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Quantitative Relationships Between Chemical Structure and Technical Properties of 4-Aminoazobenzene Sulphonic Acid Dyes

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SUMMARY

A series of new 4-aminoazobenzene dyes was synthesised. Absorption maxima and some important technical properties (lightfastness and fastness to washing) on nylon-6.6 and on wool were measured. A number of similar previously described structures were also prepared and characterised. Colour and constitution relationships in this series of dyes were established.

A statistical analysis of their fastness properties by a modified Free–Wilson method was carried out. The validity of the additive model was confirmed and quantification of substituent contributions was obtained.

1. INTRODUCTION

The structure of 4-aminoazobenzene is very popular in colour chemistry. The majority of disperse dyes are related to this family and there are a great many data in the literature concerning them.[1–3]

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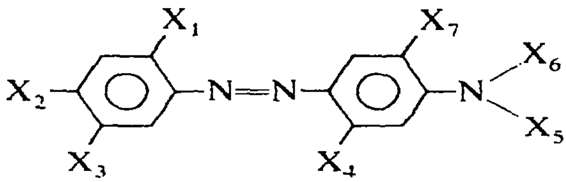
Sulphonic derivatives of 4-aminoazobenzene are much less important commercially, but patent activity indicates a continual interest in such compounds for the coloration of polyamide fibres.

Some structures have been carefully investigated because of their interesting acid–base indicator properties[4,5] (e.g. 4′-sulpho-dimethylaminoazobenzene, 'MethylOrange') but very few data are available concerning their technical properties as dyes.

Many acid dyes of general formula **Ia** are well known. In order to investigate the influence of chlorine atom substituents on the most important technical properties a series of structures of general formula **Ib**, whose distinctive feature was $X_7 = Cl$, was synthesised.



(I)

(a)	(b)
$X_1, X_3 = H, Cl, SO_3H$	$X_1, X_3 = H, Cl, SO_3H$
$X_2 = H, SO_3H$	$X_2 = H, SO_3H$
$X_4 = H, Cl, Me, NHCOMe$	$X_4 = NHCOMe, NHCOPh, NHCONHPh$
$X_5 = H, Me, Et, C_2H_4OH$	$X_5 = H$
$X_6 = H, Me, Et, C_2H_4OH, C_2H_4Cl, C_2H_4CN$	$X_6 = H$
$X_7 = H, Me, OMe$	$X_7 = Cl$

All dyes (**Ia** and **Ib**) were characterised spectrophotometrically and technical properties (lightfastness and fastness to washing) on nylon-6.6 and on wool were assessed.

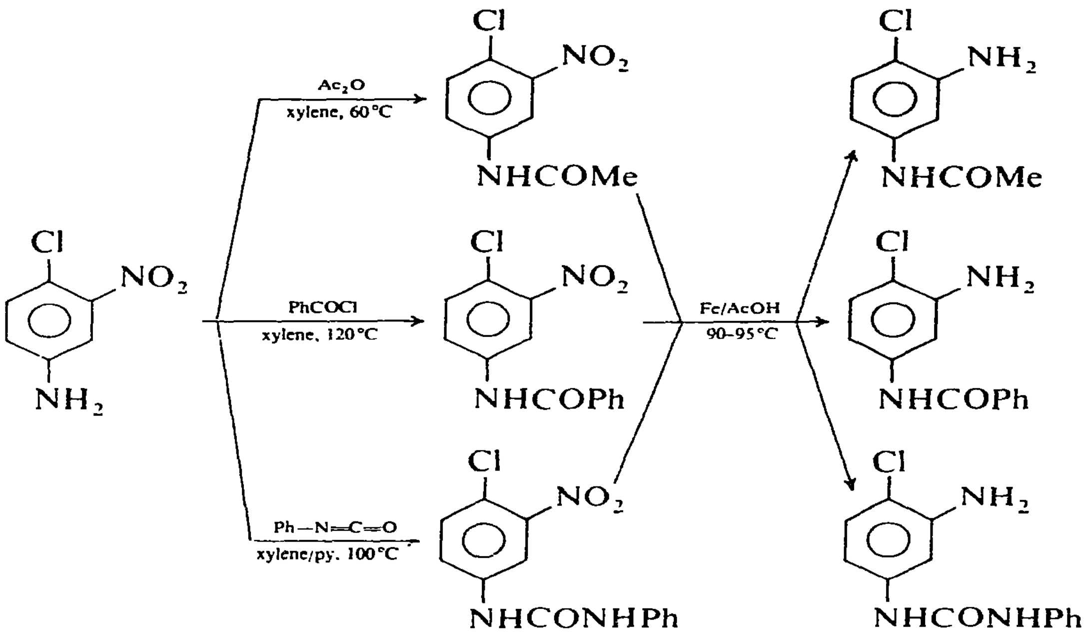
An analysis of structure–activity relationships in a series of arylazoindole sulphonic acid dyes was described in a previous paper.[6] Their technical properties (lightfastness, fastness to washing and substantivity) on nylon and on wool have been successfully correlated with substituent effects, demonstrating that the additive Free–Wilson model was appropriate for that set of dyes. The statistical approach of QSAR, previously used, is extended to 4-aminoazobenzene sulphonic acid derivatives to calculate substituent contributions to the most important technical properties. The results of the analysis indicate the most critical positions and the most active substituents affecting the technical properties of these dyes.

