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Synthesis and Properties of Acid Dye Derivatives of Arylsulphonanilides

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SUMMARY

Thirty-five acid dyes suitable for dyeing wool and polyamide fibres were synthesized, using derivatives of arylsulphonanilides prepared from o-nitrotoluene or chloronitrotoluene. As coupling components, derivatives of 1-phenyl-3-methylpyrazolone-5 and 2-naphthol were used. Fastness and colour properties of the prepared dyes were determined. It was found that some of the prepared dyes on polyamide fibres show batho- and hypso-chromic effects as well as hypo- and hyper-chromic effects during testing of their fastness to washing and to acid and alkaline perspiration.

Spectroscopic examinations and determination of pK_a of the sulphonamide and hydroxyl groups of the dyes showed that the observed changes are associated with aggregation or disaggregation of the dyes on fibres or with a change in the azo–hydrazone equilibrium. Some of the prepared dyes are characterized by very good dyeing and fastness properties.

1. INTRODUCTION

Specially selected acid dyes, apart from metal-complex dyes, represent one of the main groups of dyes used for dyeing wool and polyamide fibres. Very good dyeing properties as well as high fastness are required from these dyes. Acid dyes which can meet these requirements have been continuously studied[1,2] and in many cases descriptions have been given of attempts to synthesize new intermediates or to make use of such

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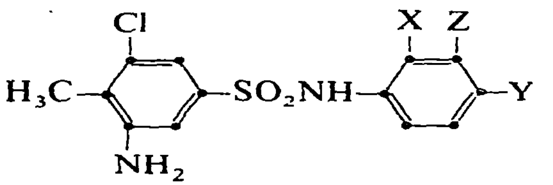
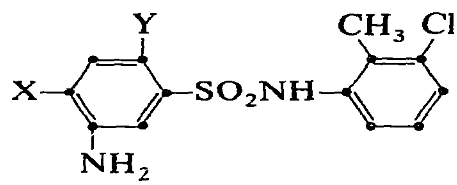
compounds as *o*-nitrotoluene or 2-chloro-6-nitrotoluene which are formed as by-products in various technological processes but which have not been, as yet, fully utilized.

The subject of this study is the synthesis and evaluation of monoazo dyes derived from the use as diazo components of amines of formulae **1**, **2**



1



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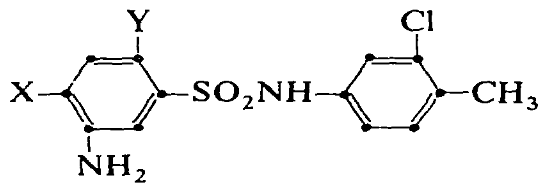


