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Synthesis and Properties of Acid Dyes Derived from 1-Phenyl-3-methyl-5-pyrazolone

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ABSTRACT

A series of yellow dyes, derived from 1-phenyl-3-methyl-5-pyrazolone and containing one or two arylsulphonamide groups were synthesized. The dyes were suitable for dyeing polyamide fibres and wool from a weakly acidic dye bath. Spectroscopic data for the dyes were evaluated and their application and fastness properties studied. The beneficial influence of the sulphonamide group on some application and fastness properties was concluded.

1 INTRODUCTION

Monoazo dyes containing one sulpho group and one arylsulphonanilide group form a large group among acid dyes. Dyes with an arylsulphonamide group dye polyamide and protein fibres from weakly acidic dyeing baths, giving a very high degree of dyebath exhaustion, and the dyeings are characterized by good fastness. In dyes of this type, the sulpho group is most often placed in the azo component, and the sulphonamide residue in the diazo component. The use as diazo component of aminoarylsulphonanilidesulphonic acids,[1] in which the sulpho group is in different positions in the anilide residue, allows the synthesis of dyes not containing sulpho- or carbonyl groups (e.g. 1-phenyl-3-methylpyrazolone) on the coupling component.

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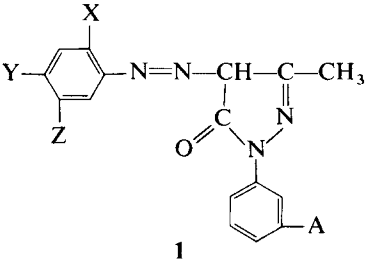
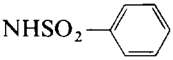
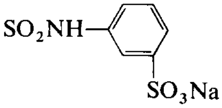
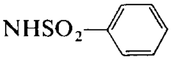
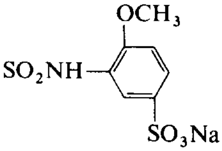
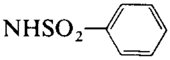
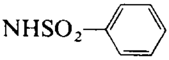
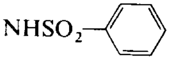
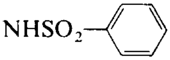
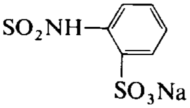
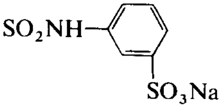
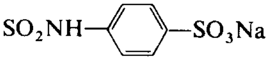
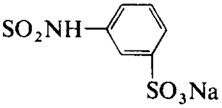
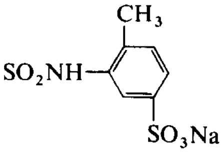
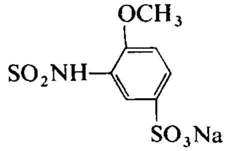
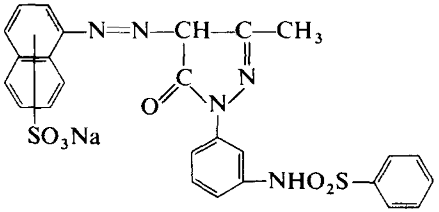


1

where

	A	X	Y	Z
D-1	 NHSO$_2$—	CH$_3$	H	 SO$_2$NH— SO$_3$Na
D-2	 NHSO$_2$—	H	CH$_3$	 OCH$_3$ SO$_2$NH— SO$_3$Na
D-3	 NHSO$_2$—	OCH$_3$	H	SO$_3$Na
D-4	 NHSO$_2$—	SO$_3$Na	H	H
D-5	 NHSO$_2$—	H	H	SO$_3$Na
D-6	 NHSO$_2$—	H	SO$_3$Na	H
D-7	H	CH$_3$	H	 SO$_2$NH— SO$_3$Na
D-8	H	CH$_3$	H	 SO$_2$NH— SO$_3$Na
D-9	H	CH$_3$	H	 SO$_2$NH——SO$_3$Na
D-10	H	H	CH$_3$	 SO$_2$NH— SO$_3$Na
D-11	H	H	CH$_3$	 CH$_3$ SO$_2$NH— SO$_3$Na