2. EXPERIMENTAL

2.1. Synthesis

Intermediates for dyes of general formula **Ib**

N-(3-Amino-4-chlorophenyl)acetamide, *N*-(3-amino-4-chlorophenyl)-benzamide and *N*-(3-amino-4-chlorophenyl)*N'*-phenylurea were prepared from 3-nitro-4-chloroaniline according to the following scheme:



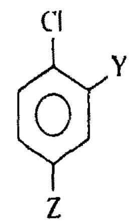
In Table 1 yields, melting points and elementary analyses of intermediates are reported. All the compounds were crystallised from ethanol.

Dyes of general formula **Ib**

The dyes were synthesised according to usual methods. They were purified by repeated washings with sodium chloride solutions and with diethyl ether until only one distinct spot was present on TLC. Final crystallisations were carried out from ethanol–water mixtures. The purified dyes still contained variable amounts (max. 10 %) of sodium chloride. Table 2 lists data for these dyes.

Dyes of general formula **Ia**, already described,[7,8] were similarly prepared.

TABLE 1
Characterisation Data of Intermediates



Structure		Yield (%)	Melting point (°C)	Empirical formula	C (%)		H (%)		N (%)		Cl (%)	
Y	*Z*				*Calcd*	*Found*	*Calcd*	*Found*	*Calcd*	*Found*	*Calcd*	*Found*
NO_2	NHCOMe	97·7	148–50	$C_8H_7ClN_2O_3$	44·77	44·46	3·29	3·39	13·05	13·07	16·52	16·47
NH_2	NHCOMe	95·0	167–69	$C_8H_9ClN_2O$	52·04	52·42	4·91	4·95	15·17	15·14	19·20	19·27
NO_2	NHCOPh	96·5	156–58	$C_{13}H_9ClN_2O_3$	56·43	56·32	3·27	3·19	10·12	9·88	12·81	12·93
NH_2	NHCOPh	96·5	159–61	$C_{13}H_{11}ClN_2O$	63·29	63·96	4·49	4·75	11·35	11·26	14·37	14·48
NO_2	NHCONHPh	91·6	190–92	$C_{13}H_{10}ClN_3O_3$	53·53	53·52	3·45	3·44	14·40	14·29	12·15	12·24
NH_2	NHCONHPh	95·3	213–15	$C_{13}H_{12}ClN_3O$	59·66	59·86	4·62	4·63	16·05	15·98	13·55	13·60

TABLE 2

Characterisation Data of Dyes of General Formula **Ib**[a]

Dye no.	Structure				Melting point (°C)	Empirical formula	C (%)		H (%)		N (%)		λ_{max} (nm)	log ε
	X_1	X_2	X_3	X_4			Calcd	Found	Calcd	Found	Calcd	Found		
1	SO_3H	H	H	NHCOPh	292 (dec)	$C_{19}H_{14}ClN_4NaO_4S$	50·39	50·22	3·12	3·23	12·37	12·25	415	4·23
2	SO_3H	H	H	NHCONHPh	250–2	$C_{19}H_{15}ClN_5NaO_4S$	48·77	48·98	3·23	3·48	14·97	14·90	424	4·29
3	H	SO_3H	H	NHCOMe	278 (dec)	$C_{14}H_{12}ClN_4NaO_4S$	43·03	43·27	3·10	3·17	14·34	14·15	419	4·37
4	H	SO_3H	H	NHCOPh	262 (dec)	$C_{19}H_{14}ClN_4NaO_4S$	50·39	50·24	3·12	3·22	12·37	12·20	423	4·38
5	H	SO_3H	H	NHCONHPh	224 (dec)	$C_{19}H_{15}ClN_5NaO_4S$	48·77	49·08	3·23	3·45	14·97	14·77	432	4·32
6	H	H	SO_3H	NHCOMe	>300	$C_{14}H_{12}ClN_4NaO_4S$	43·03	42·80	3·10	3·20	14·34	14·30	414	4·34
7	H	H	SO_3H	NHCOPh	246 (dec)	$C_{19}H_{14}ClN_4NaO_4S$	50·39	50·27	3·12	3·29	12·37	12·18	418	4·32
8	H	H	SO_3H	NHCONHPh	254 (dec)	$C_{19}H_{15}ClN_5NaO_4S$	48·77	48·61	3·23	3·38	14·97	14·77	427	4·32
9	Cl	H	SO_3H	NHCOMe	>300	$C_{14}H_{11}Cl_2N_4NaO_4S$	39·54	39·72	2·61	2·53	13·17	13·01	430	4·41
10	Cl	H	SO_3H	NHCOPh	>300	$C_{19}H_{13}Cl_2N_4NaO_4S$	46·83	46·70	2·69	2·69	11·50	11·36	434	4·24
11	Cl	H	SO_3H	NHCONHPh	225 (dec)	$C_{19}H_{14}Cl_2N_5NaO_4S$	45·43	45·24	2·81	3·04	13·94	13·77	449	4·33
12	Cl	SO_3H	Cl	NHCOMe	248 (dec)	$C_{14}H_{10}Cl_3N_4NaO_4S$	36·58	36·39	2·19	2·34	12·19	12·03	460	4·15
13	Cl	SO_3H	Cl	NHCOPh	253 (dec)	$C_{19}H_{12}Cl_3N_4NaO_4S$	43·74	43·53	2·32	2·41	10·74	10·61	453	4·24
14	Cl	SO_3H	Cl	NHCONHPh	286 (dec)	$C_{19}H_{13}Cl_3N_5NaO_4S$	42·52	42·32	2·44	2·62	13·05	12·97	473	4·33

