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Synthesis and Properties of Acid Dyes Derived from 3-Hydroxy-2-naphthanilides

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ABSTRACT

Several red acid dyes, derivatives of 3-hydroxy-2-naphthanilides have been synthesised for use in the dyeing of polyamide fibres and wool. Diazotised aminoarylsulphonanilidesulphonic acids were used as diazo components. Electronic spectra data, dying and fastness properties are reported. It was found that the solubility of the dyes and their application characteristic were positively affected by sulphonanilide groups. As confirmed by the spectroscopic measurements, the dyes are in the form of dimers in aqueous solutions, whereas in water–acetone or water–ethanol systems they are monomers of azo and hydrazone structures.

1 INTRODUCTION

The use of amines containing arylsulphonanilide groups as diazo components permits the preparation of useful acid dyes, particularly suitable for dyeing polyamide fibres. They provide level dyeings with high fastness to water, washing, perspiration and rubbing, on wool and polyamide fibres from a weakly acidic dyeing bath.

It was of interest to examine the application and fastness properties of dyes containing sulphonamide and carboxamide groups. Such dyes can be prepared by using aminoarylsulphonanilidesulphonic acids as diazo components and derivatives of 3-hydroxy-2-naphthanilides as coupling components. It was also expected that this approach could provide acid reds with bright shades difficult to obtain by other methods.

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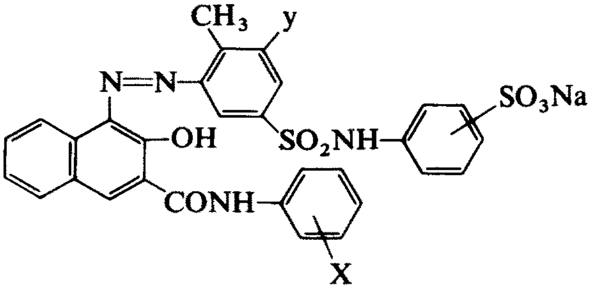
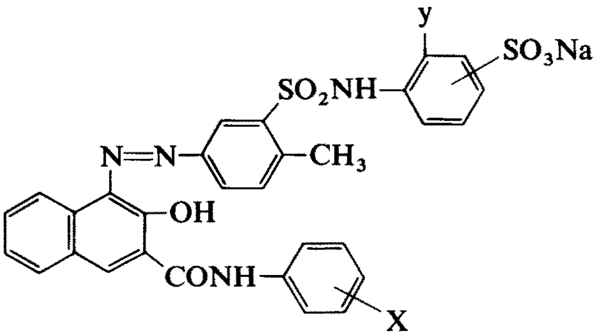


1

where:

$X = H, CH_3, OCH_3, NO_2$

$y = H, Cl$

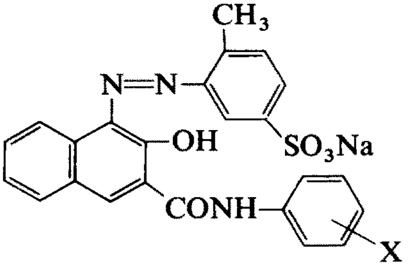


2

where:

$X = H, CH_3, OCH_3, NO_2$

$y = H, CH_3, OCH_3$



3

where:

$X = CH_3, NO_2$

The subject of this study is the synthesis of several monoazo acid dyes as shown by formulae 1, 2, and 3.

Electronic spectra data, dyeing, and fastness of the dyes were compared with reference to dyes of formula 3, which contain only a carboxamide group.