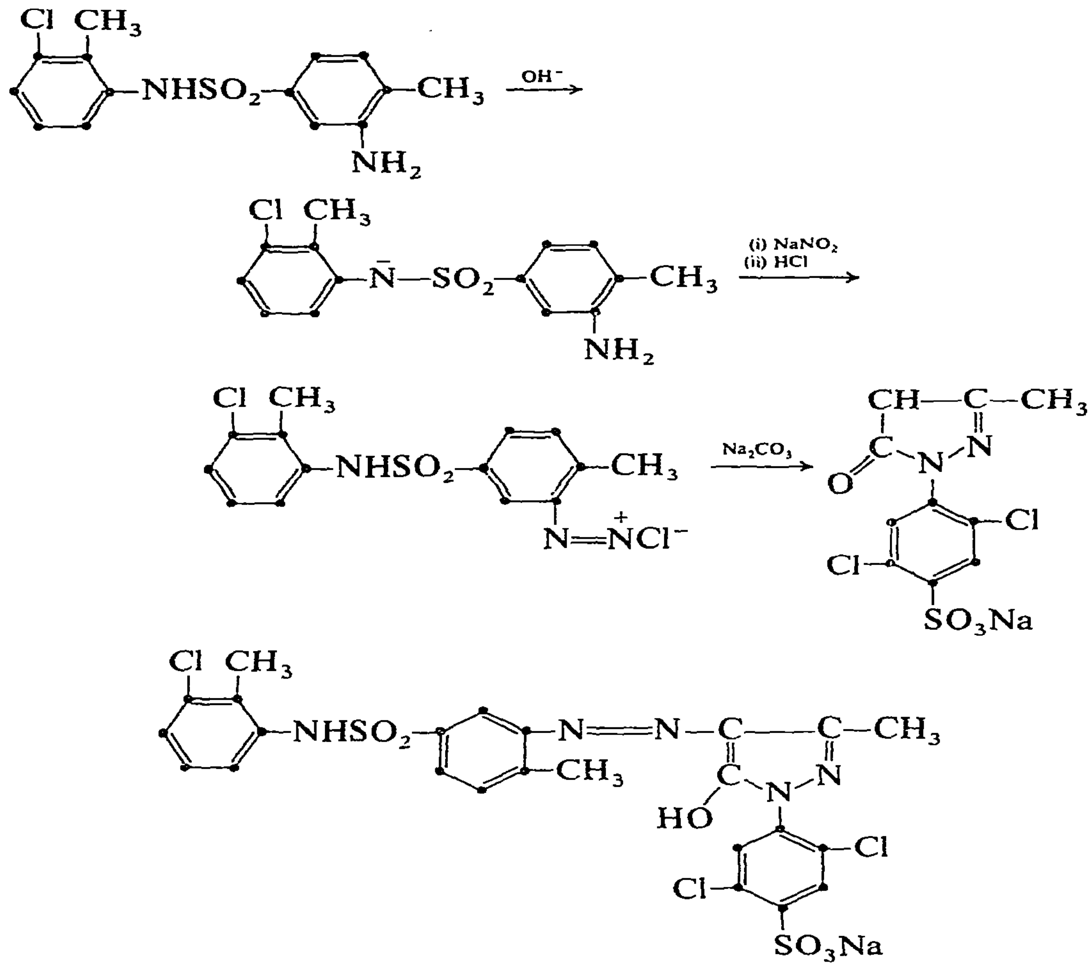
3

X and Y = H, CH_3, OCH_3 or Cl
Z = H or Cl

and **3**. The following compounds were used as coupling components: 1-(2′,5′-dichloro-4′-sulphophenyl)-3-methylpyrazol-5-one (**I**), 1-(4′-sulphophenyl)-3-methylpyrazol-5-one (**II**), 1-hydroxynaphthalene-4-sulphonic acid (**III**), 1-benzamido-8-naphtho-3,6-disulphonic acid (**IV**) and 7-amino-1-hydroxynaphthalene-3-sulphonic acid (**V**).

2. EXPERIMENTAL

The amines were prepared as previously described.[3] The coupling components were industrial products which were purified by dissolving their sodium salts in water, active carbon treatment and salting out. This procedure was repeated until chromatographically pure products were obtained. The synthesis of dyes was carried out according to general scheme 1.



Scheme 1

Diazotization of amines was carried out by the 'inverted' method, i.e. the alkaline solution of amine and sodium nitrite was dropped into hydrochloric acid and ice. Couplings with coupling components **I**, **II**, **III** and **IV** were carried out in a weakly alkaline medium and those with coupling component **V** in an acid medium (pH 3–6). The dyes were separated from the reaction mixture by salting out with sodium chloride (5–10 % by vol.) at 60–70 °C. The filtered dyes were washed with 5 % brine, dried, and subjected to vanadometric analysis. Yields of dye were in the region of 85–95 %. Purity of the prepared dyes was examined by

TABLE 1
Structure of Dyes, Paper Chromatography R_F and Purity

Dye no.	*Diazo component*				*Coupling component*	*Paper chromatography R_F*	*Purity*[a] (%)	*Colour*
	Amine	*Substituents* X	Y	Z				
D-1	1	CH_3	CH_3	H	I	0·82	63·4	Yellow
D-2	1	CH_3	H	H	I	0·80	68·4	Yellow
D-3	1	H	CH_3	H	I	0·80	66·4	Yellow
D-4	1	H	H	H	I	0·76	77·2	Yellow
D-5	1	CH_3	H	H	I	0·84	67·8	Yellow
D-6	1	H	OCH_3	H	I	0·84	84·1	Yellow
D-7	1	CH_3	H	Cl	I	0·69	91·2	Yellow
D-8	2	H	H	—	I	0·92	85·4	Yellow
D-9	2	CH_3	H	—	I	0·93	67·4	Yellow
D-10	2	H	CH_3	—	I	0·93	87·0	Yellow
D-11	3	H	H	—	I	0·90	89·6	Yellow
D-12	3	CH_3	H	—	I	0·92	84·0	Yellow
D-13	3	H	CH_3	—	I	0·92	92·7	Yellow
D-14	2	CH_3	H	—	II	0·87	77·6	Yellow
D-15	1	CH_3	CH_3	H	III	0·72	79·7	Red orange
D-16	1	CH_3	H	H	III	0·68	72·5	Red orange
D-17	1	H	CH_3	H	III	0·65	86·3	Red orange
D-18	1	H	H	H	III	0·69	91·7	Red orange
D-19	1	OCH_3	H	H	III	0·70	90·0	Red orange
D-20	1	H	OCH_3	H	III	0·70	90·0	Red orange
D-21	1	CH_3	H	Cl	III	0·55	71·6	Red orange
D-22	2	H	H	—	III	0·72	80·1	Red orange
D-23	2	CH_3	H	—	III	0·76	89·3	Red orange
D-24	2	H	CH_3	—	III	0·76	94·4	Red orange
D-25	3	H	H	—	III	0·68	71·2	Red orange
D-26	3	CH_3	H	—	III	0·72	93·4	Red orange
D-27	3	H	CH_3	—	III	0·72	95·5	Red orange
D-28	2	CH_3	H	—	V	0·72	85·5	Red
D-29	1	CH_3	CH_3	H	IV	0·44	94·5	Blue red
D-30	1	CH_3	H	H	IV	0·44	90·2	Blue red
D-31	1	H	CH_3	H	IV	0·44	96·8	Blue red
D-32	1	H	H	H	IV	0·45	97·1	Blue red
D-33	1	OCH_3	H	H	IV	0·42	93·4	Blue red
D-34	1	H	OCH_3	H	IV	0·42	91·7	Blue red
D-35	1	CH_3	H	Cl	IV	0·38	93·9	Blue red

