	461	4·61	0·90

[a] Melting points of dyes **3**, **4**, **5**, **6** are taken from Ref. 2.

The following intermediates were prepared as indicated in the references: 2-(*p*-aminophenyl)benzothiazole,[8] *N*,*N*-bis(2-cyanoethyl)aniline,[9] *N*,*N*-bis(2-cyanoethyl)-*m*-toluidine,[9] *N*,*N*-bis(hydroxyethyl)-*m*-toluidine,[10] *N*,*N*-diethyl-*m*-toluidine.[11]

Dyes **3**, **4**, **5** and **6** are described in Ref. 2 and the remainder were prepared according to the general procedure therein indicated. The crude products were crystallized from chlorobenzene and the purity of the dyes was checked by chromatography. Characterization data are reported in Table 1.

2.2 Chromatography, electronic and NMR spectra, dyeing and fastness determinations, and colour measurements

The above were carried out as indicated in Ref. 6.

3 RESULTS AND DISCUSSION

3.1 Melting points and R_f values

Several factors influence melting points of organic compounds, (e.g. polarity, geometry, size, interactions, etc.) and some trends are apparent in this present series of dyes and in comparison with previously studied dyes.[6] Thus, a methyl group in X_4 and/or cyano and hydroxy substituents in X_2 and X_3 increase melting point values, whereas a methyl group in X_1 has a lowering effect. As generally observed,[3] imidazoles are high-melting substances, due to the possibility of intermolecular hydrogen bonding. This is also confirmed by comparing the melting points of dyes having a pyridoimidazole moiety[6] with the present dyes having a benzothiazole one. In the above context, the lowest melting point is expected for the simplest compound, i.e. that having $X_1 = X_2 = X_3 = H$ and not bearing the benzothiazolyl group. Literature data[12] (m.p. 101–102°C) confirm this expectation.

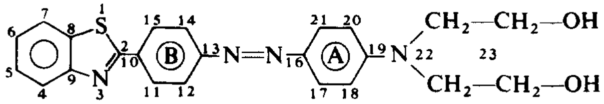
Due to their hydrophobicity, the dyes give a slight interaction with the polar substrate and therefore show very high R_f values.

3.2 ^{13}C- and ^{1}H-NMR spectra

A selected number of dyes were analysed using ^{1}H- and ^{13}C-NMR. The choice was determined by the solubility of dyes, containing two hydroxyl groups, in deuterated dimethyl sulphoxide. The overall data are given in Table 2 and Fig. 1(a) shows the ^{1}H spectrum of dye **5**. The assignment of signals of methyl protons is easy, positions 6 and 17 being adequately

TABLE 2

^{1}H- and ^{13}C-NMR Spectra^a



Position	^{1}H-NMR				^{13}C-NMR			
	Dye no.				Dye no.			
	5	6	10	11	5	6	10	11
2					165·39	165·41	166·53	166·61
					—	—	—	—
4	7·95	7·94	8·12	8·12	122·55	122·45	122·97	122·92
	(8)	(8)	(7)	(8)	(164)	(163)	(164)	(165)
5	7·37	7·34	7·47	7·46	128·27	128·14	126·73	126·70
	(8)	(8)	(8–7)^b	(8–7)^b	(162)	(160)	(161)	(162)
6			7·56	7·56	135·52	135·36	125·61	125·56
			(8–7)^b	(8–7)^b	—	—	(162)	(161)
7	7·85	7·82	8·09	8·09	121·87	121·70	122·30	122·29
	—	—	(7)	(9)	(164)	(163)	(164)	(165)
8					134·82	134·79	133·12	132·83
					—	—	—	—
9					151·54	151·49	154·14	154·62
					—	—	—	—
10					133·27	132·96	134·66	134·64
					—	—	—	—
11	8·16	8·13	8·20	8·20	128·08	127·96	128·21	128·19
	(9)	(8)	(9)	(9)	(164)	(164)	(164)	(164)
12	7·89	7·86	7·90	7·90	122·63	122·56	122·61	122·63
	(9)	(8)	(9)	(9)	(166)	(165)	(165)	(165)
13					153·97	154·44	153·74	153·75
					—	—	—	—
16					142·59	141·52	142·64	141·62
					—	—	—	—
17	7·87		7·81		125·38	140·94	125·38	140·95
	(9)		(9)		(160)	—	(160)	—
18	6·88	6·71	6·87	6·71	111·50	112·18	111·50	112·20
	(9)		(9)		(160)	(157)	(160)	(157)
19					151·90	151·88	151·56	151·54
					—	—	—	—
20	6·88	6·69	6·87	6·70	111·50	110·09	111·50	110·13
	(9)	(9)	(9)	(9)	(160)	(160)	(160)	(160)
21	7·81	7·69	7·81	7·70	125·38	116·95	125·38	116·98
	(9)	(9)	(9)	(9)	(160)	(160)	(160)	(160)
6-CH_3	2·45	2·43			21·15	21·07		
					(128)	(127)		
17-CH_3		2·66		2·66		17·20		17·94
						(127)		(127)