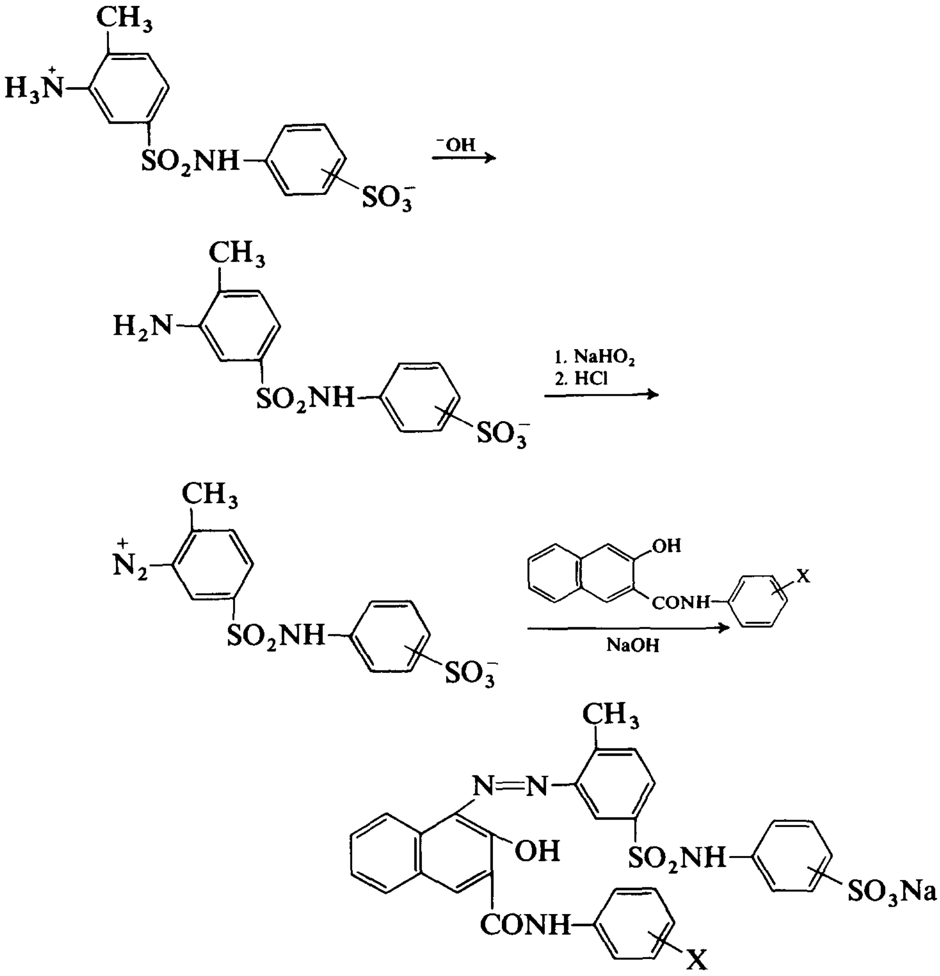
2 EXPERIMENTAL

The aminoarylsulphonanilidesulphonic acids were prepared by the previously described method.[1]

Coupling components (3-hydroxy-2-naphthanilides), being technical products, were purified by boiling in ethanol to remove traces of 3-hydroxy-

2-naphthoic acid. Their purity was confirmed by chromatography (Whatman 3 paper, eluent, pyridine:n-butanol:20% ammonia, 7:2:1 by vol).

The synthesis of dyes was carried out according to the scheme:



Diazotisation of the amines was effected by the 'inverted' procedure involving dropwise addition of an alkaline solution of the amine and sodium nitrite to ice-cooled hydrochloric acid. The coupling process was carried out in a basic system of pH 9·0–9·5 at a temperature of 0–5°C. The dyes were separated by salting out at 50–60°C. Yields were above 95%; product purity was measured by the vanadometric method and the sodium chloride content in the dried products was measured by the potentiometric method.

Relevant data are shown in Table 1.

TABLE 1
Structure of Dyes, Paper Chromatography R_f, and Purity

Dye no.	*Formula*	*Substituents*		*Position of sulphonic group*	*Paper chromatography* R_f*	*Purity*‡ (%)
		X	*y*			
D-1	1	2-OCH_3	H	3′	0·80	92·7
D-2	1	2-CH_3	H	2′	0·44	87·3
D-3	1	2-CH_3	H	3′	0·71	90·2
D-4	1	2-CH_3	H	4′	0·72	87·9
D-5	1	2-CH_3	Cl	3′	0·61	91·5
D-6	1	H	H	3′	0·84	89·7
D-7	1	3-NO_2	H	3′	0·71	90·8
D-8	2	2-OCH_3	H	2′	0·41	88·3
D-9	2	2-OCH_3	OCH_3	3′	0·81	92·1
D-10	2	2-OCH_3	CH_3	3′	0·82	91·1
D-11	2	2-CH_3	H	2′	0·57	90·0
D-12	2	2-CH_3	H	3′	0·81	87·9
D-13	2	2-CH_3	H	4′	0·77	89·3
D-14	2	2-CH_3	OCH_3	3′	0·80	91·4
D-15	2	2-CH_3	CH_3	3′	0·71	90·7
D-16	2	3-NO_2	H	2′	0·35	91·4
D-17	2	3-NO_2	H	3′	0·81	89·8
D-18	2	3-NO_2	H	4′	0·76	92·6
D-19	2	3-NO_2	OCH_3	3′	0·86	89·3
D-20	3	2-CH_3	—	—	0·37	92·4
D-21	3	3-NO_2	—	—	0·40	89·2

* Paper Whatman 3, eluent 1% brine:20% ammonia:pyridine 4:1:1 by vol.
‡ Analysis by vandometric method.