[a] Analysis by vanadometric method.

TABLE 2
Absorption Spectroscopic Maxima of the Acid Dyes Derived from Arylsulphonanilides

Dye no.	*Electronic spectral data*							
	Water		*50% Pyridine*		*50% Ethanol, pH 4·0*		*50% Ethanol, pH 10·0*	
	λ_{max} (*nm*)	ε ($dcm^3\ mol^{-1}\ cm^{-1}$)	λ_{max} (*nm*)	ε ($dcm^3\ mol^{-1}\ cm^{-1}$)	λ_{max} (*nm*)	ε ($dcm^3\ mol^{-1}\ cm^{-1}$)	λ_{max} (*nm*)	ε ($dcm^3\ mol^{-1}\ cm^{-1}$)
D-1	402	14700	422	17700	352 397	11900 16700	402	18600
D-2	401	13800	422	16800	352 396	12000 16300	401	17100
D-3	403	18300	422	18200	355 397	12000 16100	402	18600
D-4	402	18500	422	17400	354 397	12000 17600	402	19300
D-5	403	17600	422	18700	355 400	11800 17200	402	19000
D-6	403	16000	422	17400	355 399	11600 16000	403	17400
D-7	403	15300	422	16300	353 396	12100 16700	401	18300
D-8	393	14900	406	15500	350 391	12500 15400	395	16400
D-9	411	18000	411	16600	350 408	10400 17000	394	17600
D-10	407	15900	417	17400	352 409	10400 16000	392	16500

(continued)

TABLE 2—*contd.*

Dye no.	Water λ_{max} (nm)	Water ε ($dm^3\,mol^{-1}\,cm^{-1}$)	50% Pyridine λ_{max} (nm)	50% Pyridine ε ($dm^3\,mol^{-1}\,cm^{-1}$)	50% Ethanol, pH 4·0 λ_{max} (nm)	50% Ethanol, pH 4·0 ε ($dm^3\,mol^{-1}\,cm^{-1}$)	50% Ethanol, pH 10·0 λ_{max} (nm)	50% Ethanol, pH 10·0 ε ($dm^3\,mol^{-1}\,cm^{-1}$)
D-11	395	10 900	406	14 300	350	11 600	392	14 800
					391	14 100		
D-12	411	11 700	409	15 200	352	10 000	390	16 500
					407	15 400		
D-13	409	9 100	417	15 500	350	9 800	390	15 100
					407	14 600		
D-14	395	13 200	408	14 500	350	8 600	394	15 800
					399	16 100		
D-15	310	6 500	365	5 900	370	9 000	495	15 700
	495	11 400	508	14 500	497	15 900		
D-16	370	6 500	365	5 900	370	8 200	495	13 900
	495	11 400	508	14 300	498	14 800		
D-17	370	6 400	365	6 600	370	10 100	496	16 300
	495	9 800	509	16 400	498	16 700		
D-18	368	7 100	367	6 100	370	9 600	496	15 900
	493	13 300	508	16 500	497	16 200		
D-19	370	9 000	365	5 900	370	10 000	496	16 700
	494	17 600	509	16 700	498	16 900		
D-20	370	7 800	365	6 000	370	9 900	495	17 300
	494	16 700	508	17 200	497	17 600		