[a] Isolated and characterised as sodium salts.

TABLE 3
Spectroscopic Data of Dyes of General Formula **Ia**

Dye no.	*Structure*							λ_{max} (*nm*)	*log ε*
	X_1	X_2	X_3	X_4	X_5	X_6	X_7		
15	SO_3H	H	H	NHCOMe	H	H	H	415	4·23
16	H	SO_3H	H	NHCOMe	H	H	H	424	4·30
17	H	H	SO_3H	NHCOMe	H	H	H	418	4·29
18	Cl	H	SO_3H	NHCOMe	H	H	H	435	4·37
19	Cl	SO_3H	Cl	NHCOMe	H	H	H	465	4·41
20	SO_3H	H	H	NHCOMe	H	H	OMe	441	4·22
21	H	SO_3H	H	NHCOMe	H	H	OMe	464	4·25
22	H	H	SO_3H	NHCOMe	H	H	OMe	458	4·32
23	Cl	SO_3H	Cl	NHCOMe	H	H	OMe	490	4·40
24	SO_3H	H	H	NHCOMe	H	H	Me	421	4·34
25	H	SO_3H	H	NHCOMe	H	H	Me	430	4·34
26	H	H	SO_3H	NHCOMe	H	H	Me	424	4·40
27	Cl	SO_3H	Cl	NHCOMe	H	H	Me	472	4·26
28	H	H	SO_3H	H	Et	Et	H	427	4·40
29	Cl	H	SO_3H	H	Et	Et	H	444	4·47
30	Cl	SO_3H	Cl	H	Et	Et	H	470	4·48
31	H	H	SO_3H	Me	Et	Et	H	432	4·38
32	Cl	H	SO_3H	Me	Et	Et	H	449	4·39
33	Cl	SO_3H	Cl	Me	Et	Et	H	476	4·54
34	H	H	SO_3H	Cl	Et	Et	H	427	4·40
35	Cl	H	SO_3H	Cl	Et	Et	H	444	4·47
36	Cl	SO_3H	Cl	Cl	Et	Et	H	462	4·51
37	H	H	SO_3H	NHCOMe	Et	Et	H	462	4·34
38	Cl	H	SO_3H	NHCOMe	Et	Et	H	478	4·57
39	Cl	SO_3H	Cl	NHCOMe	Et	Et	H	494	4·66
40	H	H	SO_3H	H	Et	C_2H_4CN	H	412	4·36
41	Cl	H	SO_3H	H	Et	C_2H_4CN	H	427	4·24
42	Cl	SO_3H	Cl	H	Et	C_2H_4CN	H	445	4·33
43	H	H	SO_3H	H	Et	C_2H_4OH	H	423	4·43
44	Cl	H	SO_3H	H	Et	C_2H_4OH	H	440	4·45
45	Cl	SO_3H	Cl	H	Et	C_2H_4OH	H	465	4·38
46	H	H	SO_3H	H	H	H	H	396	4·25
47	H	H	H	NHCOMe	H	H	H	414	4·33
48	H	H	SO_3H	H	Me	Me	H	420	4·41
49	H	H	SO_3H	H	Et	C_2H_4Cl	H	416	4·30
50	H	H	SO_3H	H	C_2H_4OH	C_2H_4OH	H	422	4·45

TABLE 4

Technical Properties of Dyes of General Formula **Ib** (Nos. 1–14) and **Ia** (Nos. 15–46)

