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The Influence of Arylamide Groups on the Properties of Acid Dyes

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ABSTRACT

A group of dyes in a wide range of colours (yellow, red, brown) has been synthesized using derivatives of aminoarylsulphonanilide-3′,5′-dicarboxylic acid as diazo components and 1-phenyl-3-methylpyrazol-5-one, 2-naphthol, 3-hydroxy-2-naphthanilides, 2-acetylacetamido-6-ethoxybenzothiazole and 4′-chloro-2-hydroxy-3-carbazolecarboxanilide as coupling components.

The dyes, which have a very high degree of exhaustion from a dyebath at pH 5·0–6·0, can be used for dyeing polyamide, wool and natural silk fibres. It has been confirmed that introducing the amide groups (carbamide and sulphonamide) into the dye molecule significantly improves the fastness of dyeings to wet agencies. It also slightly improves the lightfastness, compared to dyes lacking the amide groups.

1 INTRODUCTION

Dyes containing amide substituents form a large group of acid dyes useful for dyeing polyamide, wool, leather and silk. These dyes are most often characterized by a high degree of exhaustion from the dyebath at relatively high pH (4–6) and the dyeings show good fastness to wet treatments such as washing, water, alkaline perspiration and rubbing. The beneficial influence of the amide groups on lightfastness is also frequently observed. For these reasons the sulphonamide and carbamide groups are often introduced into a dye molecule.[1]

The authors' previous investigations[2,3] showed that introducing arylsulphonamide groups into a dye molecule is particularly advantageous,

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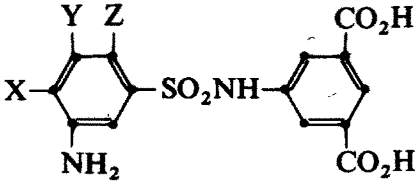
since in addition to the above properties, they also improve the solubility of dyes in water. This facilitates the application processes and improves level dyeings of polyamide fibres.

Three groups of monoazo dyes were the subject of the investigations reported here. The first group contained one amide group (sulphonamide), the second group two amide groups (sulphonamide and carbamide) and the third group comprised monoazo dyes without amide groups.

In the synthesis of the first group of dyes, the authors used the amines of formula **1**.



I

where:

	X	Y	1
A-1	H	H	H
A-2	CH_3	H	H
A-3	H	H	CH_3
A-4	Cl	H	H
A-5	CH_3	Cl	H
A-6	OCH_3	H	H

As coupling components, 1-phenyl-3-methylpyrazol-5-one (**I**) was used for all amines and, additionally, 2-naphthol (**II**) was used for the amines **A-1** and **A-2**.

In the synthesis of the second group of dyes, the amines **A-2**, **A-3**, **A-4** and **A-6** were used as diazo components. As coupling components the following 3-hydroxy-2-naphthalanilides were used: 3-hydroxy-2′-methyl-2-naphthanilide (Naphtol AS-D, **III**), 3-hydroxy-3′-nitro-2-naphthanilide (Naphtol AS-BS, **IV**), 3-hydroxy-2′-methoxy-2-naphthanilide (Naphtol AS-OL, **V**), 2-acetylacetamino-6-ethoxybenzothiazole (Naphtol AS-L 4G, **VI**) and 4′-chloro-2-hydroxy-3-carbazolecarboxanilide (Naphtol AS-LB, **VII**).

In the synthesis of the third group of dyes, which were treated as model compounds, 5-aminoisophthalic acid (**A-7**) was used as diazo component and 1-phenyl-3-methylpyrazol-5-one, 2-naphthol and Naphtol AS-D were used as coupling components.

The use of different coupling components in the synthesis of dyes not only created the possibility of observing the influence of the amide groups on the properties, but it also enabled the authors to obtain a wide range of colours (yellow, red, brown) using one group of diazo components.