D-21	370	6300	366	5800	370	9800	495	15800
	498	11600	508	15300	497	16100		
D-22	370	8700	365	6300	367	9000	494	14700
	488	18000	502	16700	492	14100		
D-23	370	7100	365	4700	370	8200	489	13800
	495	15400	509	15100	499	15600		
D-24	370	7700	365	5000	368	8900	489	13800
	495	16100	508	15600	499	15600		
D-25	368	7000	365	5400	366	8200	495	14300
	489	12600	502	14200	492	13700		
D-26	370	6000	368	5400	370	7300	492	12100
	496	9400	510	15300	498	13700		
D-27	370	6100	368	5500	368	7300	492	13100
	495	12100	508	15600	497	13100		
D-28	497	11700	517	14300	501	15400	506	15000
D-29	385	6700	385	4800	385	7800	490	12800
	514	16000	530	19500	526	19900		
D-30	385	7000	385	5000	385	8400	490	14200
	510	19600	530	21000	526	21800		
D-31	385	7100	385	4800	385	8100	489	12400
	514	20200	530	19900	525	21100		
D-32	385	7000	385	5000	385	8300	490	14500
	512	21000	530	20900	526	21800		
D-33	385	7300	385	5100	385	8400	490	14200
	511	20000	530	20900	526	21500		
D-34	385	6900	385	5000	385	8300	490	13500
	514	18800	530	20600	526	21500		
D-35	385	6800	385	4800	383	8800	490	12300
	514	11900	531	19800	526	20000		

TABLE 3
Technical Properties of the Acid Dyes Derived from Arylsulphonanilides

Dye no.	*Water*			*Washing*			*Perspiration*						*Rubbing*		*Lightfastness*	
							Alkaline			*Acid*						
	1	*2*	*3*	*1*	*2*	*3*	*1*	*2*	*3*	*1*	*2*	*3*	*Dry*	*Wet*	*1/1*	*1/3*
D-1	4–5	5	5	4†	5	5	4–5	4	4–5	$\underleftarrow{3}$	5	5	5	5	6	5
D-2	4–5	5	5	4†	5	5	4–5	4	4	$\underleftarrow{3}$	4–5	4–5	5	5	6	5
D-3	4–5	5	5	4–5	5	5	4†	4	4–5	$\underleftarrow{3}$	5	5	5	5	6	5
D-4	4–5	5	5	4†	5	5	4†	3–4	4–5	$\underleftarrow{2\text{–}3}$	5	5	5	5	5–6	5
D-5	4–5	5	5	4†	4–5	4–5	4–5	3–4	4–5	$\underleftarrow{2\text{–}3}$	4–5	4–5	5	5	6	4–5
D-6	4–5	5	5	4†	5	5	4†	3–4	4–5	$\underleftarrow{3}$	4–5	5	5	5	6	4–5
D-7	4–5	5	5	4–5	5	5	4–5	4	4–5	$\underleftarrow{2\text{–}3}$	4–5	5	5	5	5–6	4–5
D-8	4	5	5	4†	5	5	4	3–4	4	$\underleftarrow{2\text{–}3}$	4–5	5	5	5	5–6	5
D-9	4–5	5	5	4–5	5	5	4–5	4	4–5	4–5	5	5	5	5	6	5
D-10	4–5	5	5	4–5	5	5	4–5	4	4–5	4–5	5	5	5	5	6	5–6
D-11	4	5	5	4–5	5	5	4	3–4	4–5	$\underleftarrow{3}$	4–5	5	5	5	5–6	5
D-12	4–5	5	5	4–5	5	5	4–5	4	4–5	4–5	4–5	5	5	5	6	5–6
D-13	4–5	5	5	4–5	4–5	5	4–5	4–5	5	4–5	4–5	5	5	5	6	5–6
D-14	4–5	5	5	5	5	5	5	4–5	4–5	4–5	4–5	4–5	5	5	6	5
D-15	4–5	5	5	4	4–5	5	4–5	4	4–5	4–5	4–5	4–5	5	5	3–4	3

