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Effect of the sulphonic group position on the properties of urea dyes

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Abstract

Azo dyes, analogues of C.I.Direct Red 23, have been prepared, using anilinesulphonic acids as diazo components and bis-ureido-6-(naphthol-1) as a coupling component, and their colour properties have been examined, comparing them with those of a reference dye by the differential spectra method in aqueous solutions as well as by the reflectance spectra analysis on dyed wool and cotton fabrics. It has been found that the dyes under investigation may be an alternative to the presently used conventional urea dyes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Differential analysis; Urea dyes; Direct dyes; Bis-ureido-6-(naphthol-1)

1. Introduction

Urea dyes constitute quite a large group among direct dyes [1]. They are commercially manufactured exclusively by acylation of appropriate amines with phosgene [2,3]. However, the production and use of phosgene is more and more restricted due to the strong toxicity of this compound and a general reluctance to use chlorine compounds [4,5]. Therefore, it seems expedient to search for alternative methods for the preparation of urea intermediates and dyes.

In attempts to eliminate phosgene from the process of manufacturing urea intermediates and dyes, the use of diphenyl carbonate (DPC) in place of phosgene to combine two amine molecules was examined. It was found that, unlike the phosgene process, the condensation of amines with diphenyl carbonate fails to proceed in an aqueous system [5] and requires the use of excess amine. Therefore, this reagent cannot be easily used to prepare J-acid urea, a widely used intermediate product. The reason lies in the poor solubility of sulphonic acids in most organic solvents and the stability of intermediate products.

Based on the results of previous studies [5] on the optimisation of DPC condensation with aniline, a process has been developed to synthesise an analogue of J acid urea free from sulphonic groups; 6-amino-1-naphthol was condensed with DPC to prepare a new coupling component bis-ureido-6-(naphthol-1) (**5**). This compound was used for the synthesis of disazo urea dyes by coupling it with diazotised anilinesulphonic acids.

The resultant dyes would be isomers of CI Direct Red 23 (DR23), containing sulphonic groups in the diazo component and not in the coupling component. In accordance with accepted

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views [6,7], the position of the sulphonic group should not have any effect on the colour of the resultant azo dye. Nevertheless, it has turned out in practice that in many cases the presence of a sulphonic group and also its position in the dye molecule affects the colour properties of dyes [8,9].

2. Results and discussion

In order to verify the correctness of this hypothesis and to examine the possibilities of replacing J acid with its analogue free from sulphonic groups, three DR23 isomers were prepared (**8o**, **8m**, **8p**) and their colour properties examined by spectrophotometric measurements in solution and by reflection spectrophotometry of dyed wool and cotton fabrics.

A process was developed to synthesise the commercially unavailable bis-ureido-6-(naphtol-1) (**5**), an analogue of J acid urea (bis-ureido-6-(1-naphthol-3 sulphonic acid)), free from sulphonic groups. The resultant new coupling component containing a urea radical was coupled with a diazo component containing sulphonic acid groups. Using such an approach, it was expected to prepare disazo dyes with properties similar to those of known products based on carbonyl-J acid.

2.1. Synthesis of 6-amino-1-naphthol

According to literature data, 6-amino-1-naphthol (**4**) can be prepared by desulphonation of J-acid in the presence of Raney nickel in an alkaline system [10], or in an aqueous or aqueous-alkaline system under increased pressure [11,12]. It can also be prepared by electrochemical reduction of 6-nitro-1-naphthol [13] or by alkaline fusion of 2-naphthylamine-1,5-disulphonic acid (**2**) [13–17]. Due to the availability of raw materials and the simplicity of the pertinent equipment, 6-amino-1-naphthol was prepared using the latter process according to the scheme.

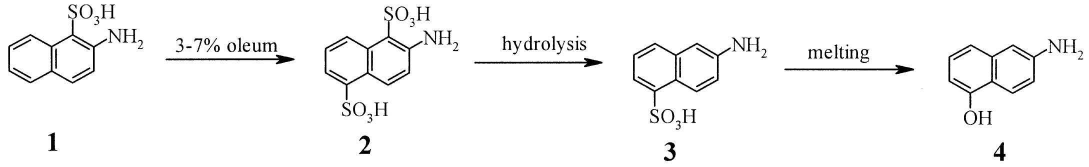
2.2. Synthesis of bis-ureido-6-(naphthol-1)

There are relatively few literature data on the preparation of bis-ureido-6-(naphthol-1) (**5**). The available processes involve the reaction of 6-amino-1-naphthol (**4**) with phosgene in an aqueous alkaline system [18], or a low-efficient desulphonation of the appropriate sulphonic acid [19].

The results of the syntheses of bis-ureido-6-(naphtol-1) (**5**) are given in Table 1.