TABLE 2—*contd.*

Position	^1H-NMR				^{13}C-NMR			
	Dye no.				*Dye no.*			
	5	**6**	**10**	**11**	**5**	**6**	**10**	**11**
22[c]					53·40 (135)	53·29 (136)	53·42 (137)	53·30 (137)
23[c]	3·60– 3·65	3·59– 3·64	3·60– 3·64	3·59– 3·64	58·22 (139)	58·31 (142)	58·27 (141)	58·33 (141)
OH	4·88	4·91	4·91	4·87				

[a] For each position, the upper line refers to chemical shifts, δ, in ppm; the numbers in parentheses refer to *J* values, in Hz.

[b] Approximate *J* values.

[c] Range of overlapped signals for protons in positions 22 and 23.

diversified, whereas only chemical shift ranges can be given for methylene protons, 22–23, due to a partial overlapping. Some interesting shielding–deshielding effects can be noted:

(1) aromatic protons in the A and B rings are deshielded by the azo group and by the benzothiazolyl residue, the latter effect being the more marked (B-ring protons are more efficiently shifted downfield, in particular proton 11);
(2) benzothiazole protons are deshielded in the order 4 > 7 > 6 > 5, in agreement with the stronger electron-attracting power of nitrogen compared with sulphur;
(3) the methyl groups determine upfield shifts, which are more appreciable in the supporting ring and considerably lower in the neighbouring B ring.

In Fig. 1(b) the ^{13}C spectrum of the same dye is reported. The assignment of carbon signals is more complex and was effected by a combination of comparison of coupled and decoupled spectra, comparison with data for simpler structures (diethylaminoazobenzene[13] and 2-phenylbenzothiazole[14]), selective decoupling of protons and comparison of effects in presence or absence of methyl groups, etc. The following general observations can be drawn:

(1) chemical shifts of the methyl and methylene carbons are well distinguishable and assignable as a function of dye structures, and ^1J(CH) shows the usual values, which also reflect, for methylene carbons, the higher electronegativity of oxygen compared with nitrogen;