D-16	4-5	5	5	4	5	5	4-5	3-4	4-5	4 ←	4-5	4-5	4-5	4-5	3-4	3-4
D-17	4-5	5	5	4	4-5	5	4	3-4	4-5	4 ←	4-5	5	4-5	4-5	4	3-4
D-18	4-5	5	5	4	5	5	4	3-4	4-5	4 ←	4-5	5	5	5	4	3-4
D-19	4-5	5	5	4	4-5	5	4-5	3-4	4-5	4-5	4-5	4-5	5	5	4	3-4
D-20	4-5	4-5	5	4	4-5	5	4-5	3-4	4-5	4-5	4-5	4-5	5	5	4	3
D-21	4-5	5	5	4-5	5	5	4-5	4-5	4-5	4 ←	5	5	5	5	3-4	3-4
D-22	4-5	4-5	5	4-5	4-5	5	4-5	3-4	4-5	4 ←	4-5	4-5	5	5	4	3
D-23	4-5	5	5	4	5	5	4-5	3-4	4-5	4-5	4-5	4-5	5	5	3-4	3-4
D-24	4-5	4-5	5	4-5	4-5	5	4-5	4	4-5	4-5	4-5	4-5	5	5	4	3-4
D-25	4-5	5	5	4	5	5	4-5	3-4	4-5	4 ←	4-5	5	5	5	4	3-4
D-26	4-5	5	5	4	5	5	4	4	4-5	4-5	5	5	5	5	4	3-4
D-27	4-5	4-5	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5	5	4-5	4-5	4	3-4
D-28	5	4-5	5	4-5	4-5	5	5	4-5	4-5	5	4-5	5	5	5	6-7	5-6
D-29	4-5	5	5	4‡	5	5	3-4‡	5	5	3-4† →	5	5	5	5	3-4	3
D-30	4-5	5	5	4‡	5	5	3-4‡	4-5	5	3-4† →	5	5	5	5	3-4	3
D-31	4-5	5	5	4‡	5	5	3-4‡	4-5	5	3† →	5	5	5	5	3-4	3
D-32	4-5	5	5	4‡	5	5	3‡	4-5	4-5	3† →	4-5	5	5	5	3-4	3
D-33	4-5	5	5	4‡	5	5	3‡	4-5	4-5	3† →	5	5	5	5	3-4	3
D-34	4-5	5	5	4‡	5	5	3‡	4	5	3† →	4-5	5	5	5	3-4	3
D-35	4-5	5	5	4‡	5	5	3‡	4-5	5	3-4† →	5	5	5	5	3-4	3

←, Hypsochromic effect; →, bathochromic effect; †, hyperchromic effect; ‡, hypochromic effect; *1*, change of shade of dyed fabric; *2*, staining nylon; *3*, staining wool.

chromatography using Whatman 3 paper and *n*-butanol–acetic acid–water (4:1:5 by vol.) as eluent. Relevant data are given in Table 1.

Absorption spectra of the dyes were taken with a Specord UV–Vis (Carl Zeiss, Jena) using as solvents water, 50% pyridine and 50% ethanol at pH 4·0 and 10·0. Pyridine was used as a highly polar and disaggregating solvent. 50% Ethanol at pH 4 and 10 was used because the washing test and the alkaline and acid perspiration tests are carried out at pH 9·3, 8·0 and 5·5, respectively. It had also been noted that below pH 4 and over pH 10 no changes in the absorption curves were observed. The results are given in Table 2.

Dyeings on knitted polyamide fabric were performed on an Ahiba apparatus (Hanau) to a strength of 1/3 or 1/1 of reference standard. The washing test was carried out in a Launder-Ometer (Atlas Electric Devices Co., Chicago). The lightfastness was estimated with a Xenotest 450. All the fastness tests were carried out according to British Standards.[4] The results are given in Table 3.

3. DISCUSSION OF RESULTS

Maximum dye uptake (94–100%) by polyamide was obtained by dyeing at pH 4–6 at a strength of 1/1 in relation to the reference standard. Dyeing at pH below 4 resulted in a slight decrease in dye uptake and at pH above 6, a considerable decrease in dye uptake was often observed. Optimal dye uptake occurred at pH 5–6. Dye uptake values in milliequivalents per kg of fibre, under the conditions used were: for yellows **D-1** to **D-14**, from 15 to 20; for oranges **D-15** to **D-28**, from 14 to 16; and for reds **D-29** to **D-35**, from 8 to 10. The effect of pH of dyebath on the degree of its exhaustion is illustrated by the data given in Table 4.