Absorption maxima of the dyes were measured in water, 50% ethanol solution, and, for some selected dyes, in water–acetone mixture with various acetone concentrations, at various pH values from 2 to 12. The measurements were performed with a Specord M-40 apparatus of Carl Zeiss-Jena within the concentration range from 2×10^{-4} to 1×10^{-6} mol/dcm^3. The results are listed in Tables 2 and 3 and illustrated in Figs 1, 2, 3, and 4.

Using dyes D-2, D-4, D-7, D-20 and D-21, at 2% depth on polyamide fibres, the dyebath exhaustion was examined at various pH values from 4·0 to 7·0 and liquor ratio of 1:40. The results are given in Table 4.

Polyamide-fibre knitted-fabric samples dyed to the 1/3 and 1/1 strength of reference specimen were used for colour-fastness determinations. Tests of dye fastness to water, acidic and alkaline perspiration, dry and wet rubbing, and washing at 40°C were carried out with the above samples.

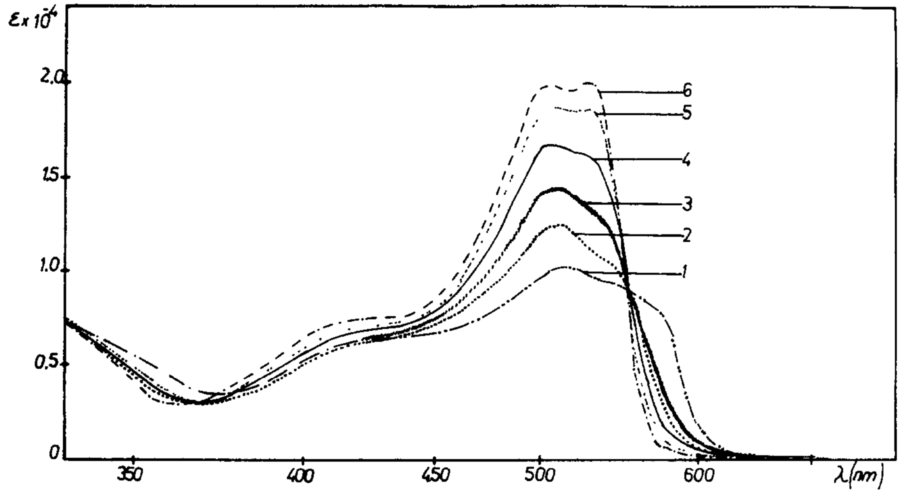


Fig. 1. Absorption spectra of dye D-3 in water and water–acetone solution at 20 ± 1 C. Dye concentration 5×10^{-5} mol/dcm^3. 1, water (— · —— · —), water–acetone: 2, 90:10 by vol (·······), 3, 80:20 by vol (▮▮▮), 4, 70:30 by vol (————), 5, 60:40 by vol (···········), 6, 10:90 by vol (— — · —).

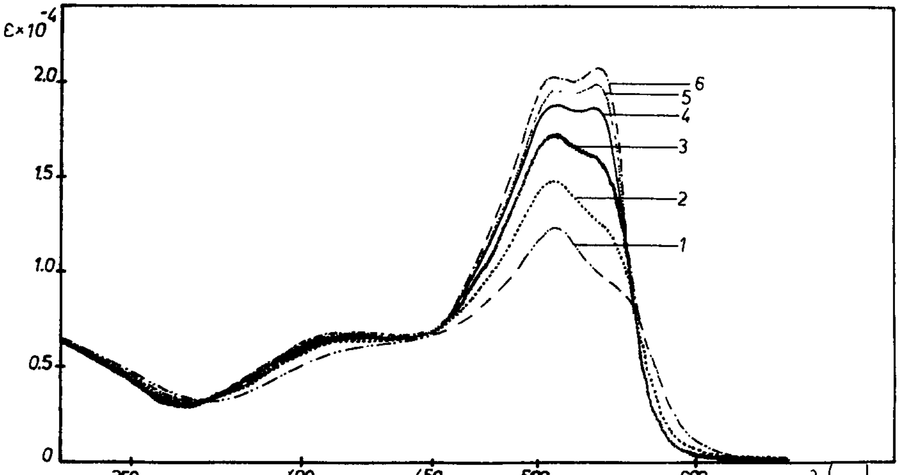


Fig. 2. Absorption spectra of dye D-20 in water and water–acetone solution at 20 ± 1 C 1, water (— · · — · · —), water–acetone: 2, 90:10 by vol (·······), 3, 80:20 by vol (▮▮▮), 4, 70:30 by vol (————), 5, 60:40 by vol (···········), 6, 10:90 by vol (— —· —).