	A	X	Y	Z
D-12	H	H	CH_3	
D-13	NO_2	CH_3	H	SO_3Na
D-14	NO_2	OCH_3	H	SO_3Na



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	Position of sulphonic group
D-15	4
D-16	7
D-17	8

A series of monoazo acid yellow dyes, derivatives of 1-phenyl-3-methyl-5-pyrazolone, which differ in the orientation of the sulpho- and arylsulphoanilide groups, was chosen as the subject of this study. The structure of the dyes is given by the general formulae **1** and **2** shown above.

The objective of the investigation was to obtain a group of acid dyes of interest from a theoretical and technological point of view. The variations in the structure of the dyes should make it possible to investigate structural influences on the physical–chemical, application and end-use properties.

2 EXPERIMENTAL

The acid dyes D-1 to D-17 were prepared by diazotization of the appropriate amines and coupling with pyrazolone derivatives in a basic medium (pH 9·0–9·5) at 0–5°C. The dyes were separated from the reaction medium by salting out with sodium chloride at 50–60°C.

The dye yields were over 90%; dye content in the dry product was determined by the vanadometric method and sodium chloride content by the potentiometric method. The purity of the dyes was examined by

TABLE 1
Some Properties of Dyes Derived from 1-Phenyl-3-methyl-5-pyrazolone

Dye no.	*Mol. wt.*	*Purity*[a] *(%)*	*Paper chromatography*[b] R_f	*Electronic spectra data* *Water*		*50% Ethanol*		*Acetone–0·01N NaOH 50:50 by vol.*	
				λ_{max} (nm)	ε (dm^3/(mol cm))	λ_{max} (nm)	ε (dm^3/(mol cm))	λ_{max} (nm)	ε (dm^3/(mol cm))
D-1	704	91·6	0·85	399	16 400	399	20 600	401	17 800
D-2	734	80·4	0·91	397	15 600	397	18 600	402	15 200
D-3	565	80·3	0·78	418	14 000	420	16 000	408	14 000
D-4	535	89·3	0·79	393	17 800	394	19 000	395	16 000
D-5	535	93·1	0·83	392	18 200	394	19 600	399	16 000
D-6	535	82·5	0·81	394	16 000	398	17 800	408	14 000
D-7	549	89·0	0·70	397	17 800	399	19 500	400	18 600
D-8	549	83·7	0·86	397	20 100	399	21 700	399	16 400
D-9	549	86·9	0·82	397	18 700	399	20 300	400	16 000
D-10	549	73·1	0·86	396	20 000	398	21 400	400	17 200
D-11	563	94·4	0·87	396	19 300	398	22 000	400	17 600
D-12	579	89·6	0·87	396	20 800	398	21 600	400	17 200
D-13	439	96·2	0·46	402	19 000	406	19 000	398	18 200
D-14	455	97·1	0·48	419	19 000	424	19 000	400	16 900
D-15	585	96·4	0·70	437	12 000	438	16 000	450	18 000
D-16	585	94·7	0·62	427	12 000	433	14 800	443	16 400
D-17	585	93·1	0·73	363	12 000	363	16 400	369	18 000

[a] Analysis by vandometric method.

[b] Paper Whatman 3, eluent pyridine : 25% ammonia : 1% brine 1 : 1 : 8 by vol.

chromatography using Whatman 3 paper and, as eluent, pyridine : 20% ammonia : 1% sodium chloride (1 : 1 : 8 by vol.).

Dye content in the dry product, R_f values and λ_{max} in water, 50% ethanol and 50% acetone at different pH from 2 to 13 are given in Table 1 and in Figs 1–5.