The results of the syntheses showed that the reaction course and the purity of the obtained (**5**)

8o	*orto-*
8m	*meta-*
8p	*para-*



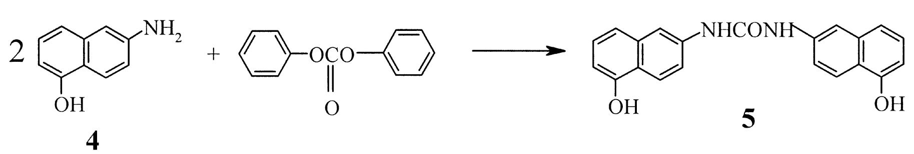


Table 1
Synthesis yields of dyes 157

No.	Catalyst	*o*-Dichlorobenzene	2-Methoxyethanol	Quinoline
		Yield [%]		
1	—	16.3	8.0	19.8
2	*p*-*N*,*N*-dimethylaminepyridine	52.3	—	[a]
3	*p*-Toluenesulfonic acid	44.2		22.1
4	Nicotinic acid	52.0	[a]	

[a] Tarry products, impossible to separate and identify.

depend to a great extent on the type of solvent used as reaction medium. In quinoline, tarry products are formed, being difficult to identify, while in 2-methoxyethanol, the process proceeds with a lower yield than that in *o*-dichlorobenzene.

It was found that the best reaction conditions include *o*-dichlorobenzene as solvent at a temperature of 180°C in the presence of an alkaline catalyst. The type of catalyst is not so important, and differences in yield amount to about 8% depending on the catalyst type.

*2.3. Synthesis of dyes **6** and **8***

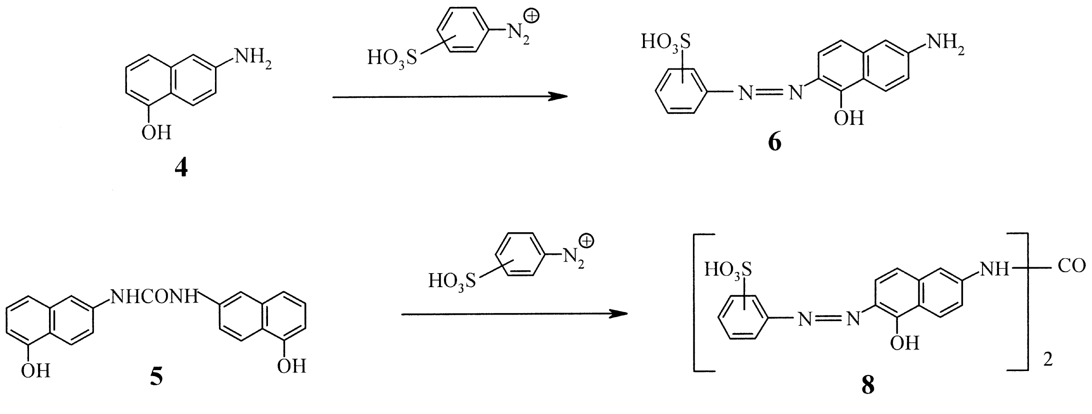
The syntheses of the monoazo dyes **6** and the disazo dyes **8** were carried out according to the scheme.

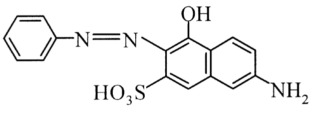
Dyes **6** were prepared by coupling diazotised orthanilic, metanilic and sulphanilic acids with **4**, while dyes **8** were obtained by coupling the same diazo components with **5**. Dyes in which the sulphonic acid groups are in positions *ortho*-(**6o**, **8o**), *meta*-(**6m**, **8m**) or *para*-(**6p**, **8p**) in relation to the azo bond, were used to examine the effect of the sulphonic group position on the colour properties of the dyes. In a comparative examination, model compounds were used, such as appropriate urea dye prepared from J-acid urea (C.I.Direct Red 23, CI 29160) (**DR23**) containing a sulphonic group in the naphthalene skeleton, and a reference monoazo dye **St**.

Samples of wool and cotton fabrics were dyed and spectra were taken in aqueous solutions at pH 7 and 10. The analysis was carried out by the differential absorption spectra method in aqueous solutions and the reflectance spectra method on wool and cotton woven fabrics [20].