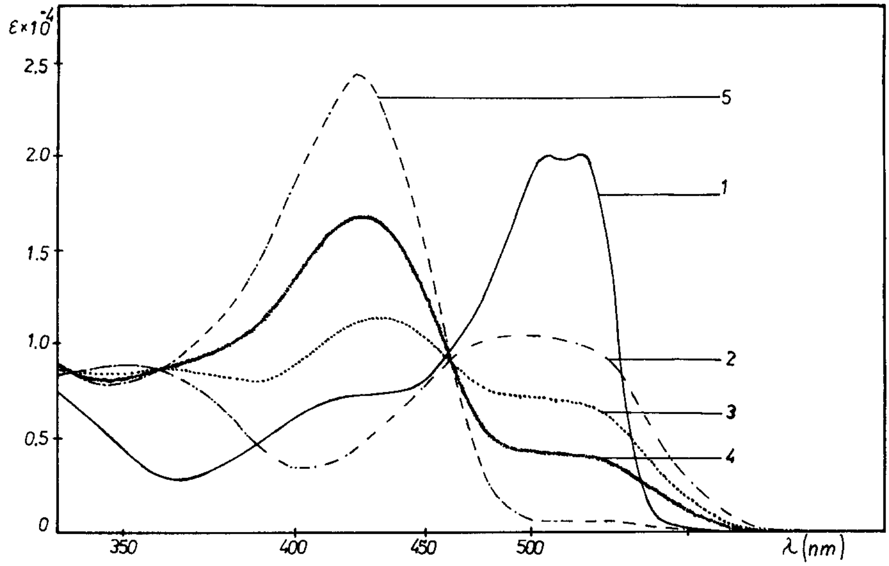


Fig. 3. Absorption spectra of dye D-3 in water–acetone, 50:50 by vol, and 0·01N NaOH–acetone 50:50 by vol at 20 ± 1°C. 1, water–acetone (———), 0·01N NaOH–acetone, 2, directly after preparing the solution (— · — · · —), 3, after 2 h (·······), 4, after 5 h (▬), 5, after 24 h (— — — · —).

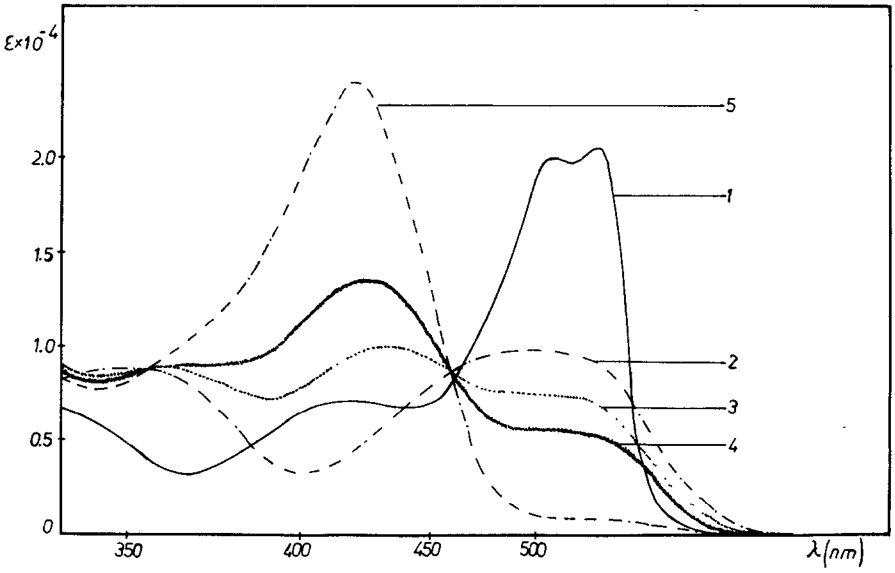


Fig. 4. Absorption spectra of dye D-20 in water–acetone, 50:50 by vol and 0·01N–NaOH–acetone, 50:50 by vol at 20 ± 1°C. 1, water–acetone (———), 0·01N NaOH–acetone, 2, directly after preparing the solution (— · — —), 3, after 2 h (·······), 4, after 5 h (▬), 5, after 24 h (— —·—).