Dye no.	*Colour of dyeing*	*Lightfastness* *Nylon*	*Lightfastness* *Wool*	*Fastness to washing*[a] *Nylon (60°C)*			*Wool (40°C)*			*Notes*
1	Yellow	6	5–6	3	3	3	2–3	3	2–3	
2	Yellow	6	5	3–4	3–4	3–4	3	2–3	2–3	
3	Yellow	6	4–5	3	3–4	3–4	2	3	3	
4	Reddish yellow	5–6	5	3–4	3	2–3	3	3	3	
5	Orange	5–6	4–5	3–4	3–4	3–4	3	3	3	
6	Yellow	6	4–5	2–3	3–4	3–4	2	3–4	3	Phototropic
7	Yellow	6	5	3–4	2–3	2–3	3	3	3	Phototropic
8	Yellow	6	4–5	3–4	2–3	2–3	3	3	3	Phototropic
9	Yellow	6	5	3	4	3	2	4	3–4	
10	Reddish yellow	5–6	5	3–4	4	3–4	3	3–4	3–4	
11	Reddish yellow	5–6	4–5	4	3–4	3	3	3	3	
12	Orange	6	5	3–4	3	2–3	3	3–4	2–3	
13	Orange	6	5	3–4	2–3	2–3	3–4	4	3	
14	Orange	5–6	4–5	4	3	3	3–4	3–4	2–3	
15	Brownish yellow	4–5	4	3–4	4	4	1–2	3–4	3	Phototropic
16	Brownish yellow	4–5	4	3–4	4	3–4	1–2	3	2–3	
17	Yellow	5	4	3–4	4	4	1–2	3	3	
18	Reddish yellow	5–6	4–5	3–4	4	3–4	2	2–3	2–3	
19	Orange	5–6	4–5	4	4	3–4	2–3	2–3	2–3	
20	Orange	5	3	2–3	4	3–4	1–2	3–4	3	
21	Orange	5	3	2	3–4	3–4	2	3–4	3	
22	Orange	5	3	2–3	3–4	3–4	2	3–4	3	
23	Red	5–6	3–4	3	3	3	3	3	2–3	
24	Greenish yellow	5	4–5	4	4	4	1–2	4	3–4	
25	Yellow	5	4–5	3–4	4–5	4	2	2–3	2–3	
26	Yellow	5–6	4–5	3–4	4–5	4	2	2–3	2–3	
27	Orange	5–6	5	4	3–4	3	3	3	3	
28	Yellow	5	4–5	3–4	3–4	3–4	2	2	2–3	
29	Reddish yellow	5–6	4–5	3–4	4	2–3	2–3	2	2	
30	Yellowish red	6	5	4	3–4	3	3	2–3	3	
31	Reddish yellow	5–6	4–5	4	4	3–4	2–3	2–3	2–3	
32	Orange	5–6	4–5	3–4	4	2–3	3	2–3	2–3	
33	Yellowish red	5–6	4–5	4	4	3	3–4	3	3	
34	Yellow	5–6	4–5	4	4	3–4	2–3	2–3	2–3	
35	Reddish yellow	5–6	4–5	4	4	3–4	3	3	3	
36	Yellowish red	5–6	4–5	4	4	3–4	3–4	3–4	3–4	
37	Reddish yellow	5	4	3–4	4	3–4	2	2–3	2–3	
38	Orange	5–6	4–5	3–4	4	3	2–3	2–3	2	
39	Reddish orange	5–6	5	4	3–4	3	3	2–3	3	
40	Yellow	5	4–5	3–4	4	4	1–2	3	3	
41	Yellow	5–6	4–5	4	4	3–4	2	2	2	
42	Orange	6	5	4	4	3–4	2–3	2–3	2–3	
43	Yellow	4–5	4	3–4	4	3–4	2	2–3	2–3	
44	Reddish yellow	4–5	3–4	3–4	4	3–4	2	2–3	2–3	
45	Yellowish red	4	3–4	3–4	3–4	3–4	2–3	2–3	2–3	
46	Yellowish green	4–5	4	3–4	3–4	3–4	2	3–4	3–4	Phototropic

[a] 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 for nylon and of cotton for wool.

2.2. Spectra

Electronic absorption spectra of dyes (sodium salts) in methanol (10^{-5}–10^{-6} M) were recorded on a Pye–Unicam SP 1800 spectrophotometer. The spectral parameters of dyes **1b** are listed in Table 2, those of dyes **1a** in Table 3.

2.3. Dyeings and fastness determinations

Dyeings were carried out as indicated in ref. 6.

Lightfastness (xenon lamp) and fastness to washing were assessed according to standard methods (ISO).[9] Table 4 lists the technical properties on nylon-6.6 and on wool.

2.4. Calculations

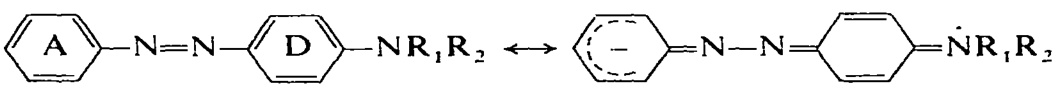
Calculations were carried out on an IBM 370/158 computer, using the stepwise procedure of the SPSS programs.[10]

3. RESULTS AND DISCUSSION

3.1. Visible absorption maxima

Many data relative to the visible absorption spectra of aminoazobenzenes are available from the literature.[11–14]

Aminoazobenzene dyes can be classed as donor–acceptor chromogens.[15] Mesomeric equilibria involve two extreme canonical forms (**II** and **III**). According to the resonance theory bathochromic movements



(II) (III)

of λ_{max} are expected when electron-withdrawing groups are present in ring A and/or when electron-donor groups are present in ring D. Analyses of experimental data often reveal irregularities, mainly because of steric complications. Additivity of substituent effects is not generally observed.