The use of 5-aminoisophthalic acid in the synthesis of acid dyes suitable for dyeing polyamide fibres and wool from a weakly acidic dyebath was an additional objective of the investigations.

2 EXPERIMENTAL

2.1 General

All amines used in the syntheses of the dyes were prepared as previously described.[4] The coupling components 1-phenyl-3-methylpyrazol-5-one and 2-naphthol were pure products (POCh). The remaining components (Naphtols AS) were technical products, whose purity was checked by paper chromatography (Whatman 3 paper, eluent, pyridine:*n*-butanol:20% ammonia, 7:2:1 by vol.). They were additionally purified by boiling in ethanol, filtering hot and washing the deposit with ethanol.

The synthesis of dyes was carried out as follows: diazotization of the amines was carried out by the 'inverted' method, i.e. an alkaline solution of amine (pH 7·5) and sodium nitrite was dropped into hydrochloric acid and ice. The coupling reaction was carried out in an alkaline medium at pH 8·5–9·0 with 1-phenyl-3-methylpyrazol-5-one and at pH 9·0–9·5 with the remaining coupling components. The temperature was maintained between 0 and 5°C. The dyes were separated from the reaction mixture by salting out with sodium chloride at 50–60°C. The content of dyes in the dried products was determined by the vanadometric method. The sodium chloride content was determined by the potentiometric method. The structure, determinations of dye content in the product, R_f value (PC) and colour are shown in Table 1.

Electronic spectra of the dyes were measured in 50% ethanol, water and 1% sodium chloride using a Specord M-40 (Carl Zeiss-Jena) at a concentration 2×10^{-5} mol/dm^3. The results are listed in Table 2.

To test the suitability of the dyes for dyeing polyamide and to determine their application properties, the degree of exhaustion from the dyebath at pH 4·0, 5·0 and 6·0 was determined. Dyeings on knitted polyamide fabric were performed on a Roaches Engineering Ltd (England) dyeing machine in a dyebath at a liquor ratio 1:40, using 2% of pure dye in proportion to fibre. Dyeings were carried out according to current standards. The results are listed in Table 3.

Fastness tests were done on polyamide fibre dyed to a strength of 1/3 and

TABLE 1
Structure of Dyes, Paper Chromatography R_f and Purity

Dye no.	*Diazo component amine*	*Coupling component*	*Molecular weight*	*Paper chromatography* R_f[a]	*Purity (%)*	*Colour*
D-1	**A-1**	**I**	565	0·90	93·5	Reddish yellow
D-2	**A-2**	**I**	579	0·90	89·6	Reddish yellow
D-3	**A-3**	**I**	579	0·89	92·7	Reddish yellow
D-4	**A-4**	**I**	599·5	0·90	91·0	Reddish yellow
D-5	**A-5**	**I**	613·5	0·82	92·0	Reddish yellow
D-6	**A-6**	**I**	595	0·90	93·7	Reddish yellow
D-7	**A-1**	**II**	535	0·89	91·2	Orange
D-8	**A-2**	**II**	549	0·88	90·7	Orange
D-9	**A-2**	**III**	682	0·59	90·7	Red
D-10	**A-3**	**III**	682	0·72	91·3	Red
D-11	**A-6**	**III**	698	0·74	88·9	Red
D-12	**A-2**	**IV**	713	0·54	87·3	Bluish red
D-13	**A-2**	**V**	698	0·62	89·9	Red
D-14	**A-2**	**VI**	683	0·81	92·3	Greenish yellow
D-15	**A-6**	**VI**	699	0·80	89·4	Greenish yellow
D-16	**A-2**	**VII**	742·5	0·24	97·7	Brown
D-17	**A-4**	**VII**	764	0·25	98·0	Brown
D-18	**A-7**	**I**	410	0·70	82·3	Reddish yellow
D-19	**A-7**	**II**	380	0·58	86·3	Orange
D-20	**A-7**	**III**	513	0·26	94·3	Red

[a] Paper Whatman 3, eluent, 1% brine:20% ammonia:pyridine, 8:1:1 by vol.