TABLE 2

Absorption Maxima of Acid Dyes Derived from 3-Hydroxy-2-naphthanilides

Dye no.	*Water*		*Electronic spectral data* *50% ethanol*		*50% acetone, pH 12*	
	λ_{max} (*nm*)	ε_1 ($dcm^3\ mol^{-1}\ cm^{-1}$)	λ_{max} (*nm*)	ε ($dcm^3\ mol^{-1}\ cm^{-1}$)	λ_{max} (*nm*)	ε ($dcm^3\ mol^{-1}\ cm^{-1}$)
D-1	420·9	6 400	422·1	6 800		
	507·3	10 300	507·8	21 300		
			531·2	21 000		
D-2	421·7	6 300	424·3	6 800		
	515·0	10 200	509·0	18 500		
			533·8	18 700		
D-3	421·6	6 300	422·3	6 800	421·6	24 100
	514·4	10 200	510·2	20 000		
			534·2	20 000		
D-4	425·6	6 200	425·9	6 900		
	515·5	10 000	509·2	20·200	421·6	23 800
			530·8	20 200		
D-5	424·5	6 300	425·0	7 200		
	512·6	11 000	502·6	21 000		
			527·6	21 000		
D-6	421·8	6 200	423·4	7 200		
	506·3	10 100	506·3	21 300		
			531·6	21 300		
D-7	421·6	5 200	420·8	7 000		
	505·0	11 500	501·0	19 500	423·4	24 000
			525·6	19 700		

(*continued*)

TABLE 2—*contd.*

Absorption Maxima of Acid Dyes Derived from 3-Hydroxy-2-naphthanilides

Dye no.	*Water*		*Electronic spectral data* *50% ethanol*		50% *acetone, pH 12*	
	λ_{max} (*nm*)	ε ($dcm^3\,mol^{-1}\,cm^{-1}$)	λ_{max} (*nm*)	ε ($dcm^3\,mol^{-1}\,cm^{-1}$)	λ_{max} (*nm*)	ε ($dcm^3\,mol^{-1}\,cm^{-1}$)
D-8	422·0	6 400	422·6	7 000		
	514·0	10 600	508·9	21 000		
			532·0	21 200		
D-9	424·3	6 400	424·3	6 800		
	514·0	10 500	508·9	20 800		
			532·0	21·000		
D-10	424·3	6 400	424·3	6 800		
	513·7	10 400	509·3	20 600		
			532·7	20 800		
D-11	420·9	6 400	423·0	6 800		
	513·0	10 400	509·2	19 800		
			532·0	20 000		
D-12	420·9	6 400	422·8	6 800		
	513·0	10 800	509·0	21 000		
			532·0	21 200		
D-13	425·6	6 200	424·3	6 900		
	515·0	10 800	509·0	21 000		
			530·8	21 000		

	421·6	6 300	423·0	6 800		
D-14	514·4	10 600	508·6	21 200		
			530·8	21 200		
	421·7	6 400	422·8	6 800		
D-15	513·0	10 700	509·0	20 200		
			530·8	20 300		
	420·9	5 100	420·6	6 800		
D-16	505·0	11 900	505·4	18 800		
			529·0	18 800		
	421·6	5 000	421·0	6 900		
D-17	505·1	11 800	502·3	20 600		
			527·1	20 800		
	420·8	5 000	422·0	6 800		
D-18	505·1	11 800	502·0	20 000		
			527·0	20 000		
	422·0	4 900	422·0	6 800		
D-19	505·0	12 000	503·0	20 800		
			527·0	20 000		
	423·8	6 800	422·3	7 100		
D-20	515·5	12 900	514·4	20 600	421·6	24 000
			538·9	20 900		
	412·3	6 300	414·0	6 400		
D-21	424·3	7 300	506·0	18 600		
			529·7	18 800	423·4	23 500