The degree of exhaustion of the dyes was examined with respect to the dye bath pH, using 1% dye in relation to polyamide fibre. Dyeing was carried out using a dyeing machine manufactured by Roaches Engineering Ltd (England), in dye baths at pH 4·0, 5·0, 6·0 and 7·0 and a liquor ratio 1 : 40. The results are given in Table 2.

For selected dyes (D-1, D-5, D-8, D-13, D-16), absorption curves were obtained using 1% dye with respect to polyamide. Dyeings were carried out at pH 6·0 and a liquor ratio 1 : 40. Absorption curves are given in Fig. 6.

To study end-use fastness, dyeings on knitted polyamide fabric were performed to a strength of 1/3 or 1/1 of reference standard. Dyeings to a

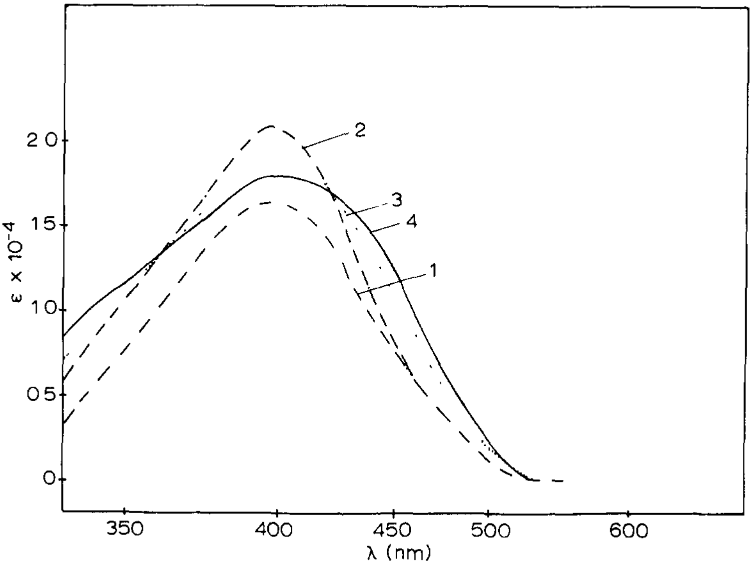


Fig. 1. Absorption spectra of dye D-1 in: 1, water (— · · — · ·); 2, water pH 2–10: acetone 50 : 50 by vol. (— · — · —); 3, water pH 11 : acetone 50 : 50 by vol. (······); 4, water pH 12 : acetone 50 : 50 by vol. (——).

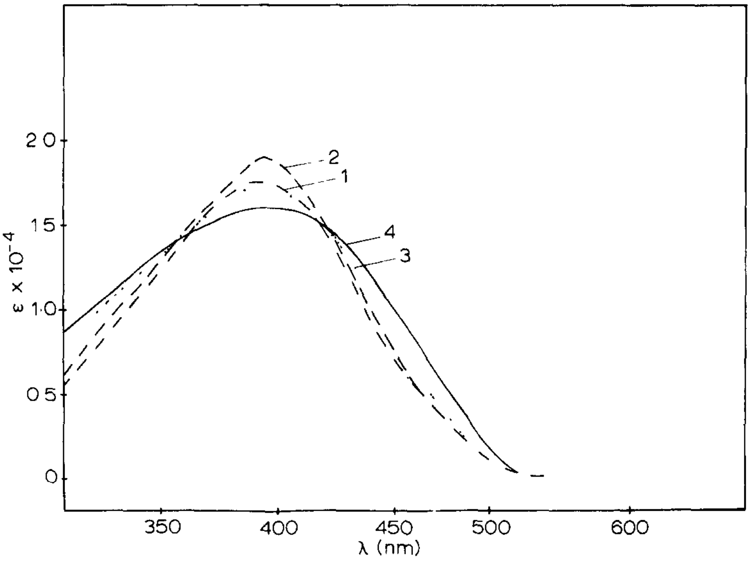


Fig. 2. Absorption spectra of dye D-4 in: 1, water (— · · — · ·); 2, water pH 2–10: acetone 50 : 50 by vol. (— · — · —); 3, water pH 11 : acetone 50 : 50 by vol. (······); 4, water pH 12 : acetone 50 : 50 by vol. (——).