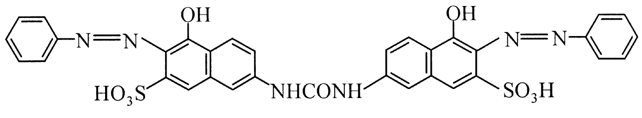
3. Differential analysis of absorption and reflectance spectra

The relationship between the absorption bands of reference dye DR23 (C.I.Direct Red 23) and





St



DR23 (C.I. Direct Red 23; CI 29160)

dyes **6** and **8** was assessed by differential analysis. The differences in areas under absorption curves were used as a measure of this relationship. Such an approach allows one to show not only the differences in position of maxima λ_{max}, but also makes it possible to perform analysis over the remaining absorption ranges. The analysis was carried out within a useful absorbance range of the dyes under investigation when $A > 0$, i.e. within 280–650 nm for spectra in solution and within 270–700 nm for reflectance spectra on dyed fabric samples. The difference in the oscillator strengths was assessed on the basis of the following formulae:

$$\Delta S = S_{St} - S_i \text{ or } \Delta S = S_{DR23} - S_I$$

where: S_{St}—area under the absorption curve of the monoazo dye **St**; S_i, S_I—area under the absorption curve of monoazo dye **6o**, **6m**, **6p** or disazo dye **8o**, **8m**, **8p**; ΔS—difference in areas under absorption curves; S_{DR23}—area under the absorption curve of C.I. Direct Red 23.

Comparison of areas under the absorption curve (ΔS) corresponds to the difference in the values of oscillator strength f expressed in terms of units under the absorption curves, of reference dye (S_{St}) which is a product of the coupling of aniline to J-acid (**St**) and the examined dye (S_i or S_I). Thus, the ranges of changes and discrepancy between absorption intensities vs the wavelength were determined.

Prior to the comparison, the spectra were converted so that the values of absorbance of reference dye (A_{St}) or the direct dye A_{DR23} and of the examined dyes (A_i, A_I) were equal to the λ_{max} of C.I. Direct Dye 23. Using this approach, one can avoid the necessity of taking absorption spectra at precisely defined concentrations. Such a procedure made it possible to carry out the analysis without knowing the concentrations of the dyes under comparison. The analysis of the reflectance spectra of dyed wool and cotton fabrics was performed in a similar way.

4. Absorption spectra in aqueous solutions at pH = 7 and pH = 10

The spectral analysis of aqueous solutions of the monoazo dyes **6o**, **6m** and **6p** and of the disazo dyes **8o**, **8m**, **8p** was carried out within the range 280–700 nm. C.I. Direct Red 23 (**DR23**) or (2-phenylazo)-3-sulpho-6-amino-1-naphthol (**St**) were used as reference dyes. The results obtained are given in Table 2.

Standardisation of the spectra of the monoazo dyes **6** was performed at wavelengths 482 and

Table 2
Differential analysis of aqueous dye solutions

		Monoazo dyes					Disazo dyes			
		pH 7		pH 10			pH 7		pH 10	
		λ_{max}	ΔS	λ_{max}	ΔS		λ_{max}	ΔS	λ_{max}	ΔS
o-SO_3H	**6o**	462	−56.3	480	−90.2	**8o**	449	−150.5	463	−101.5
m-SO_3H	**6m**	464	−131.0	482	−270.6	**8m**	461	−159.6	478	−171.4
p-SO_3H	**6p**	467	−91.9	505	−252.5	**8p**	467	−119.4	483	−114.1
	St	**482**		**478**		**DR23**	**499**, *522*		**495**, *532*	