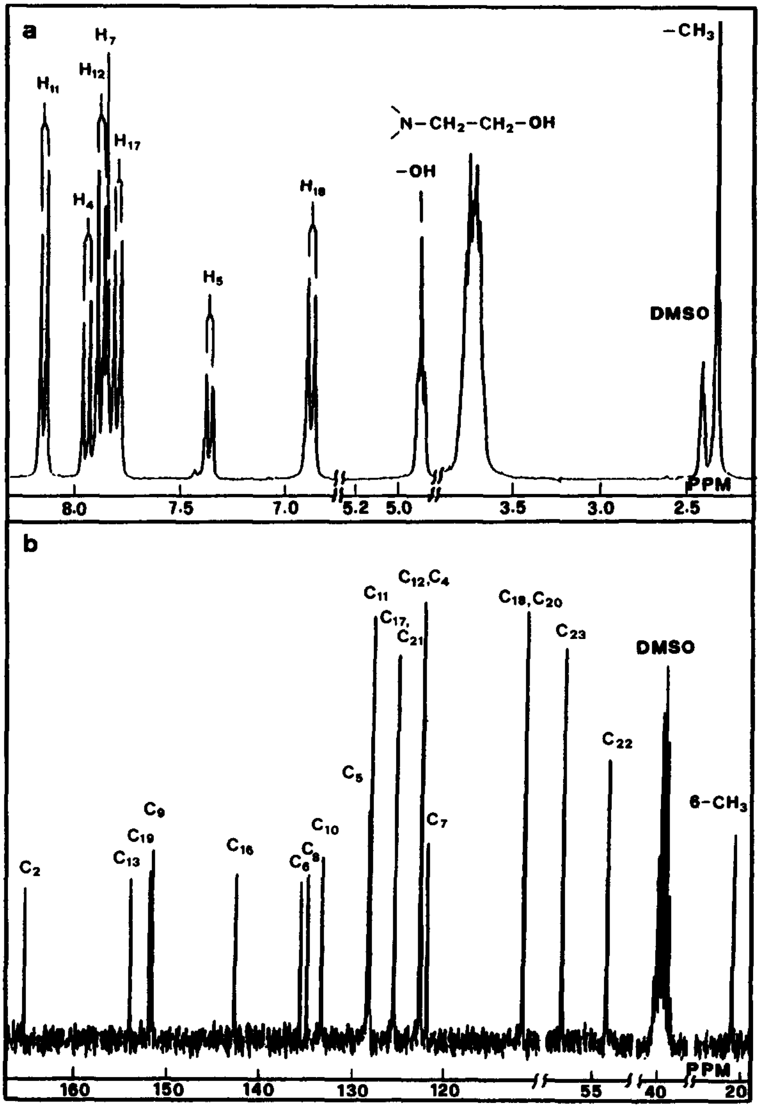


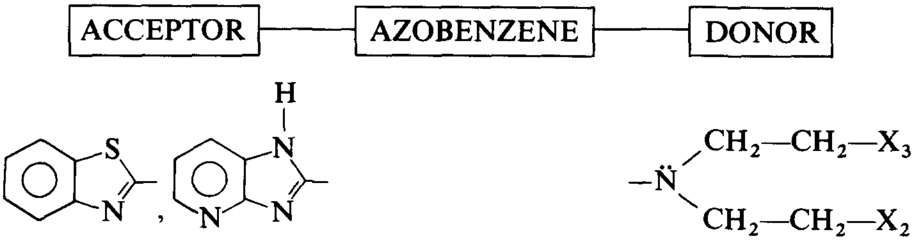
Fig. 1. NMR spectra of dye 5 (formula in Table 2): (a) ^1H; (b) ^{13}C.

(2) the extreme positions in the spectra are respectively represented by carbon-2 (downfield) and carbons-18–20 (upfield), as expected on the basis of charge distribution; also $^1J(CH)$ values, higher in ring B than in A, sustain this observation;

(3) the presence of a methyl in the 17-position influences in a different way the equidistant positions, owing to probable different bond orders, i.e. 17–18 and 17–16; the same trend, even though subdued, is shown by a methyl group in the 6-position.

3.3 Electronic absorption spectra

The idea of considering the present dyes as donor–acceptor substituted azobenzenes is strongly sustained by spectroscopic data. Furthermore, the concept of comparing hetaryls with more usual substituents is now widely accepted in the current literature.[15] It is useful here to report absorption data[12] of reference compounds having the general formula **I** but not bearing



the acceptor hetaryl moiety. Substituents X_1, X_2, X_3, λ_{max}(nm), log ε, are given:

H, H, H, 416, 4·47; H, OH, OH, 407, 4·47;
H, CN, CN, 382, 4·29; CH_3, CN, CN, 392, 4·41.