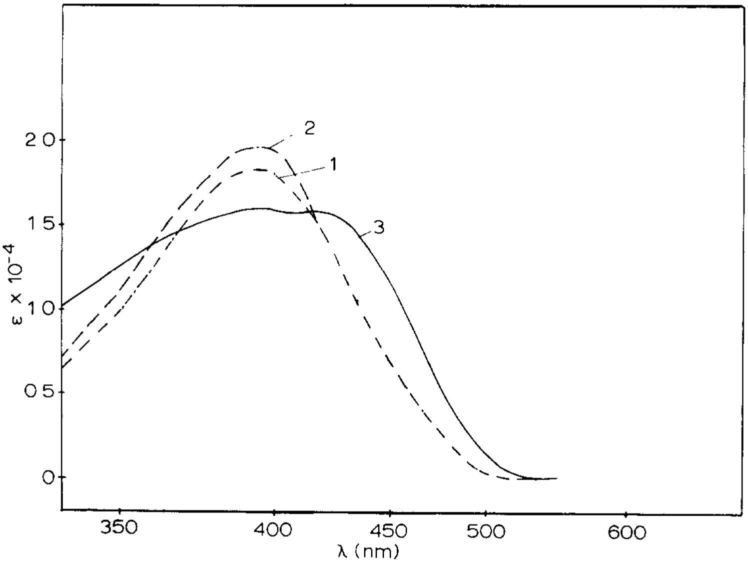


Fig. 3. Absorption spectra of dye D-5 in: 1, water (— · · — · ·); 2, water pH 2–10: acetone 50 : 50 by vol. (— · — · —); 3, water pH 11, 12: acetone 50 : 50 by vol. (———).

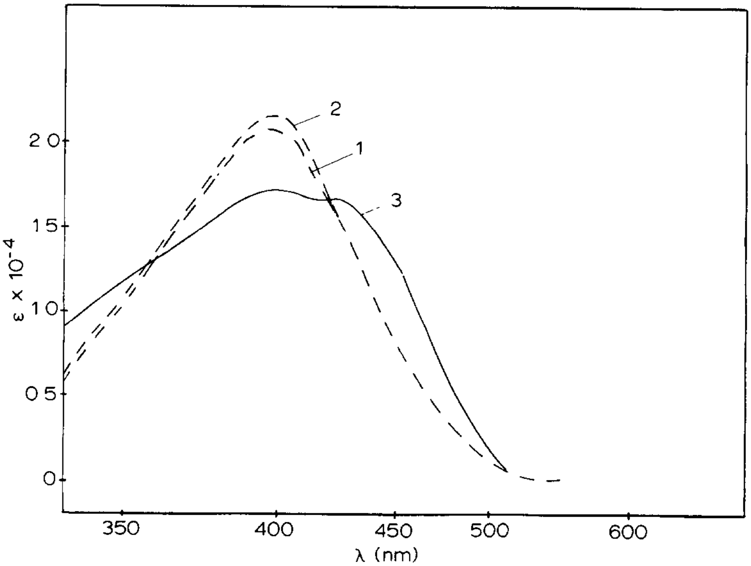


Fig. 4. Absorption spectra of dye D-12 in: 1, water (— · · — · ·); 2, water pH 2–10: acetone 50 : 50 by vol. (— · — · —); 3, water pH 11, 12: acetone 50 : 50 by vol. (———).