TABLE 3

Dependence of Dye Molar Absorption on Concentration in Solution

Dye no.	*Concentration of dyes (mol/dcm^3)*	*Electronic spectral data*			
		Water		*50% ethanol*	
		λ_{max} (*nm*)	ε (*dcm^3 mol^{-1} (cm^{-1})*)	λ_{max} (*nm*)	ε (*dcm^3 mol^{-1} (cm^{-1})*)
D-3	2×10^{-4}	514·4	10 100		
	1×10^{-4}	514·4	10 200	510·2	19 000
	5×10^{-5}	514·4	10 500	510·2	20 000
	2×10^{-5}	514·4	10 500	510·2	20 600
	1×10^{-5}	514·4	11 400	510·2	20 800
	5×10^{-6}	515·3	11 600	509·2	21 000
	2×10^{-6}	517·6	11 600	509·2	21 000
	1×10^{-6}	519·8	11 600	509·2	21 000
D-4	2×10^{-4}	515·5	9 250		
	1×10^{-4}	515·5	9 500	509·2	18 200
	5×10^{-5}	515·5	9 700	509·2	19 200
	2×10^{-5}	515·5	10 000	509·2	20 200
	1×10^{-5}	516·5	10 000	509·2	20 200
	5×10^{-6}	516·5	10 200	509·2	20 600
	2×10^{-6}	518·7	10 500	509·2	20 800
	1×10^{-6}	518·7	11 000	509·2	20 800
D-7	2×10^{-4}	505·0	11 000		
	1×10^{-4}	505·0	11 000	501·0	18 600
	5×10^{-5}	505·0	11 000	501·0	19 000
	2×10^{-5}	505·0	11 500	501·0	19 500
	1×10^{-5}	505·0	11 500	501·0	20 000
	5×10^{-6}	505·0	12 000	501·0	20 400
	2×10^{-6}	505·0	12 500	501·0	20 800
	1×10^{-6}	505·0	12 500	501·0	21 000
D-20	2×10^{-4}	516·5	10 900		
	1×10^{-4}	516·5	11 550	514·4	19 200
	5×10^{-5}	515·5	11 900	514·4	20 300
	2×10^{-5}	515·5	12 900	514·4	20 600
	1×10^{-5}	514·4	13 500	514·4	20 800
	5×10^{-6}	512·3	16 500	514·4	21 000
	2×10^{-6}	512·3	18 000	514·4	21 000
	1×10^{-6}	512·3	19 200	514·4	21 000

TABLE 4
Relationship between Dyebath Exhaustion and pH

Dye no.	*pH*			
	4·0 (%)	*5·0* (%)	*6·0* (%)	*7·0* (%)
D-3	99·5	99·4	99·2	90·6
D-4	99·9	99·7	99·3	99·2
D-7	95·0	94·3	90·2	68·9
D-20	90·3	87·7	77·3	71·5
D-21	85·0	84·1	69·4	49·6

Light-fastness was tested in a Xenotest 150S (Heraeus). The results are given in Table 5.

3 RESULTS AND DISCUSSION

Brilliant red dyes suitable for dyeing polyamide fibre and wool were obtained by coupling diazotised aminoarylsulphonanilidesulphonic acids with 3-hydroxy-2-naphthanilides. The dyes with sulphonamide groups showed good solubility, to an extent that makes them applicable under technical conditions. The dyes derived from aminoarylsulphonanilide-3′ and 4′-sulphonic acids had a solubility of 50–80 g/dcm^3, while a solubility of 20–30 g/dcm^3 was shown by the dyes from aminoarylsulphonanilide-2′-sulphonic acid. The water-solubility of the reference dye D-20 was 7 g/dcm^3 and that for D-21 3 g/dcm^3, which makes them unsuitable for application under technical conditions.

Our dyeing experiments showed that dyes derived from the anilide, toluidide, and *o*-anisidide of 3-hydroxy-2-naphthoic acid were almost completely exhausted from the dyebath. Derivatives of the 3′-nitroanilide of 3-hydroxy-2-naphthoic acid showed somewhat lower exhaustion; for example, the degree of exhaustion of D-7 was 95·0% and 90·2% at pH 4·0 and 6·0, respectively. Dyes without sulphonamide groups exhausted from the dyebath to a much lower extent, e.g., the corresponding values for D-21 are 85% and 69·4% at pH 4 and 6, respectively, which illustrates the beneficial effect of the sulphonamide groups. It should be further noted that dyes with such substituents give level dyeings on polyamide fibres, which is not possible with the reference dyes, regardless of the pH of the dyebath.

The dyes containing sulphonamide groups have very good fastness to water, washing, perspiration, and rubbing, while the reference dyes D-20 and D21 show somewhat lower fastness.