1/1 of reference standard. The lightfastness was estimated on a Xenotest (Heraeus-Hanau, Germany). The remaining fastness tests were carried out in accord with normal standards. The results are listed in Table 4.

2.2 Typical dye syntheses: Dye D-1

2-Toluidine-4-sulphonanilide-3′,5′-dicarboxylic acid (10·5 g, 0·03 mol) was dissolved in 80 cm^3 of water whilst adding sodium hydroxide (2·4 g, 0·06 mol). A 4M solution of sodium nitrite (7·5 cm^3) was added, and the mixture was dropped into 30% hydrochloric acid (12 cm^3) and ice (50 g). The reaction mixture was stirred for 2 h at 0–5°C. 1-Phenyl-3-methylpyrazol-5-one (5·3 g, 0·03 mol), sodium hydroxide (2·4 g) and sodium carbonate (6·0 g) were dissolved in 140 cm^3 of water. After cooling to 0°C, the diazo liquor was dropped in over 0·5 h, maintaining the temperature at 0–5°C.

After stirring for 5 h, the solution was heated to 60°C and 25 g of sodium

TABLE 2
Electronic Spectral Data

Dye no.	*50% ethanol*		*Water*		*1% brine*	
	λ_{max} (*nm*)	ε_{max} (*dm*^{3}*/mol cm*)	λ_{max} (*nm*)	ε_{max} (*dm*^{3}*/mol cm*)	λ_{max} (*nm*)	ε_{max} (*dm*^{3}*/mol cm*)
D-1	388·0	19 900	385·0	16 700	386·8	10 800
D-2	397·3	20 100	394·4	15 900	398·7	10 600
D-3	396·8	20 500	395·6	16 300	396·2	11 300
D-4	391·1	20 200	389·8	17 100	396·0	11 200
D-5	392·9	20 200	391·1	16 900	396·8	11 300
D-6	410·3	20 100	409·0	18 500	415·8	12 100
D-7	486·4	19 600	482·4	9 800	485·2	9 800
D-8	496·0	19 300	496·1	9 600	492·8	9 400
D-9	527·1	22 300	511·0	9 200	504·0	7 400
D-10	524·9	22 200	514·2	9 700	507·0	8 700
D-11	539·6	21 800	517·3	11 100	518·7	8 700
D-12	533·2	23 000	536·0	11 000	520·6	9 300
D-13	531·0	21 000	506·1	10 800	518·6	8 300
D-14	392·5	18 600	381·1	14 700	384·2	10 200
D-15	398·7	18 600	392·6	14 400	393·7	10 400
D-16	507·1	20 400	499·1	11 000	517·1	10 100
D-17	495·8	19 800	515·5	11 000	516·1	10 800
D-18	396·2	19 800	391·8	17 000	392·1	15 000
D-19	489·2	19 300	486·4	17 200	487·1	13 600
D-20	524·1	22 000	496·1	10 600	507·1	9 700

chloride was added. After cooling to 25°C, the precipitated dye was filtered and washed with 100 cm^3 of 3% brine. Yield 18·5 g. According to the vanadometric analysis, the product contained 89·6% of dye.

2.3 Typical dye synthesis: Dye D-15

2-Anisidine-4-sulphonanlide-3′,5′-dicarboxylic acid (11·0 g, 0·03 mol) was dissolved in 80 cm^3 of water and 2·4 g of sodium hydroxide. Sodium nitrite (4 M, 7·5 cm^3) was added and, after cooling to 0–5°C, the mixture was dropped into 30% hydrochloric acid (12 cm^3) and ice (50 g). The reaction mixture was stirred for 2 h at 0–5°C.