Considering these data and those reported in Table 1, the following generalizations can be drawn:

(1) the absorption maxima of dyes **1–11** fall into three groups, viz. (a) those having $X_2 = X_3 = H$, absorbing at longer wavelengths (470–482 nm), (b) those having $X_2 = X_3 = OH$, absorbing at intermediate wavelengths (451–459 nm), and (c) those having $X_2 = X_3 = CN$, absorbing at shorter wavelengths (425–430 nm);
(2) the same order of decrease in the donor ability (proportional to the electron-withdrawing power of substituents) is observed for reference compounds;
(3) the hetaryls behave as moderate acceptors and the effects of benzothiazolyl (this paper) and of imidazolylpyridine[6] are not essentially different;
(4) the presence of the methyl group at X_1 in all the series is accompanied by a slight (3–12 nm) but consistent bathochromic shift, thus indicating a reinforcement of the effect exerted by the main donor.

3.4 Dyeing properties

The dyes were found to be suitable for the dyeing of polyamide and polyester fabrics and gave satisfactory dyebath exhaustion, levelling and colour yields. Some dyeings showed a slight tendency to phototropic changes. Table 3

TABLE 3
Fastness Properties of Dyes[a]

Dye no.	*Washing*[b]									*Perspiration*[b]						*Acid/Alkali*		*Tetrachloro-ethylene*[b]			*Rubbing*		*Light*
	60°C			*95°C, 30 min*			*95°C, 4 h*			*pH 5*			*pH 8*								*Dry*	*Wet*	
1	*	4–5	*	4–5	4	4–5	3	2–3	4–5	*	*	*	*	*	*	*	*	*	*	*	*	*	3–4
2	*	4	*	4	3	4–5	2–3	2	4–5	*	*	*	*	*	*	*	*	*	*	*	*	*	4–5
3	*	*	*	3	3–4	4–5	2–3	3	4–5	*	*	*	*	*	*	*	*	*	*	*	*	*	4
4	*	*	*	4	4	*	3	3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4–5
5	*	4	*	2–3	2	4	2	1–2	4	*	*	*	*	*	*	*	*	*	*	*	*	*	3
6	*	4	*	2–3	2	4	2	1	4	*	*	*	*	*	*	*	*	*	*	*	*	*	3–4
7	*	4	*	3–4	3	4–5	3	3	4–5	*	*	*	*	*	*	*	*	*	*	*	*	*	2–3
8	*	4	*	3	1–2	4–5	2	1–2	4	*	*	*	*	*	*	*	*	*	*	*	*	*	3
9	*	*	*	3	3–4	4–5	2–3	3	4–5	*	*	*	*	*	*	*	*	*	*	*	*	*	5–6
10	*	3–4	*	2–3	2	4	2–3	2	4	*	*	*	*	*	*	*	*	*	*	*	*	*	3
11	*	3–4	*	3	2	3	2–3	1	3	*	*	*	*	*	*	*	*	*	*	*	*	*	3–4
1	*	*	*	*	*	*	*	3–4	*	*	*	*	*	*	*	*	*	*	*	*	3	3–4	3
2	*	*	*	*	*	*	*	3–4	*	*	*	*	*	*	*	*	4–5	*	*	*	4–5	*	2
3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4
4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	2–3	3–4	3–4
5	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3–4	*	*	*	4–5	*	2
6	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	4–5	*	1–2
7	*	*	*	*	*	*	*	4	*	*	*	*	*	*	*	*	4	*	*	*	4–5	*	2
8	*	*	*	*	*	*	*	4	*	*	*	*	*	*	*	*	3–4	*	*	*	4–5	*	2
9	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4
10	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4–5	*	2
11	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	4–5	*	2

[a] The first set of data refers to polyamide, the second to polyester.