The fastness of dyed knitted polyamide fabrics to water, washing, alkaline and acid perspirations and rubbing were found to be very high irrespective of degree of sulphonation in the coupling component. Only the fastness to alkaline perspiration showed some variation. Several dyes stained the accompanying wool fibre to a slight extent, while some of them coloured polyamide fibres. During the fastness testing, particularly to washing and to acid and alkaline perspirations, many dyes showed changes in hue or depth, depending on the coupling components used as well as substituents present in diazo components. Dyes derived from 1-(4′-sulpho-2′-,5′-dichlorophenyl)-3-methylpyrazolone-5 (**I**) as coupling

TABLE 4
The Effect of pH of Dyebath on the Degree of Exhaustion: Dyes on Polyamide Fibre

Dye no.	*pH*			
	4	*5*	*6*	*7*
D-7	99	99	90	69
D-14	98	97	94	75
D-18	97	94	88	63
D-28	100	100	99	97
D-29	95	94	87	61

component and amine **1** (**D-1** to **D-7**) and amine **2** (**D-8**) as diazo components, showed hyperchromic effects during testing the fastness to washing (increase in the dye strength and its brightness). This phenomenon was also observed in the case of three yellow dyes during the testing of their fastness to alkaline perspiration. However, during the testing of the fastness to acid perspiration, a hypsochromic effect was observed without changes in depth of shade. These effects were observed to a considerably less extent with dyes derived from 1-naphthol-4-sulphonic acid. Dyes **D-16** to **D-18, D-21, D-22** and **D-26** showed a slight hypsochromic effect during testing of the fastness to acid perspiration. Polyamide fibres dyed with dyes prepared from 1-benzamido-8-naphthol-3,6-disulphonic acid (**IV**) during testing of the fastness to washing and alkaline perspiration show a clear hypochromic effect, and during testing of the fastness to acid perspiration, distinct bathochromic and hyperchromic effects.

These effects are not associated with dye stripping during the fastness testing procedure since there was no or little staining of accompanying fibres and no coloration of the test solutions. Thus, the observed effects may be due to changes in the dye structure on the fibre or to the dye–fibre interaction.

Changes in the absorption spectrum of azo dyes can result from a change in equilibrium between the azo and hydrazone structures,[5–9] changes in the acid–base equilibrium, aggregation of dyes,[10–12] and the solvent used for measurements.[13]

Skulski, Burowoy, Keleman and others have shown that the absorption spectrum of a simple benzene–azonaphthalene system for the azo structure is, in many cases, considerably different from that for the hydrazone structure, although as follows from the quantum calculations of Keleman,[8] this transition is of a low energy value (about 2 kcal mol^{-1}). The stability of one of the structures is associated, first of all, with the charge value on the nitrogen atom of the azo bond or the oxygen atom of the hydroxyl group. This charge depends on the substituents present in the dyes. Both structures are stabilized with the intramolecular hydrogen bond of a six-membered chelate ring in which the hydrogen shift from nitrogen to oxygen and vice versa does not change its steric structure, thus giving a high mobility to the equilibrium state unless external factors such as crystallinity, pH or aggregation stabilize one of the structures.

Spectroscopic measurements of dyes **D-1** to **D-35** (except **D-28**) showed that in 50% ethanol at pH 4 and in water there is an additional absorption band in the short-wavelength part of the spectrum, with quite a high intensity in comparison with the main absorption band. In the case of pyrazolone dyes, this band is hidden and becomes visible in the differential spectrum (dye solution as a reference at pH 10) at 350–355 nm. For dyes prepared from 1-naphthol-4-sulphonic acid, this band appears at 370 nm, and for those prepared from 1-benzamido-8-naphthol-3,6-disulphonic acid, at 385 nm. The band disappeared completely in 50% ethanol at pH 10, while in 50% pyridine it was present in many cases but with relatively low intensity. All the dyes in pyridine solution showed a bathochromic effect in comparison with aqueous solutions and ethanol solutions at pH 4 and 10, that is due to solvolysis of solvent. The molar absorption for the pyrazolone dyes was highest in ethanol solution at pH 10, much the same in pyridine, somewhat lower in ethanol at pH 4, and in many cases, considerably lower in water.

The molar absorption of the dyes derived from 1-naphthol-4-sulphonic acid, in pyridine solution, was similar to that in ethanol at pH 4 and 10, but was often considerably lower in water. On the other hand, the molar absorption of dyes prepared from 1-benzamido-8-naphthol-3,6-disulphonic acid was highest in ethanol solution at pH 4, much the same in pyridine solution, and similar or lower in water, but almost twice as low in ethanol solution at pH 10 in comparison with that in ethanol at pH 4. This effect is brought about by aggregation in alkaline media and is confirmed by the simultaneous hypsochromic effect which suggests the existence of 'sandwich' type aggregates.

Different λ_{max} values were observed for dye solutions at pH 4 and 10. The pyrazolone dyes, in which amine **1** was used as the diazo compound, in alkaline medium show a slight bathochromic effect, about 5 nm, in relation to solutions at pH 4. This was also observed in dyes **D-8** and **D-11** synthesized from amines **2** and **3**. These dyes have no methyl group. Introducing such a group into this ring brings about a reverse effect. In alkaline medium, these dyes (**D-9**, **D-10**, **D-12** and **D-13**) showed hypsochromic shifts of 14–17 nm in comparison with their solutions in acid medium.