Our spectroscopic data, related to sulphonic derivatives, agree with Hallas's analysis.[12] Small bathochromic effects are observed for substitution by a sulpho group (X_1, X_2, X_3 positions) in the sequence *para* (9–10 nm), *meta* (4 nm), *ortho* (1 nm). The effect exerted by the chlorine substituent is opposing: if present in the A ring it causes a remarkable red shift whereas in the D ring a weak, or not appreciable, hypsochromic shift is produced (X_1, $\Delta\lambda$ 15–17 nm; $X_1 + X_3$, $\Delta\lambda$ 26 or 41–42 nm; X_4, $\Delta\lambda$ 0 nm, with exception for no. 36 vs no. 30, $\Delta\lambda$ −8 nm; X_7, $\Delta\lambda$ 4–5 nm). The methyl group has a bathochromic effect in both X_4 (5–6 nm) and X_7 (6–7 nm) positions. The methoxy group (in X_7) causes large movements of the visible band towards longer wavelengths (25–26 or 40 nm). The acylamino groups (in X_4) also give rise to considerable red shifts: acetylamino $\Delta\lambda$ 22–24 or 34–35 nm; benzoylamino (vs acetylamino) $\Delta\lambda$ 4 nm (exception for no. 13, $\Delta\lambda$ −6 nm); phenylureido (vs acetylamino) $\Delta\lambda$ 13 nm (for no. 11, $\Delta\lambda$ 19 nm).

Substitution at the nitrogen of the 4-amino group affects its basicity and consequently λ_{max}. The order of the observed bathochromic effect is as follows: ethyl, $\Delta\lambda$ 15–16 or 21–22 nm; methyl, $\Delta\lambda$ 12 nm; β-hydroxyethyl, $\Delta\lambda$ 11–12 nm; β-chloroethyl $\Delta\lambda$ 4–5 nm; β-cyanoethyl, $\Delta\lambda$ −1–0 nm. Values for ethyl, methyl and β-hydroxyethyl groups have been obtained by halving $\Delta\lambda$ values of the corresponding *N*,*N*-dialkyl derivatives, whereas those for β-chloroethyl and β-cyanoethyl have been obtained as differences. From the above data one can note the higher efficiency of the methyl substitution at the nitrogen (X_5, X_6) as compared with substitution at the aromatic carbons (X_4, X_7).

3.2. Quantitative structure–activity relationships analysis

The statistical approach of QSAR analysis is applied to the technical properties of dyes of general formula **Ib** and **Ia**, listed in Table 4.

As in the previous analysis[6] the method used is the Fujita–Ban modification of the Free–Wilson technique.[16,17]

A set of linear equations of the form (1) were solved,

$$A_i = \sum_p \sum_s C_{i,ps} + \mu \qquad (i = 1, 2, \ldots, n) \tag{1}$$

where A_i is the value of the examined property of the member i of a series of n congeners; C is the contribution of the substituent s,

TABLE 5
Matrix Used for Calculation of Group Contributions (Eqns 2–5)

Dye no.	X_1		X_2	X_3		X_4					X_5	X_6			X_7		
	SO_3H	Cl	SO_3H	SO_3H	Cl	Me	Cl	$NHCOMe$	$NHCOPh$	$NHCONHPh$	Et	Et	C_2H_4CN	C_2H_4OH	Me	Cl	OMe
1	1								1							1	
2	1									1						1	
3			1					1								1	
4			1						1							1	
5			1							1						1	
6				1				1								1	
7				1					1							1	
8				1						1						1	
9		1		1				1								1	
10		1		1					1							1	
11		1		1						1						1	
12		1	1		1			1								1	
13		1	1		1				1							1	
14		1	1		1					1						1	
15	1							1									
16			1					1									
17				1				1									
18		1		1				1									
19		1	1		1			1									
20	1							1									1
21			1					1									1
22				1				1									1
23		1	1		1			1									1
24	1							1							1		
25			1					1							1		
26				1				1							1		
27		1	1		1			1							1		
28				1							1	1					
29		1		1							1	1					
30		1	1		1						1	1					
31				1		1					1	1					
32		1		1		1					1	1					
33		1	1		1	1					1	1					
34				1			1				1	1					
35		1		1			1				1	1					
36		1	1		1		1				1	1					
37				1				1			1	1					
38		1		1				1			1	1					
39		1	1		1			1			1	1					
40				1							1		1				
41		1		1							1		1				
42		1	1		1						1		1				
43				1							1			1			
44		1		1							1			1			
45		1	1		1						1			1			
46				1													

dependent on the position p; μ represents the activity of the constant portion (parent structure) of the series. The examined properties are lightfastness and fastness to washing on nylon and on wool.

The matrix used for the analysis is given in Table 5, where the presence of each substituent in any position is indicated by the number 1. The results are given in Tables 6–10.