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

reports the fastness data. Due to the very crowded occurrence of excellent scores, the table has been drawn using asterisk to indicate the maximum score of 5 (lightfastness is excluded, being measured on a 1–8 scale).

The present series contains some dyes of potential practical interest, i.e. dyes **3** and **9** on polyester, particularly when considering the low cost of their precursors. Some general trends can also be noted, namely:

(1) the excellent behaviour of all dyes is shown in the fastnesses to tetrachloroethylene, to acid and basic perspiration, and to acetic acid on both the substrates, to sodium carbonate, dry and wet rubbing on polyamide and to washing (60°C and 95°C for 30 min) on polyester;
(2) a general comparison between the two substrates shows a slightly better fastness to light on polyamide (CN groups are improving factors) and a reverse situation where other fastnesses are concerned;
(3) the general behaviour of the present series of dyes, allowing for better results from wet treatments, closely follows the behaviour of the analogous imidazo[4,5-*b*]pyridine derivatives.[6]

3.5 Colour assessment

The colour of dyed fabrics was assessed in terms of tristimulus colourimetry. In Table 4 the values for chromaticity coordinates, luminance factor, Helmholtz coordinates (λ_D, λ_C, $P\%$), and the positions of colours in the CIELAB colour solid, are reported.

The comment on the above parameters is substantially the same as for the series previously considered,[6] with minor variations. The main conclusions are:

(1) higher lightness of colouration is obtained on polyester than on polyamide, improved by substituents (OH, CN) in X_2 and X_3 and absence of methyl in X_1;
(2) the bathochromic shift of λ_D is promoted by methyl in X_1, whereas a cyano substituent in X_2 and X_3 gives the lowest λ_D values.

3.6 Photofading of dyes

With the present series of dyes, we carried out an extensive investigation on the photofading of dyes on substrates as a function of irradiation time. The final goal of this research could be the proposal of a colourimetric method for assessing lightfastness, which is more precise and free from subjective interferences than traditional procedures.[16]

The dyed specimens to be tested (about 5–7 swatches for each dyeing) were

TABLE 4
Colour of Dyed Fibres[a]

Dye no.	*Chromaticity coordinates*		*Luminance factor Y (%)*	*Helmholtz coordinates*			*CIELAB coordinates*		
	x	*y*		*Dominant wavelength* λ_D *(nm)*	*Complementary dominant wavelength* λ_c *(nm)*	*Purity P (%)*	*L**	*a**	*b**
1	0·51	0·40	47·56	590	487	75·8	74·5	39·7	65·1
2	0·55	0·37	33·66	597	489	79·6	64·7	55·3	60·6
3	0·46	0·44	64·68	580	481	74·7	84·3	11·9	74·2
4	0·44	0·43	69·41	580	481	62·2	86·7	10·9	59·9
5	0·54	0·40	40·69	592	488	82·1	70·0	47·0	69·7
6	0·56	0·37	31·71	598	489	82·5	63·1	56·7	63·3
7	0·53	0·40	44·33	591	487	81·4	72·5	43·0	71·2
8	0·54	0·38	31·28	597	489	76·9	62·7	51·0	56·1
9	0·49	0·43	55·66	584	484	79·8	79·4	24·8	76·5
10	0·55	0·39	38·46	594	488	82·4	68·4	50·0	68·4
11	0·56	0·37	31·36	598	489	81·6	62·8	56·5	61·7
1	0·53	0·41	44·34	590	487	81·3	72·5	41·7	71·2
2	0·54	0·33	35·88	595	489	79·4	66·4	50·7	62·3
3	0·46	0·46	66·02	579	481	76·8	85·0	9·8	77·9
4	0·45	0·43	64·24	581	482	67·6	84·1	13·2	64·4
5	0·48	0·42	56·06	585	485	73·3	79·6	25·7	67·3
6	0·50	0·41	47·98	588	486	72·7	74·3	34·6	61·9
7	0·52	0·41	44·90	590	487	80·1	72·8	40·1	69·9
8	0·53	0·38	38·37	597	489	76·9	68·3	47·0	57·9
9	0·48	0·44	59·39	584	484	79·8	81·5	18·3	74·8
10	0·49	0·42	53·43	594	488	82·4	78·1	28·3	70·8
11	0·51	0·41	44·61	598	489	81·6	72·6	38·0	64·8

[a] The first set of data refers to polyamide, the second to polyester.