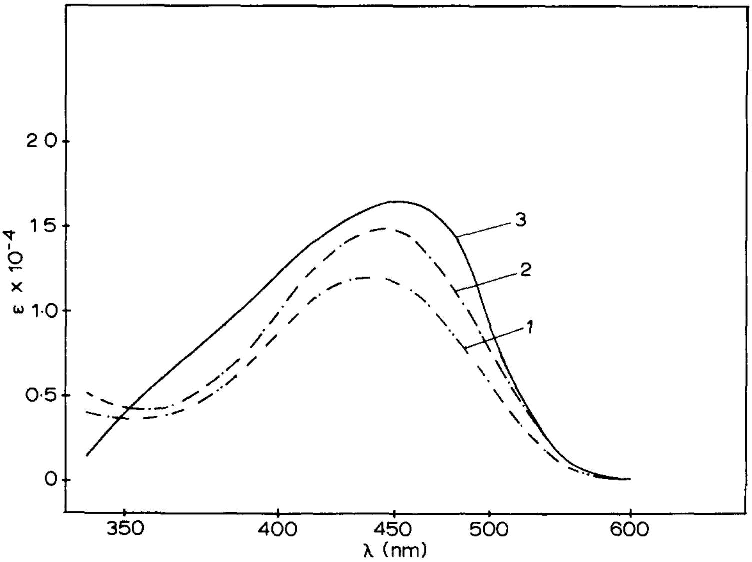


Fig. 5. Absorption spectra of dye D-16 in: 1, water (— · · — · ·); 2, water pH 2–10: acetone 50 : 50 by vol. (— · — · —); 3, water pH 11, 12: acetone 50 : 50 by vol. (———);

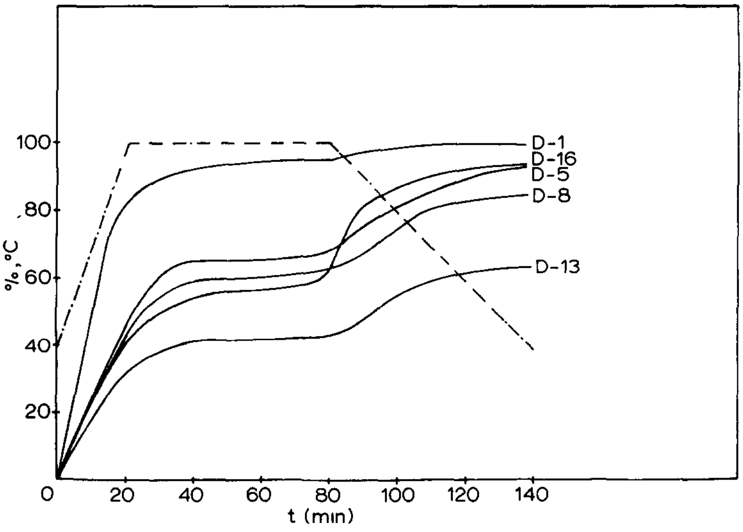


Fig. 6. Absorption curves of dye derivatives of 1-phenyl-3-methyl-5-pyrazolone (——); dyeing temperature (— · — · —).

TABLE 2
Dependence of the Bath Exhaustion on pH

Dye no.	*Exhaustion (%) as various pH values*			
	4·0	*5·0*	*6·0*	*7·0*
D-1	100	99·9	99·8	88·0
D-2	100	99·8	99 6	88·6
D-3	99·9	98·7	96·7	75·0
D-4	99·9	99·4	96·7	81·2
D-5	99·9	98·3	94·3	71·1
D-6	99·9	98·9	96·3	76·4
D-7	99·9	99·2	94·6	76·0
D-8	99·0	96·8	84·7	58·1
D-9	99·5	98·3	88 9	66·0
D-10	99·5	98·5	86·6	65·8
D-11	99·7	98·7	90·0	68·2
D-12	99·9	98·9	89·6	70·0
D-13	92·7	85·0	64 3	48·6
D-14	90·8	83·8	62·7	47·3
D-15	100	99 3	93 5	88·5
D-16	100	99·4	94·1	89·3
D-17	—	—	—	—

strength of 1/1 were carried out to test the fastness to water, acidic and alkaline perspiration, dry and wet rubbing and washing at 40°C. The lightfastness was estimated with a Xenotest 150 S (Heraus Hanau, Germany). Results are given in Table 3.