The substitution pattern of this series of dyes imposes the following limitations on the analysis:

(a) Cl at the X_3 position appears always as a pair with Cl at X_1;
(b) the *geminal* substitution at X_5 and X_6 always occurs simultaneously;
(c) the substituents at X_7 are always accompanied by an acylamino substituent at X_4.

The net effects of Cl at X_3 and of the substituents at X_5, X_6 and X_7 cannot therefore be assessed.

Lightfastness

Equations 2 and 3 (of the form 1) were formulated relating the lightfastness on nylon and on wool respectively to the most significant variables. The correlation is good for eqn 3, poorer for eqn 2.

Eqn	*Fibre*	n^a	k^b	R^c	s^d	R^{2e}	F^f	
2	Nylon-6.6	46	15	0·871	0·306	75·8	6·27	(+ + +)
3	Wool	46	15	0·942	0·235	88·7	15·60	(+ + +)

[a] Number of compounds used for the regression analysis.
[b] Number of explanatory variables entered in the regression equation; the explanatory variables were allowed to enter the regression if they exceeded an F value of 0·1.
[c] Multiple correlation coefficient.
[d] Standard deviation of estimate.
[e] Percentage of the variance of the dependent variable explained by the regression equation.
[f] F-ratio and significance level: (+ + +) $P < 0{\cdot}001$.

The low correlation coefficient of eqn 2 is not surprising if the small variance of lightfastness values (2 units) and the usual experimental error (0·5 units) are taken into account.

Tables 6 and 7 list the calculated contributions of the parent

TABLE 6
Calculated Group Contributions to Lightfastness on Nylon, Based on $C_H = 0.00$ (Eqn 2)

Position	*Substituent*	C^a	s^b	F^c	R^2 *change*^{d}
X_1	Cl	0·12	0·13	0·87	5·0
X_2	SO_3H	−0·15	0·19	0·65	1·1
X_3	Cl	0·32	0·20	2·38	0·6
	SO_3H	0·05	0·17	0·08	0·1
X_4	Me	0·12	0·24	0·23	0·1
	Cl	0·12	0·24	0·23	0·1
	NHCOMe	0·06	0·20	0·09	0·1
	NHCOPh	−0·12	0·29	0·16	0·7
	NHCONHPh	−0·22	0·29	0·56	0·9
X_5	Et	0·42	0·19	4·71 (+)	9·8
X_6	C_2H_4CN	0·12	0·24	0·23	0·1
	C_2H_4OH	−1·05	0·24	19·4(+ + +)	20·8
X_7	Cl	1·05	0·20	27·0(+ + +)	33·8
	Me	0·34	0·20	2·91	1·7
	OMe	0·22	0·20	1·18	1·1
Parent structure (μ)		4·80			

[a] Calculated group contributions, based on $C_H = 0.00$.
[b] Standard deviation for each explanatory variable.
[c] *F*-ratio and significance level: (+ + +) $P < 0.001$; (+ +) $P < 0.01$; (+) $P < 0.05$.
[d] Percentage of the total variance accounted for by each explanatory variable.

structure (μ) and of the substituents included in the correlation equations. In Table 10 are shown the calculated lightfastness values of the dyes, obtained by summing the contributions in Tables 6 and 7, and the residuals.

The results of the analysis suggest the following considerations:

(a) the validity of the additive model to account for the dependence of lightfastness on the structural features for this set of dyes;
(b) the important contribution of the parent structure (μ), higher for nylon than for wool, and the generally low effect of substitution;
(c) the most important positions are X_7 and X_5–X_6: they account for nearly 37% (X_7) and 31% (X_5, X_6) of the total variance for nylon and 55% (X_7) and 18% (X_5, X_6) for wool; some importance can also be attributed to the X_4 position for wool (*ca* 10% of the total variance);

TABLE 7
Calculated Group Contributions to Lightfastness on Wool, Based on $C_H = 0.00$ (Eqn 3)

Position	*Substituent*	C^a	s^a	F^a	R^2 *change*[a]
X_1	SO_3H	0·22	0·14	2·41	0·6
	Cl	0·12	0·10	1·30	0·6
X_3	Cl	0·22	0·16	1·97	4·2
X_4	NHCOPh	0·25	0·22	1·29	9·7
	NHCOMe	−0·08	0·16	0·24	0·1
	Me	−0·12	0·18	0·44	0·1
	Cl	−0·12	0·18	0·44	0·1
	NHCONHPh	−0·25	0·22	1·20	0·4
X_5	Et	0·35	0·15	5·46(+)	1·3
X_6	C_2H_4CN	0·05	0·18	0·06	0·3
	C_2H_4OH	−0·96	0·18	27·0(+ + +)	16·6
X_7	Cl	0·60	0·16	14·6(+ + +)	1·9
	Me	0·45	0·16	8·49(+ +)	3·1
	OMe	−1·05	0·16	45·6(+ + +)	49·6
Parent structure (μ)		4·10			

[a] See Table 6 for definition.

(d) from the examination of the statistically significant substituents it is clear that the Cl at X_7 plays the most important positive role and the C_2H_4OH at X_6 the most negative one on both the substrates; a strong negative influence is exerted by OMe at X_7 on wool; a moderate positive effect is displayed by Et at X_5;

(e) the three positions X_1, X_2, X_3, for the SO_3H group do not appear to differ significantly.