TABLE 5

Data for Regression $P\%/t$ According to Eqn (1) (see text)[a]

Dye no.	*Lightfastness (BO2)*	$B \times 10^3$ *(slope)*[d]	$\sigma_B \times 10^3$[b]	$A \times 10^3$ *(intercept)*	$\sigma_A \times 10^3$[b]	r[c]
1	3–4	2·4	0·1	−3	4	0·996
	3	3·0	0·5	−10	9	0·954
2	4–5	1·6	0·1	0	2	0·998
	2	6·1	0·5	−10	11	0·989
3	4	2·2	0·1	3	4	0·997
	4	2·2	0·2	−11	11	0·986
4	4–5	2·1	0·1	−1	4	0·997
	3–4	2·7	0·2	7	8	0·990
5	3	2·7	0·2	−5	5	0·993
	2	6·1	0·2	5	5	0·998
6	3–4	2·9	0·2	−9	6	0·992
	1–2	8·3	0·5	12	10	0·992
7	2–3	3·5	0·1	6	4	0·998
	2	5·3	0·3	−7	5	0·995
8	3	3·5	0·1	1	3	0·998
	2	5·5	0·3	−7	5	0·995
9	5–6	1·0	0·1	−3	4	0·993
	4	1·9	0·1	0	3	0·999
10	3	2·6	0·2	−2	7	0·982
	2	6·5	0·5	5	9	0·992
11	3–4	2·5	0·2	−8	11	0·982
	2	6·6	0·5	9	9	0·992

[a] For each dye, values in the upper line refer to polyamide, in the lower to polyester.

[b] Standard deviation.

[c] Correlation coefficient.

[d] B in h^{-1}.

irradiated in a Xenotest 150 for increasing times, ranging from 3 to 100 h, depending on their lightfastnesses. The colour parameters of the exposed samples at various times and of the original dyed fabrics were then measured. In our first approach we have focused our attention on changes of percentage purity, $P\%$, it being understood that other colour parameters could be investigated as part of future developments of this approach. We have thus obtained a set of 22 linear plots, reported in Table 5, corresponding to the general eqn (1) which describes the dependence of the relative purity on time, i.e. a fading rate curve

$$\frac{P_0 - P_t}{P_0} = Bt + A \tag{1}$$

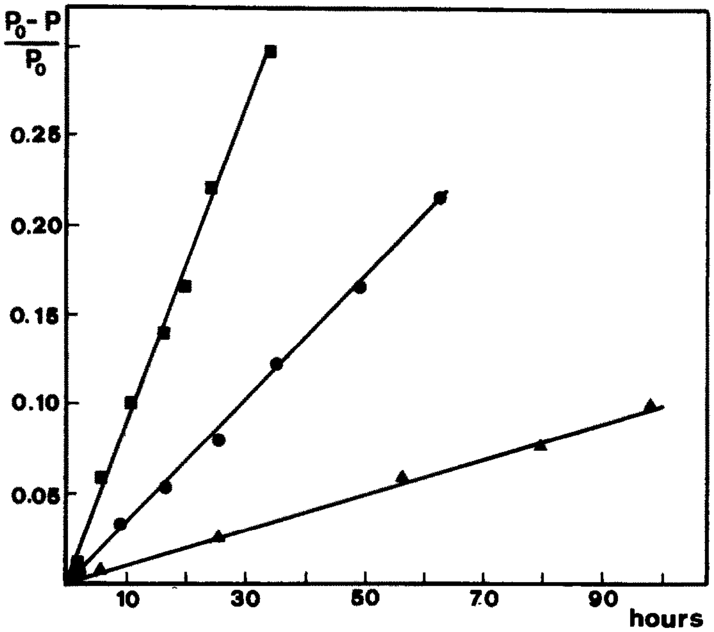


Fig. 2. Variation of relative percentage purity with time: ■, dye **6** on polyester; ●, dye **8** on polyamide; ▲, dye **9** on polyamide.