3 DISCUSSION

As shown by the fastness testing, a number of the dyes are characterized by very bright shades, dyeing polyamide fibres and wool from a weak acid dye bath.

The application examinations (Table 2) showed the beneficial influence of the arylsulphonanilide group on the degree of absorption of the dyes. Dyes containing arylsulphonanilide groups at pH 4–6 show practically quantitative uptake. Dyes containing two arysulphonanilide groups had the highest dye uptake values. Dyes containing one arylsulphonanilide group (irrespectively of its orientation in either the coupling or diazo component) showed a slightly lower dye uptake. However, in the model dyes without arylsulphonanilide groups (D-13 and D-14), a considerably lower dye uptake was observed at the same pH.

TABLE 3

Technical Propeties of the Acid Dyes Derived from 1-Phenyl-3-methyl-5-pyrazolone

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	7	6
D-2	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6	5–6
D-3	5	4	5	5	5	5	5	4	5	5	4	5	5	5	4–5	4
D-4	5	4	5	4–5	5	5	5	4	5	5	4	5	5	4–5	6	5
D-5	5	4	5	4–5	5	5	5	3–4	4–5	5	4	5	5	5	5–6	4–5
D-6	5	4	5	5	5	5	5	4	4–5	5	4	5	5	5	5–6	4–5
D-7	5	4–5	4–5	5	5	5	5	4–5	4–5	5	4–5	4–5	5	5	7	6
D-8	5	3–4	4–5	5	5	5	5	3	4	5	3	4	5	5	7	6
D-9	5	4	4–5	5	5	5	5	4	4–5	5	3–4	4–5	5	5	7	6
D-10	5	3–4	4–5	5	5	5	5	4	4–5	5	3–4	4–5	5	5	6–7	5–6
D-11	5	3–4	4–5	5	5	5	5	4	4–5	5	4	4–5	5	5	6–7	5–6
D-12	5	3–4	4–5	5	5	5	5	4	4–5	5	4	4–5	5	5	6–7	5–6
D-13	5	2	3	4–5	4–5	5	5	2	3	5	2	3	5	4–5	5–6	4–5
D-14	5	2	3	4–5	4–5	5	5	2	3	5	2	3	5	4–5	5	4–5
D-15	5	4–5	5	5	5	5	5	4–5	5	5	4–5	5	5	5	3–4	3
D-16	5	4–5	5	5	5	5	5	4–5	5	5	4–5	5	5	5	3	2–3
D-17	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

1—change of shade of dyed fabric; 2—staining nylon; 3—staining wool.

Introducing the arylsulphonanilide group into the molecule of a dye increases its affinity for polyamide fibre. This is illustrated by the absorption curves presented on Fig. 6. The dye D-1, containing two arylsulphonanilide groups, has the highest affinity and the highest dyeing rate at pH 6·0. The lowest affinity, at the pH, was shown by the model dye, the difference being 50%. However, the orientation of the sulpho- and arylsulphonamide groups in the dye molecule also has an influence on the affinity for polyamide fibres. This is illustrated by the absorption curves for the dyes D-5 and D-8.

As is shown by the absorption curves, a considerable amount of dye is adsorbed by the polyamide fibre during the cooling of the dye bath. For this reason, it can be presumed that during this period dyes are adsorbed by forming aggregates on the fibre. Among the dyes containing one arylsulphonanilide group dye D-16 has the highest absorption during the cooling of the dye bath, and at the same time shows a very strong tendency to aggregation in water (Table 1).

It should be underlined that in spite of the high dye affinity to polyamide fibres, dyes containing arylsulphonanilide groups provide level dyeings on polyamide fibres. Also the presence of sulphonanilide groups positively influences the fastness of the dyes.