Dyes prepared from 1-naphthol-4-sulphonic acid showed a slight bathochromic effect in ethanol solution at pH 4 in comparison with their ethanol solutions at pH 10. The pyridine solutions showed a bathochromic shift of about 10–11 nm in comparison with ethanol solutions at pH 4. However, dyes derived from 1-benzamido-8-naphthol-3,6-disulphonic acid showed a bathochromic shift of 36 nm in ethanol solution at pH 4 in comparison with alkaline solutions, and their pyridine solutions a bathochromic shift of 4 nm in relation to solutions in ethanol at pH 4. It can be assumed that the observed changes in λ_{max} are brought about by the change in the azo–hydrazone equilibrium, ionization of sulphamide groups, dye aggregation or ionization of hydroxyl groups. Therefore, the pK_a values of the following model compounds were determined: 3-chloro-4-methyl-5-nitrosulphonylanilide (pK_a = 8·95), 3-nitro-4′-methylsulphonyl-3-chloro-4-methylanilide (pK_a = 9·18), 1-naphthol-4-sulphonic acid (pK_a = 8·24), and 1-(4′-sulpho-2,5-dichlorophenyl)-3-methylpyrazol-5-one (pK_a = 6·55). For several dyes, pH values at which the hydroxyl groups were completely ionized were determined, viz. **D-4**, pH = 9·50; **D-12**, pH = 9·8; **D-18**, pH = 9·70; **D-26**, pH = 9·90; and **D-32**, pH = 10·40.

These measurements show that in 50% ethanol at pH 4 the dyes exist in the hydrazone structure, and at pH 10 in the azo structure; at the same time, the sulphonamide and hydroxyl groups are ionized, resulting in bathochromic effect and λ_{max} close to the hydrazone structure.

Previous studies[5,6,8] have shown a difference between the azo and hydrazone structures of from 30 to 70 nm. In the case of the dyes **D-29** to **D-35** in 50% ethanol solutions at pH 10, the hypsochromic effect is associated with aggregation, although the absorption curve suggests some contribution of the hydrazone structure (a small absorption band at 385 nm). On the other hand, in 50% pyridine this group of dyes exists in the hydrazone structure. However, dyes **D-1** to **D-27** appear to exist in an ionized azo structure and the shape of their spectra is similar to those in ethanol at pH 10. The shape of the spectra in aqueous solutions shows that the dyes exist in the hydrazone structure. Thus, the appearance of a new band within the short-wavelength part of the dye spectrum suggests that the dye assumes the hydrazone structure. It may be accepted that it is associated with the coupling component in which a hydrazoquinone system appears. Only the absorption curve of dye **D-28** shows no important differences under the influence of pH and with change in solvent.

The spectroscopic examinations and observed changes in shades of dyed polyamide fibres indicate that the dyes, in many cases, as for example **D-29** to **D-35**, are fixed in the aggregated form and can undergo further aggregation or disaggregation, which is shown in the hypo- or hyper-chromic effects and accompanying hypso- or batho-chromic effects.

These dyes **D-29** to **D-35** during testing of fastness to washing and alkaline perspiration undergo further aggregation (alkaline medium) giving a hypochromic effect. During the testing of fastness to acid perspiration, however, they are disaggregated, showing a hyperchromic effect. At the same time, their hydrazone structure is stabilized resulting in the observed bathochromic effect.

Dyes **D-1** to **D-6** and **D-8**, during testing of fastness to washing, and dyes **D-3**, **D-4** and **D-6** during testing of fastness to alkaline perspiration, show the hyperchromic effect, which suggests that they are disaggregated under these conditions due to ionization of the sulphonamide group. On the other hand, dyes **D-1** to **D-8**, **D-11**, **D-16** to **D-18**, **D-21**, **D-22** and **D-25** during the testing of fastness to acid perspiration show the hypsochromic effect, which reveals their further aggregation on the fibre (head-to-tail aggregates).

As is shown by the fastness values (Table 3), when using *o*-nitrotoluene and its chloro derivatives for dye synthesis, it is possible to prepare very useful acid dyes with bright shades which can be successfully used for dyeing polyamide and protein fibres. Of particular interest are yellows **D-2**, **D-3**, **D-9**, **D-10**, **D-12**, **D-13** and **D-14**. They show high fastness to light as well as to wet treatments.