2-Acetylacetamido-6-ethoxybenzothiazole (8·34 g, 0·03 mol) and sodium hydroxide (2·4 g) were dissolved in 100 cm^3 of water. After cooling to 0°C the diazo liquor was run in over 0·5 h; pH 9·0–9·5 was maintained by addition of 30% sodium hydroxide (6·5 mol). The coupling reaction was carried out at

TABLE 3
Relationship Between Dyebath Exhaustion and pH

Dye no.	*pH*		
	4·0 (%)	*5·0* (%)	*6·0* (%)
D-1	98·6	95·4	50·7
D-2	99·6	96·0	53·4
D-3	99·8	97·3	54·8
D-4	99·0	97·6	54·6
D-5	99·9	97·6	55·0
D-6	98·9	96·0	53·2
D-7	99·0	98·2	50·3
D-8	99·3	98·4	53·2
D-9	100·0	99·4	87·8
D-10	100·0	99·5	88·2
D-11	99·9	99·3	87·6
D-12	99·8	99·0	85·6
D-13	99·9	99·4	87·6
D-14	99·9	99·6	88·2
D-15	99·8	99·6	88·9
D-16	100·0	99·8	90·2
D-17	100·0	99·8	90·4
D-18	85·0	64·5	38·6
D-19	84·6	61·8	37·3
D-20	96·8	94·6	50·9

0–5°C for 4 h. After this time the mixture was heated 60°C and 20 g of sodium chloride was added. After cooling to 25°C the dye was filtered and washed with a 1% brine (50 cm^3). Yield 22·5 g. Purity of the product 89·4% (according to the vanadometric analysis).

3 DISCUSSION OF RESULTS

As anticipated, the use of aryloaminosulphonanilide-3′,5′-dicarboxylic acids and the selected coupling components led to the formation of dyes having a wide range of bright colours. However, their dyeing and application properties were quite different. Dyebath exhaustion at pH 4–6 showed large differences between the groups of dyes containing one or two amide groups, compared to the dyes lacking the amide groups. The results showed that during dyeing of polyamide fibre from a dyebath at pH 4·0, all dyes containing the amide groups were almost completely exhausted

TABLE 4
Fastness Properties of Acid Dyes

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

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

(98·6–100%). Only the dyes derived from 5-aminoisophthalic acid as diazo component exhausted to a lower extent (84·6–98·8%). With dyeing at pH 5·0, the degree of exhaustion was slightly lower, although still very high, the corresponding values being 95·4–99·8% for the dyes containing the amide groups, but only 61·8–64·5% for the dyes lacking the amide groups.

During dyeing at pH 6·0, a clear distinction in the adsorption of dyes was observed. The dyes of the first group, i.e. those containing only one amide group, either sulphonamide or carbamide, showed adsorption only between 50·3–55·0%, but dyes containing two such amide groups were adsorbed between 87·0 and 90·4%. The model dyes without amide groups (**D-18**, **D-19**) only adsorbed between 37·3 and 38·6%.

These results clearly show that the presence of the amide groups in the dye molecule has an advantageous influence on the degree of adsorption by the polyamide fibre from the dyebath at a relatively high pH (5·0–6·0). This dye property often gives level dyeings on polyamide and covers irregularities, which is an additional advantage.

Fastness tests show quite large differences among the obtained dyes (Table 4). From the data presented in Table 4, wet fastness to water and perspiration are quite good (4, 4–5, 5) in the case of the dyes with one amide group (sulphonamide) in the diazo component, in which 1-phenyl-3-methylpyrazol-5-one (**D-1** to **D-6**) or 2-naphthol (**D-7**, **D-8**) are coupling components. However, their fastnesses are clearly lower than those of the second group of dyes, with two amide groups (**D-9** to **D-17**). In this group of dyes, the wet fastnesses are generally 5, and only in a few cases 4–5. The dyes of the third group, which have 5-aminoisophthalic acid as diazo component, show significantly lower fastness. Even their fastnesses to rubbing are relatively low (3–4, 4, 4–5) compared to the other two groups of dyes, which have a very good fastness (5) and only in a few cases (**D**-16, **D-17**) was the fastness to wet rubbings (4–5).