Dyes containing two sulphonanilide groups (D-1 and D-2) are characterized by very high wet fastness (to water, washing, perspiration, rubbing), which is illustrated in Table 3. Moreover, all dyes containing one arylsulphonanilide group showed much higher wet fastness than that of the model dyes D-13 and D-14.

The light fastness of the dyeings varied between 3 and 7. The diazo component considerably influenced the lightfastness of the dyeings, the lowest fastness being observed with derivatives of naphthylaminesulphonic acids (3–4 for D-15 and 3 for D-16) and also for derivatives of *o*-anisidine-4-sulphonic acid (4–5 for D-3). Dyes derived from toluidinesulphonanilidesulphonic acids (D-1, D-2 and D-7 to D-12) showed very high light-fastness.

The differences in light fastness existing in this group of dyes will be the subject of further investigation.

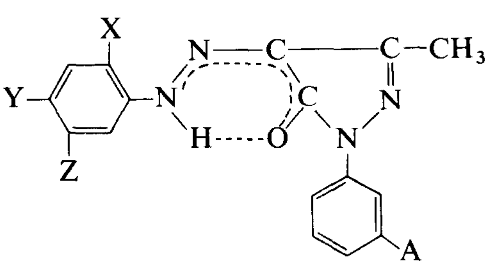
During fastness testing to alkaline and acid perspirations and washing, many azo dyes show changes in shade of the dyed polyamide fibre; hypo-, hyper-, hypso- and bathochromic effects can be observed. As a result, in many investigations, these effects have been shown to be caused by the change of equilibrium between the azo and hydrazone configurations, the change of acid–base equilbrium, or the aggregation of the dye. For these reasons, interpretation of absorption spectra of azo dyes in which the above equilibrium states can occur is difficult and ambiguous.

Spectroscopic examination of dye solutions in 50% ethanol, 50% acetone, and also in 50 % pyridine and 50% DMF show one absorption band in the range of 390–440 nm (Figs 1–5). According to Yasuda's investigations[2,3] the occurrence of this band can be due to the hydrazone structure of the dye stabilized by intramolecular hydrogen bond. The existence of the intramolecular hydrogen bond is confirmed by IR investigations (valence vibrations of the CO group occur at lower frequencies). In these presently investigated dyes, valence vibrations of the CO group also occur at lower frequencies (1645–1655 cm^{-1}) than for pyrazolones. In 1-(3'-*N*-benzenesulphonamide)phenyl-3-methyl-5-pyrazolone, valence vibrations of the CO group occur at 1700 cm^{-1}, and for 1-(3'-nitrophenyl)-3-methyl-5-pyrazolone at 1705 cm^{-1}. The hydrazone structure of pyrazolone dyes has also been confirmed by Lycka[4] (^{19}F-NMR investigations) and by Yamamoto and co-workers[5] (^{15}N-NMR investigations).

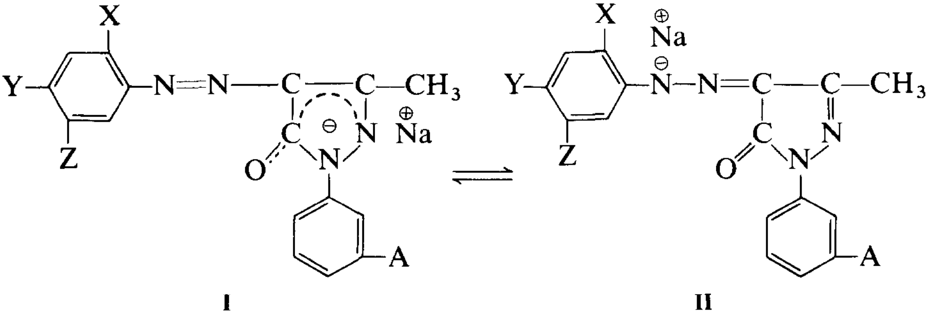
On examination of the products from the coupling aniline derivatives with 1-phenyl-3-methyl-5-pyrazolone, Schwander[6] formulated a hypothesis that these dyes occur in the form of different tautomers, in chloroform as hydrazones, and in polar solvents (dimethylsulphoxide or pyridine) as a mixture of hydrazone and azo. Grecu and co-workers[7] suggest that the azo- or hydrazone structure is stabilized by substituents situated in the diazo component.