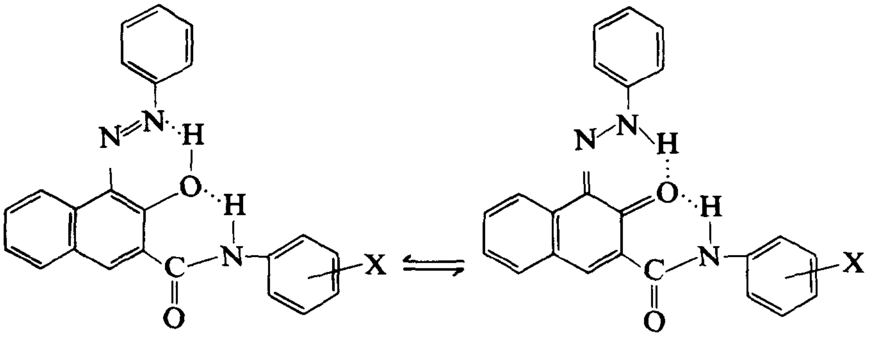
TABLE 5
Fastness Properties of Acid Dyes Derived from 3-Hydroxy-2-naphthanilides

Dye no.							*Perspiration*									
	Water			*Washing*			*Alkaline*			*Acid*			*Rubbing*		*Light-fastness*	
	1	*2*	*3*	*1*	*2*	*3*	*1*	*2*	*3*	*1*	*2*	*3*	*Dry*	*Wet*	*1/1*	*1/3*
D-1	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5–6	4–5
D-2	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5
D-3	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5
D-4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5
D-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5–6	4–5
D-6	5	5	5	5	5	5	5	5	5	5	4–5	5	5	5	5	4
D-7	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	3–4
D-8	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5–6	4–5
D-9	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5–6	4–5
D-10	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5–6	4–5
D-11	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5
D-12	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5
D-13	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5
D-14	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5–6	4–5
D-15	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5
D-16	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	3–4
D-17	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	3–4
D-18	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	3–4
D-19	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	3–4
D-20	5	4–5	5	5	5	5	5	5	5	5	5	5	5	4–5	4	3–4
D-21	5	4–5	5	5	5	5	5	5	5	5	5	5	5	4–5	3–4	3–4

1, Change of shade of dyed fabric; 2, staining nylon; 3, staining wool.

Light-fastness of the dyes varied from 5–6 to 3–4, and was considerably affected by the nature of the coupling component. The highest fastness values were shown by derivatives of 2′-methoxyanilide and the lowest by the 3′-nitroanilide of 3-hydroxy-2-naphthoic acid. The diazo component also has a significant influence; dyes with sulphonamide groups have much higher light-fastness than the corresponding reference dyes D-20 and D-21.

The electronic spectra of the dyes in 50% ethanol and 50% acetone show two absorption bands (Table 2, Figs 1 and 2), at 420–425 nm (I) and at 502–532 (II). According to the results of Burawoy,[2] Skulski,[3-5] Kelemen,[6-9] Ball, Nicholls,[10] and Stepanov,[11-13] the first brand is relatable to the azo structure, and the other to the hydrazone configuration. However, about 25% of the dye remains in the azo structure.



I II

It is interesting to note that the shift in absorption maxima of the dyes between the azo and hydrazone structure is accompanied by a bathochromic shift of about 100 nm. Such a large bathochromic effect is not usually observed in derivatives of benzene, pyridone, and pyrazolone and is associated with the presence of the naphthoquinoimine moiety in the hydrazone structure of the dye.

The hydrazone band is resolved into two maxima, 502–510 nm and 527–534 nm (Figs 1 and 2).

Hsieh and his co-workers[14] in their spectroscopic studies on 4-(3′,5′-dinitro-2′-hydroxyphenylazo)-3-hydroxy-2-naphthanilide and its sodium salt have found that separation of that band is brought about by the monomer–dimer equilibrium.

In the dyes under investigation, the presence of sulphonamide and carbamide groups favours aggregation, while the sulphonic group should facilitate non-aggregated molecules in solution. These assumptions are confirmed by spectroscopic measurements of aqueous dye solutions, in which the dyes are in the form of aggregates, mostly dimers, being stable even when diluted (1×10^{-6} mol/dcm^3). In contrast, the reference dye D-20 is disaggregated as its concentration decreases. The absorption spectra of dyes in water–acetone or water–ethanol solutions (above 50% of organic solvent) show that the dyes are practically disaggregated, and hence the absorption spectra correspond to the monomeric-dye molecule.