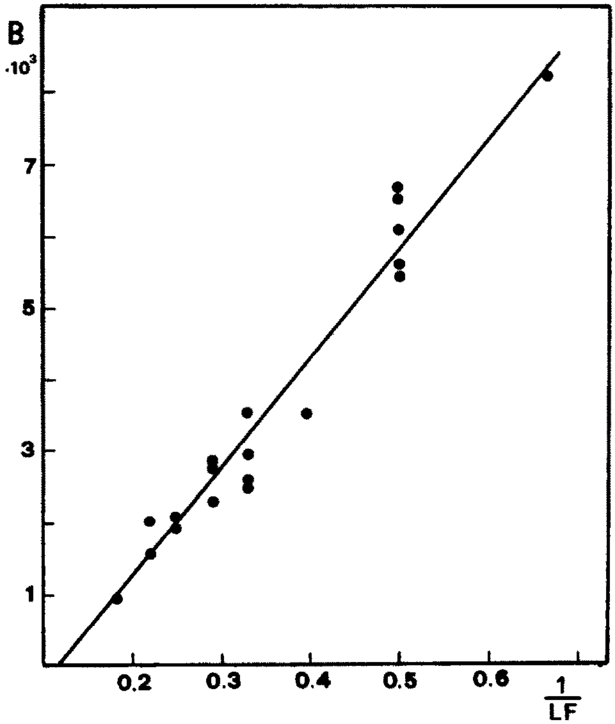


Fig. 3. Plot of B [slope in eqn (1), h^{-1}] versus reciprocal of light fastness (1/LF): The points correspond to regressions in Table 5.

where P_0 = percentage purity of non-irradiated samples;
P_t = percentage purity at time t;
t = time of irradiation (hours);
B = slope of the regression line;
A = intercept of the regression line.

The statistical parameters of the resultant linear correlations are shown in Table 5, and the correlation coefficients, r, confirm the linear relationships. Figure 2 depicts three of the various rate plots, chosen as representative examples of low-, medium- and high-lightfastness dyes.

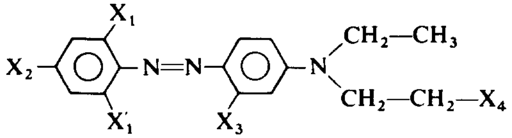
Using these results, we have extended the correlations to include the more usually employed fastness scores derived from the traditional blue standard scale. The slopes B in Table 5, which represent fading rates on a semi-quantitative level, were then plotted against the reciprocal of the lightfastnesses rating (LF) assessed according to the BO2 standard test. The resulting correlation is represented by the straight line (Fig. 3), whose statistical parameters (eqn 2), confirm satisfactorily the linear relationship. The direct correlation between B and LF was also examined but gave less satisfactory results.

$$B = 0\cdot0018 + 0\cdot0153\ (1/\mathrm{LF}) \qquad (2)$$

$$[r = 0\cdot978;\ \sigma\ (\text{slope}) = 0\cdot0007;\ \sigma\ (\text{intercept}) = 0\cdot0003]$$

The question remains as to the general applicability of the above relationship to other dyes, which might allow an accurate assessment of

TABLE 6
Data for Regression $P\%/t$ According to Eqn (1) (see text)