Among oranges and reds, dyes **D-26**, **D-24**, **D-19**, **D-35** and **D-30** are distinguishable by their exceptional colour brightness and shades difficult to obtain by other methods. Therefore, despite relatively low fastness to light, dyes of this type find their use in the ranges recommended for dyeing wool and polyamide fibres by many manufacturers.

A very high rating should be given to dye **D-28** in which 7-amino-1-naphthol-3-sulphonic acid (**IV**) is used as the coupling component. This dye shows no visible changes in shade on fibre during fastness testing. Other isomeric dyes prepared from amines **1–3** and acid **V** show similar fastness and colour properties. They represent a very valuable group of acid dyes.

4. EXAMPLES OF SYNTHESES

4.1. Dye D-10

2-Aminotoluene-4-sulphone-3′-chloro-2′-methylanilide (9·3 g, 0·03 mol) was dissolved in 110 cm^3 of water whilst adding sodium hydroxide (1·2 g, 0·03 mol). A 4 M solution of sodium nitrite (7·5 cm^3) was added and the whole slowly added into 30% hydrochloric acid (12 cm^3) and ice (50 g). The reaction mixture was stirred for 2 h at 0–5 °C. 1-(2′,5-Dichloro-4′-sulphophenyl)-3-methylpyrazol-5-one (10·4 g, 0·03 mol) and sodium carbonate (6·5 g) were dissolved in 140 cm^3 of water. After cooling to 0 °C, the above diazo compound was added over 30 min, maintaining a temperature of 0–5 °C and pH 9–9·5. After stirring for 3 h, the solution was heated to 60 °C and 30 g of sodium chloride was added. On cooling to 25 °C, the precipitated dye was filtered and washed with 150 cm^3 of 3% brine. Yield, 21·4 g. Vanadometric analysis showed the product contained 87% of pure dye. The remaining dyes (except **D-28**) were prepared and analysed in a similar manner.

4.2. Dye D-28

The diazotization of 2-aminotoluene-4-sulphone-3′-chloro-2′-methylanilide was carried out as in Section 4.1. 7-Amino-1-naphthol-3-sulphonic acid (7·2 g, 0·03 mol) and sodium hydroxide (1·2 g, 0·03 mol) were dissolved in 150 cm^3 of water. The solution was added to the diazo liquor. After stirring for 1·5 h at 3–5 °C, 20 cm^3 of sodium acetate (30%) was added over 3 h to pH = 5·3, and stirring continued for a further 3 h at 4–6 °C. The dye suspension was then slowly heated to 60 °C and sodium carbonate was added to pH 8·5 (foaming). To the clear solution of dye, sodium chloride (38 g) was added. After cooling to 25 °C, the precipitated dye was filtered and washed with 5 % brine (160 cm^3). Yield, 18·6 g. Vanadometric analysis showed that the product contained 85·5 % of pure dye.

REFERENCES

1. K. Venkataraman, *The chemistry of synthetic dyes*, Vol. 3, Chapter VI, pp. 249–301, New York and London, Academic Press (1970).
2. ICI, British Patent 1331261 (1970), 1484869 (1974), 1446069 (1973), 1489752 (1974); Ciba-Geigy, Polish Patent 136874 (1976); Bayer, British Patent 1442540 (1973), GFR Patent 2526172 (1976); Mitsubishi, Japanese Patents 49125671 (1973), 50034030 (1973); Toms River Chem. Corp., US Patent 3637338 (1970).
3. J. Kraska and K. Blus, *Dyes and Pigments*, **2**, 1–10 (1981).
4. *Standard methods for the determination of the colour fastness of textiles and leather*, Bradford, Society of Dyers and Colourists (1978).
5. L. Skulski, *Zeszyty Naukowe Politechniki Warszawskiej*, No. 140 (1966).
6. A. Burawoy, A. G. Salem and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952).
7. R. J. Ott, U. Widmer and H. Zollinger, *J. Soc. Dyers Colourists*, **73**, 33 (1957).
8. J. Keleman, *Dyes and Pigments*, **2**, 73–91 (1981).
9. P. Ball and C. H. Nichols, *Dyes and Pigments*, **3**, 5–26 (1982).
10. J. Kraska and W. Czajkowski, *Roczniki Chemii*, **50**, 845–56 (1976).
11. M. R. Padhye, *Colourage Annual*, 115 (1969).
12. J. Kraska and J. Sokołowska-Gajda, *Przem. Chem.*, **58**, 87–90 (1979).
13. C. N. R. Rao, *Ultra-violet and visible spectroscopy. Chemical applications*, London, Butterworths (1975). Polish edition, Wrocław, PWN (1982).