The lightfastness of other dyes of the series (not tested) containing the analysed substituents may be calculated from the group contributions listed in Tables 6 and 7. It follows that the dyes with the greatest calculated fastness on nylon should have Cl at X_7 and Et at X_5 (not included in the present analysis). In the case of wool, due to the smallness of the positive contribution values, it is difficult to suggest structures having higher fastness than those already tested.

Fastness to washing

Colour change data were used for the regression analysis. Equations 4 and 5 give satisfactory correlations, as judged from the statistical tests.

TABLE 8
Calculated Group Contributions to Fastness to Washing on Nylon, Based on $C_H = 0.00$ (Eqn 4)

Position	*Substituent*	C^a	s^a	F^a	R^2 *change*[a]
X_1	Cl	0·11	0·08	1·82	1·1
X_2	SO_3H	−0·07	0·10	0·51	0·2
X_3	Cl	0·34	0·13	6·36(+)	12·8
X_4	NHCONHPh	0·72	0·14	26·8(+ + +)	7·8
	NHCOPh	0·42	0·14	9·14(+ +)	4·0
	Cl	0·33	0·13	5·97(+)	2·5
	Me	0·16	0·13	1·44	0·4
X_6	C_2H_4CN	0·16	0·13	1·44	0·7
	C_2H_4OH	−0·17	0·13	1·64	1·4
X_7	Me	0·16	0·12	1·84	0·4
	Cl	−0·61	0·12	25·7(+ + +)	8·4
	OMe	−1·08	0·12	79·2(+ + +)	45·9
Parent structure (μ)		3·51			

[a] See Table 6 for definition.

TABLE 9
Calculated Group Contributions to Fastness to Washing on Wool, Based on $C_H = 0.00$ (Eqn 5)

Position	*Substituent*	C^a	s^a	F^a	R^2 *change*[a]
X_1	Cl	0·27	0·08	13·1(+ +)	3·0
	SO_3H	−0·27	0·10	7·39(+)	1·3
X_3	Cl	0·55	0·12	22·0(+ + +)	32·9
X_4	NHCONHPh	0·83	0·17	24·5(+ + +)	0·9
	NHCOPh	0·73	0·17	18·9(+ + +)	2·0
	Me	0·43	0·14	9·96(+ +)	0·8
	Cl	0·43	0·14	9·96(+ +)	2·2
	NHCOMe	−0·14	0·12	1·36	21·8
X_5	Et	−0·01	0·16	0·01	4·2
X_6	Et	0·40	0·14	8·57(+ +)	10·8
	C_2H_4CN	0·17	0·14	1·35	0·2
X_7	Cl	0·30	0·12	6·57(+)	12·4
	Me	0·31	0·12	7·07(+)	1·3
	OMe	0·31	0·12	7·07(+)	0·5
Parent structure (μ)		1·80			

[a] See Table 6 for definition.