X_1	X_1'	X_2	X_3	X_4	*Light fastness (BO2)*	$B \times 10^3$ (*slope*)[c]	$\sigma_B \times 10^{3}$[a]	$A \times 10^3$ (*intercept*)	$\sigma_A \times 10^{3}$[a]	r[b]
H	H	CN	H	H	5	1·1	0·1	−8	9	0·987
H	H	CN	CH_3	H	5	1·2	0·1	−6	7	0·999
Br	H	H	H	CN	6–7	0·64	0·04	11	10	0·990
Cl	Cl	H	H	CN	7	0·06	0·01	5	5	0·980
Cl	Cl	H	CH_3	CN	7	0·07	0·02	4	6	0·984
NO_2	H	H	H	OH	4	1·9	0·2	7	5	0·997

[a] Standard deviation.
[b] Correlation coefficient.
[c] B in h^{-1}.

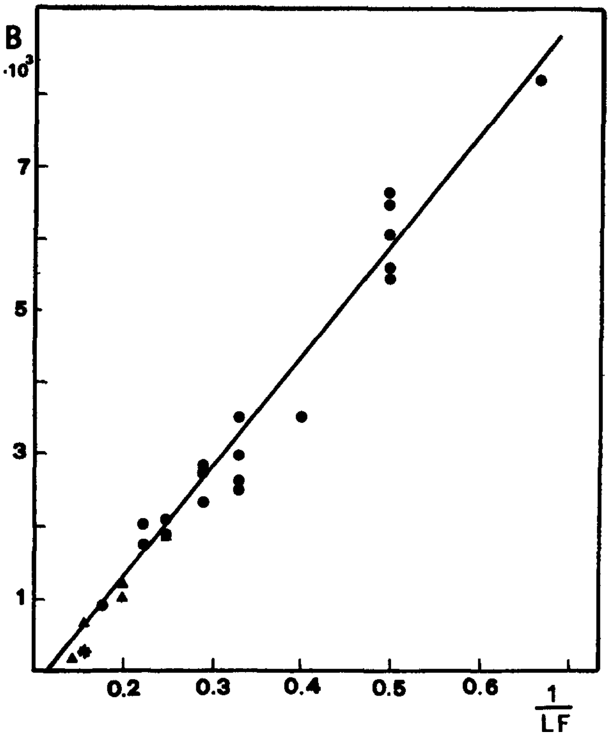


Fig. 4. Plot of B [slope in eqn (1), h^{-1}] versus reciprocal of light fastness (1/LF): ●, points corresponding to regressions in Table 5; ▲, points corresponding to regressions in Table 6; ▲*, two overlapped points.

lightfastness by a direct colourimetric procedure, completely free of subjective interferences. Further investigations in this area will form part of our future research programmes. Preliminary encouraging results were obtained using data for polyester taken from our files and derived from different sources. Table 6 shows the data, which extend the correlation to dyes of higher fastness, and Fig. 4 shows the overall plot of data from Tables 5 and 6. The correlation equation (3) is practically unchanged and the correlation coefficient is slightly improved.

$$B = -0{\cdot}0019 + 0{\cdot}0156\ (1/\mathrm{LF}) \tag{3}$$

$$[r = 0{\cdot}985;\ \sigma\ (\mathrm{slope}) = 0{\cdot}0005;\ \sigma\ (\mathrm{intercept}) = 0{\cdot}0002]$$

4 CONCLUSIONS

Aminophenyl-benzothiazoles and dialkylanilines were used in the synthesis of a series of heterocyclic disperse azo dyes. Studies on the properties of these dyes were made with respect to the following parameters:

(1) the assignment of signals in ^1H- and ^{13}C-NMR spectra and correlation of spectral parameters with structure;
(2) the interpretation of electronic spectra data in terms of a general 'donor–acceptor–azobenzene' chromogen, with hetaryls in the role of acceptors;
(3) dyeing and fastness properties which, as a whole, were found to be very satisfactory;
(4) the possible introduction of an instrumental procedure for assessing lightfastness on a standard scale.

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