In the investigated dyes, a large influence of substituents on the λ_{max} value was observed, e.g. introducing a methoxy group into the ortho-position to the azo group (D-3, D-14) causes a bathochromic shift of approximately 20–25 nm; a very strong bathochromic effect is observed with dyes D-15 and D-16, derived from naphthylaminesulphonic acids.

The conclusion can be drawn that during the coupling of diazotized aromatic amines in a basic environment (pH 9–9·5) with derivatives of 1-phenyl-3-methyl-5-pyrazolone, dyes which can be described by a delocalized structure, containing an azo-hydrazone equilibrium, are obtained.



This system is very stable. Absorption curves in 50% acetone do not change within the pH from 2 to 10. However, after adding NaOH to the pH 11 (solution of acetone : 0·001N NaOH 50 : 50 by vol.) or to the pH 12 (solution of acetone : 0·01N NaOH 50 : 50 by vol.), the absorption decreases and simultaneously splits into two maxima (Figs 3 and 4). Part of the dye exists in an ionized azo structures (I) and part in an ionized hydrazone structure (II), which is in accord with the investigations of Bell[8] and Zheliu.[9]



The mutual relationship of the azo and hydrazone structures depends upon the substituents situated in the aryl ring of the diazo component, particularly in the ortho-position to the azo group, e.g. the position of the sulpho group in the ortho-position (dye D-4) or the meta-position (dye D-5) (Figs 2 and 3) or the position of the methyl group in the ortho-position (dye D-1) and the para-position (dye D-12) (Figs 1 and 4).

In aqueous solution, the dyes are partly aggregated, which is favoured by the presence of the sulphonanilide group, although the influence of the orientation of the sulphonanilide group is not clear. Dyes in which the sulphonanilide group is situated at some distance in the diazo component from the disaggregating sulpho group undergo higher aggregation (D-3 ÷ D-6).

The molar absorption of dyes derived from naphthylaminesulphonic acids (D-15 and D-16) is low in water as well as in 50% ethanol. Above pH 10, in 50% acetone, ionization of the hydrazone system and simultaneous disaggregation of dye occurs.

Because of the steric hindrance of the sulpho group, compound D-17 has absorption outside the visible region (λ_{max} occurs at 363–369 nm), i.e. in the region of the absorption of naphthylaminesulphonic acids. This compound exists in the hydrazone form, without an intramolecular hydrogen bond. Carbonyl vibrations occur at the same frequencies and have similar intensity as do 1-(3'-*N*-benzenesulphonamide)phenyl-3-methyl-5-pyrazolone.

4 CONCLUSIONS

A range of yellow acid dyes derived from 1-phenyl-3-methyl-5-pyrazolone and containing one or two arylsulphonanilide groups have been synthesized. Dyes containing the arylsulphonanilide group are useful for dyeing polyamide and wool from a weakly acidic dye bath. The presence of the arylsulphonanilide group increases the dye affinity for polyamide giving level dyeings, and also enhances the fastness of the dyeings (to water, perspiration, wet rubbing).

From the results of spectroscopic examinations, in aqueous solution the dyes are partly aggregated. On the other hand, in 50% ethanol solution and in acetone, they occur in a disaggregated form, with a stable hydrazone-azo configuration over the pH range 2–10, and their spectra are characterized by one absorption maximum. Only from pH 11 and above do the dyes undergo ionization and their spectra are then characterized by two absorption maxima, one due to the ionized azo structures, the other to the ionized hydrazone structure.

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