TABLE 10
Calculated Values of Properties and Residuals

Dye no.	Fastness to light				Fastness to washing			
	Nylon		Wool		Nylon		Wool	
	Calcd[a]	Δ[b]	Calcd[a]	Δ[b]	Calcd[a]	Δ[b]	Calcd[a]	Δ[b]
1	5·73	0·27	5·18	0·32	3·32	−0·32	2·55	−0·05
2	5·63	0·37	4·68	0·32	3·62	−0·12	2·65	0·35
3	5·76	0·24	4·62	−0·12	2·82	0·18	1·99	0·01
4	5·58	−0·08	4·95	0·05	3·24	0·26	2·85	0·15
5	5·48	0·02	4·45	0·05	3·54	−0·04	2·95	0·05
6	5·96	0·04	4·65	−0·15	2·89	−0·39	1·96	0·04
7	5·78	0·22	4·98	0·02	3·32	0·18	2·82	0·18
8	5·68	0·32	4·48	0·02	3·62	−0·12	2·92	0·08
9	6·08	−0·08	4·77	0·23	3·01	−0·01	2·23	−0·23
10	5·90	−0·40	5·10	−0·10	3·43	0·07	3·09	−0·09
11	5·80	−0·30	4·60	−0·10	3·73	0·27	3·19	−0·19
12	6·20	−0·20	4·96	0·04	3·27	0·23	2·82	0·18
13	6·02	−0·02	5·29	−0·29	3·69	−0·19	3·68	−0·18
14	5·92	−0·42	4·79	−0·29	3·99	0·01	3·78	−0·28
15	4·86	−0·36	4·25	−0·25	3·51	−0·01	1·39	0·11
16	4·71	−0·21	4·02	−0·02	3·44	0·06	1·69	−0·19
17	4·91	0·09	4·06	−0·06	3·51	−0·01	1·66	−0·16
18	5·03	0·47	4·17	0·33	3·62	−0·12	1·93	0·07
19	5·15	0·35	4·36	014	3·89	0·11	2·52	−0·02
20	5·08	−0·08	3·20	−0·20	2·42	0·08	1·70	−0·20
21	4·93	0·07	2·98	0·02	2·35	−0·35	2·00	0·00
22	5·13	−0·13	3·01	−0·01	2·42	0·08	1·97	0·03
23	5·37	0·13	3·31	0·19	2·80	0·20	2·83	0·17
24	5·20	−0·20	4·70	−0·20	3·67	0·33	1·70	−0·20
25	5·05	−0·05	4·48	0·02	3·60	−0·10	2·00	0·00
26	5·25	0·25	4·51	−0·01	3·67	−0·17	1·97	0·03
27	5·49	0·01	4·81	0·19	4·05	−0·05	2·83	0·17
28	5·26	−0·26	4·48	0·02	3·51	−0·01	2·19	−0·19
29	5·39	0·11	4·60	−0·10	3·62	−0·12	2·46	0·04
30	5·50	0·50	4·79	0·21	3·89	0·11	3·05	−0·05
31	5·38	0·12	4·36	0·14	3·67	0·33	2·62	−0·12
32	5·50	0·00	4·48	0·02	3·78	−0·28	2·90	0·10
33	5·62	−0·12	4·66	−0·16	4·05	−0·05	3·48	0·02
34	5·38	0·12	4·36	0·14	3·84	0·16	2·62	−0·12
35	5·50	0·00	4·48	0·02	3·95	0·05	2·90	0·10
36	5·62	−0·12	4·66	−0·16	4·21	−0·21	3·48	0·02
37	5·33	−0·33	4·41	−0·41	3·51	−0·01	2·06	−0·06
38	5·45	0·05	4·52	−0·02	3·62	−0·12	2·33	0·17
39	5·57	−0·07	4·71	0·29	3·89	0·11	2·91	0·09
40	5·38	−0·38	4·53	−0·03	3·67	−0·17	1·62	−0·12
41	5·50	0·00	4·64	−0·14	3·78	0·22	1·90	0·10
42	5·62	0·38	4·83	0·17	4·05	−0·05	2·48	0·02
43	4·21	0·29	3·53	0·47	3·34	0·16	1·79	0·21
44	4·34	0·16	3·64	−0·14	3·45	0·05	2·06	−0·06
45	4·45	−0·45	3·83	−0·33	3·71	−0·21	2·65	−0·15
46	4·85	−0·35	4·13	−0·13	3·51	−0·01	1·80	0·20

[a] Values calculated from group contributions in Tables 6–9 respectively.
[b] Δ = Observed − calculated value. Observed values are reported in Table 4. Intermediate values on the scale have been expressed by adding 0·5 to the lowest value (e.g. 1–2 = 1·5).

Eqn	*Fibre*	*n*	*k*	*R*	*s*	R^2	*F*
4	Nylon-6.6	46	12	0·924	0·207	85·5	16·1(+ + +)
5	Wool	46	14	0·972	0·175	94·5	34·6(+ + +)

Tables 8 and 9 list the contributions of the parent structure and of the most significant substituents. The calculated values of fastness of each congener and the residuals are listed in Table 10.

The data in Tables 8 and 9 show some differences in the behaviour of dyeings on nylon and wool:

(a) the contribution of the parent structure is high for nylon, low for wool;
(b) X_7 is the most active position for nylon (*ca* 55% of the total variance); X_3 and X_4 are the most important ones for wool (*ca* 33% and 28% respectively of the total variance);
(c) if one examines the statistically significant substituents at the various positions, NHCONHPh, NHCOPh and Cl at X_4, and Cl at X_3, appear to be the most positive substituents for both the fibres; OMe and Cl at X_7 have a negative effect for nylon.

As already observed for lightfastness, the three positions for the SO_3H group appear to be indistinguishable.

From values in Table 8 the greatest calculated fastness on nylon corresponds to dyes with Cl at X_3, NHCONHPh at X_4, Me or H at X_7 (not contained within the present series). The dyes with the greatest fastness on wool, calculated from values in Table 9, are those with Cl at X_3, NHCONHPh or NHCOPh at X_4, Cl, Me or OMe at X_7 (some of which were included in the present analysis).

4. CONCLUSIONS

The effect of substituents on some important properties of 4-aminoazobenzene sulphonic acid dyes (50 members) has been examined. As expected, the long-wavelength absorptions were considerably affected by substituents, and strong bathochromic shifts (max. 98 nm) were obtained with suitable substitution patterns. Colour on dyeings on nylon-6.6 and on wool varied in the yellow–red range.

Lightfastness and fastness to washing data of dyed fabrics were analysed by the Fujita–Ban modification of the Free–Wilson approach, previously used in a series of arylazoindole sulphonic acid dyes. Also in this case good quantitative structure–property relationships were found and additivity of substituent contributions was confirmed. For this set of dyes lightfastness (both for nylon and for wool) and fastness to washing (for nylon) had high levels for the parent structure, with minor substituent effects. Fastness to washing for wool, which showed a low level for the parent structure, was positively influenced by weighty substituents.

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