Lightfastness was considerably affected by the nature of the coupling component, but the influence of the diazo component was small, although apparent.

The dyes derived from 5-aminoisophthalic acid had lightfastness values lower than those of the dyes with the amide groups. The yellow dyes derived from Naphtol AS-L 4G (**D-14** and **D-15**) showed the highest lightfastness (7, 7) and similar fastness was shown by the yellow dyes derived from 1-phenyl-3-methylpyrazol-5-one (6 and 7) or (6–7, 7). Dye **D-5**, containing the methoxy group *ortho* to the azo group, showed lightfastness 5–6, 6, and the 5-aminoisophthalic acid derivative **D-18** had fastness of only 5, 6. The lowest lightfastness values were shown by the dyes having 2-naphthol as the coupling component, viz. 3, 4 for **D-7** and **D-8**, and 3, 3–4 for **D-19** (diazo component 5-aminoisophthalic acid). On the other hand, the use of

Naphtols AS as coupling components and amines containing a sulphonamide group as diazo components significantly improved the lightfastness of the dyeings to 4, 4–5 for **D-9** to **D-11**. With Naphtol AS-LB as coupling component, the lightfastness was 5,6 (**D**-16 and **D-17**) which, for an acidic brown, is a high value.

Electronic spectra of the dyes were measured in 50% ethanol, water and 1% sodium chloride in order to investigate the influence of the dye structure on the λ_{max}, molar absorption and aggregation. In 50% ethanol at concentrations from 2×10^{-6} mol/dm^3 to 2×10^{-4} mol/dm^3, the solutions were in accord with the Lambert–Beer law, irrespective of the number of amide groups in the molecule. In water and 1% brine solution they showed a high tendency for aggregation. The dyes derived from 1-phenyl-3-methylpyrazol-5-one containing one amide group (sulphonamide) showed a lowering of molar absorption by 10–20% in water (**D-1** to **D-6**), and by 50% in 1% brine, so under these conditions they are practically dimers. The dye with one carbamide group (**D-20**) occurs as a dimer in water and 1% brine. The dyes containing two amide groups, i.e. the 3-hydroxy-2-naphthoic and 2-hydroxycarbazole-3-carboxylic acid derivatives (**D-9** to **D-13** and **D-16** to **D-17**) showed an approximate 50% reduction in the molar absorption in water, and therefore, under these conditions, they form dimers. In 1% brine the dyes of this group showed even slightly higher aggregation, particularly some of the 3-hydroxy-2-naphthoic acid derivatives (**D-9** to **D-13**).

The dyes derived from 2-acetylacetamido-6-ethoxybenzothiazole showed a slightly lower tendency to aggregation in water solutions with molar absorption lowering by *c.* 20–25%, and in 1% brine solutions full dimerization could be observed. In the dyes of the third group lacking the amide groups (**D-18** to **D-19**) showed a considerably lower tendency to aggregation and even in 1% brine, molar absorption lowered by only *c.* 25–30% compared to the dyes in 50% ethanol.

4 CONCLUSION

The results clearly show that the use of derivatives of the aminoarylsulphonanilide-3′,5-dicarboxylic acid (formula **1**) in the synthesis of acid dyes opens the possibility of preparing a large group of dyes suitable for dyeing polyamide fibres, wool and silk. These dyes are characterized by a very high degree of exhaustion from a weakly acidic dyebath (pH 5·0–6·0). At the same time they give permanent colours, good wet fastness and they cover well the irregularities of polyamide fibres.

The authors confirmed the earlier observations that introducing amide groups into the dye molecule considerably improves the fastness of the dyeings to wet factors, especially if there are two amide groups. Lightfastness is also improved, although to a smaller extent (0·5–1 degree), compared to the dyes lacking the amide groups.

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