Disaggregation of dimers is revealed, as a rule, by doubling or increase in absorption if the Lambert–Beer law holds good. The dyes under study satisfy the law within a wide concentration range in water–acetone or water–ethanol systems. The λ_{max} at 530 nm present in the hydrazone band cannot therefore be ascribed to a dimer. This band is associated with the naphthoquinoimine system occurring in the hydrazone structure. The separation of the hydrazone band in the absorption spectrum suggests that the hydrazone structure occurs in two polar forms with quite a high stability. One may assume that the naphthoquinoimine configuration is maintained in both forms, since a shift to the azo structure would change the character of the absorption curve. Examination of the pH effect on the absorption curve of dyes D-3 and D-20 in 50% acetone shows that the absorption curve is not changed over the pH range from 2 to 10, but, when the pH is increased to 12 by adding NaOH (acetone: 0·01 N NaOH, 50:50 by vol) absorption in the hydrazone band is decreased by 50% with simultaneous disappearance of the absorption in the azo band. This would indicate the formation of that structure which is stabilized by the dimer. However, this structure alters with time; the hydrazone band disappears gradually, and the azo band starts to appear, reaching a maximum after 24 h, accompanied by complete disappearance of the hydrazone band. The molar absorption reaches a maximum, which suggests that the anion of the azo structure formed is a monomer. Absorption curves (measured against time) show an isosbestic point at $\lambda = 460{\cdot}4$ nm for dyes D-3 and D-20, which would point to changes taking place inside the dye molecule. Under these conditions, the dye possesses an azo structure, with the hydroxy group being in anionic form. Reneutralisation of the dye solution brings about a decrease in absorption, and formation of aggregates of the azo structure, since λ_{max} is not changed. Only heating of the solution results in the hydrazone structure. Spectroscopic measurements confirm the high stability of the dyes within a wide range of pH, and consequently the exceptional high wet-fastness of dyeings (acidic and alkaline perspiration, water).

Which structure of the dyes is responsible for the separation of the hydrazone band and the tendency to form stable dimers will be the subject of further studies.

4 CONCLUSION

By coupling diazotised aminoarylsulphonanilidesulphonic acids with 3-hydroxy-2-naphthanilides a group of useful brilliant red acid dyes was obtained. These dyes are suitable for dyeing polyamide fibres from a weakly acidic dyebath, owing to their high levelling power. The dyes have good water-solubility and their wet fastness (to water, washing, perspiration, and rubbing) is very high.

Spectroscopic measurements indicate that, in aqueous solution, the dyes are in the form of aggregates with a hydrazone configuration, whereas, in aqueous acetone or aqueous-ethanol (50:50 by vol), they are disaggregated. The dye structure is not affected by changes in pH from 2 to 10; only at pH 11 or above do the dyes shift to an azo configuration.

REFERENCES

1. Blus, K. & Kraska, J., *Dyes and Pigments*, **9** (1988) 305.
2. Burawoy, A., Salem, A. G. & Thompson, A. R., *J. Chem. Soc.*, **12** (1952) 4793.
3. Skulski, L. & Urbański, T., *Bull. Acad. Pol. Sci.*, **10** (1960) 561.
4. Skulski, L., *Wiązanie wodorowe*, PWN, Warsaw, 1963, p. 73.
5. Skulski, L. & Urbański, T., *Rocz. Chem.*, **36** (1962) 801.
6. Kelemen, J., *Dyes and Pigments*, **2** (1981) 73.
7. Kelemen, J., Moss, S., Souter, H. & Winkler, T., *Dyes and Pigments*, **3** (1982) 27.
8. Kelemen, J., Kormany, G. & Rihs, G., *Dyes and Pigments*, **3** (1982) 249.
9. Kelemen, J., Moss, S. & Glitsch, S., *Dyes and Pigments*, **5** (1984) 83.
10. Ball, P. & Nicholls, C. H., *Dyes and Pigments*, **3** (1982) 5.
11. Traver, V. F., Stepanov, B. J. *et al.*, *Zh. Org. Khim.*, **16**(5) (1980) 1047.
12. Stepanov, B. J., Traver, V. F. *et al.*, *Zh. Org. Khim.*, **17**(6) (1981) 1291.
13. Traver, V. F., Stepanov, B. J. *et al.*, *Zh. Org. Khim.*, **21**(3) (1985) 579.
14. Hsieh, B. R., Desilets, D. & Kazmaier, P. M., *Dyes and Pigments*, **14** (1990) 165.