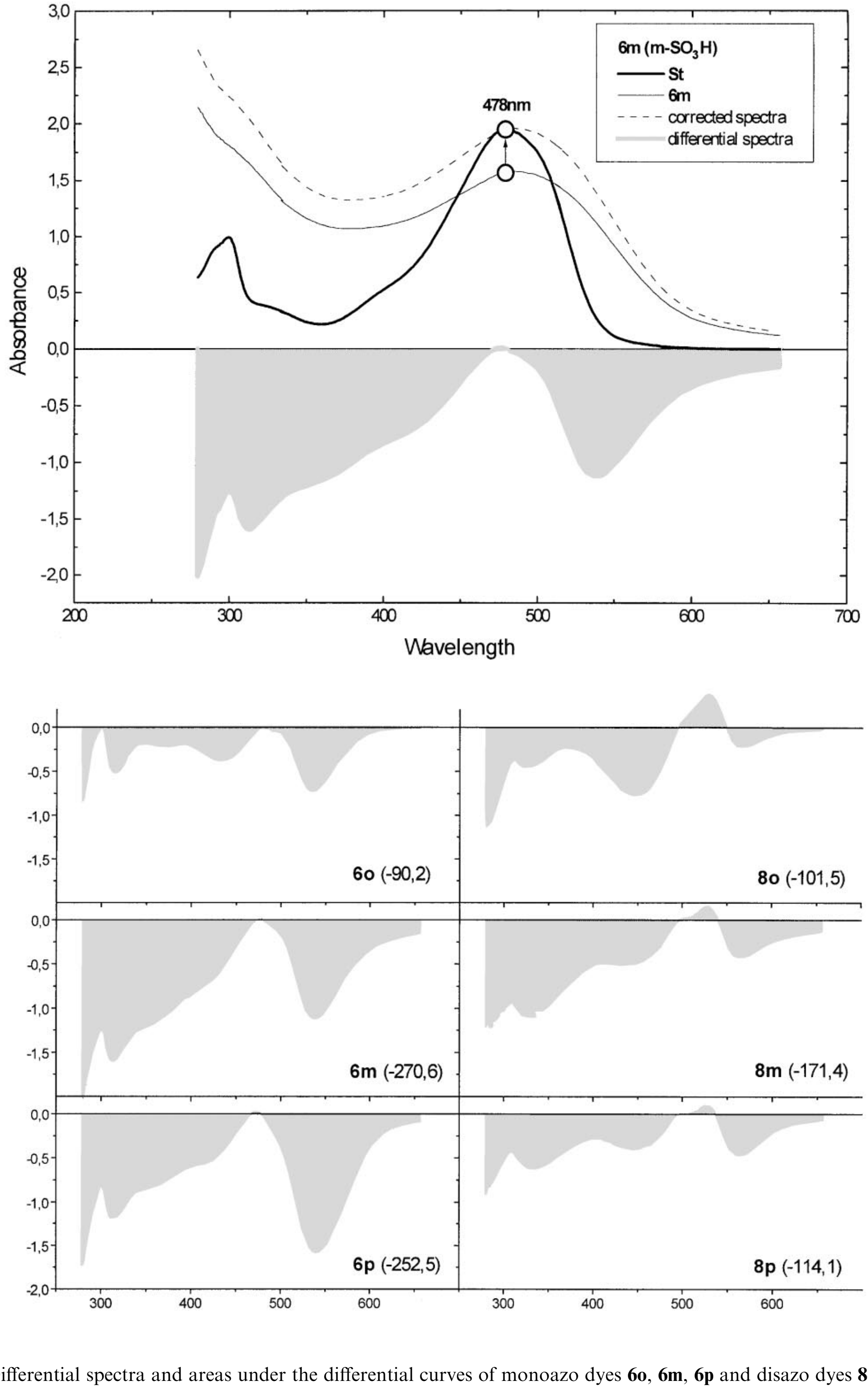


Fig. 1. Differential spectra and areas under the differential curves of monoazo dyes **6o**, **6m**, **6p** and disazo dyes **8o**, **8m**, **8p**.

Table 3
Differential analysis of reflectance spectra on wool

	Monoazo dyes			Disazo dyes		
		λ_{max}	ΔS		λ_{max}	ΔS
o-SO_3H	**6o**	503	−27.5	**8o**	495	−14.7
m-SO_3H	**6m**	486	−34.4	**8m**	490	−49.6
p-SO_3H	**6p**	502	−33.3	**8p**	487	−29.5
	St	**503**		DR23	528	

478 nm, while that for the disazo dyes **8** was carried out at 499 and 495 nm.

Reference dyes **St** and **DR23** in solutions of various pH show a low sensitivity to the system alkalinity. This makes them different from the dyes under investigation, in which at pH = 7 a hypsochromic effect takes place in relation to the spectra taken at pH = 10, i.e. when the dyes are in an ionised form. This effect seems to be associated with ionisation of the hydroxyl group, as well as with the effect on the spectrum of the ionised sulphonic acid group.

The effect of the sulphonic acid group is considerable and, in the extreme case, amounts to 38 nm (dye **6p**). The ΔS values of the *meta*-derivatives are also characteristic, being in all the examined cases higher that those for *ortho*- and *para*-isomers. This confirms the conclusion that the sulphonic acid groups in the examined dyes in aqueous solutions not only improve solubility, but also they participate in electronic interaction with the azo system and can affect the spatial structure of dye molecules.

A pictorial example of the standardisation of the spectrum of dye **6m** is shown in Fig. 1. For all the remaining dyes only differential spectra are shown.

In the case of the analysis of the spectral characteristics of monoazo dyes, one should take into account the fact that in the preparation of urea derivatives, the spatial structure of the obtained dyes are changed, while the urea system can partly transfer the electronic interaction between the two parts of the dye. Owing to the differential analysis its identification is possible only in a quantitative way.

Analysis of the data indicates, in most cases, that the best agreement with respect to the spectral characteristics is between the *ortho*-isomers and those of C.I. Direct Red 23. Probably, the sulphonic acid group in an *ortho*-position to the azo bond provides the molecule with additional stabilisation (**8o**), which is shown by different values of ΔS for dyes **8m** and **8p**, and particularly for the *meta*-derivative **8m**.

5. Reflectance spectra on wool and cotton

The reflectance analysis of the dyed wool and cotton fabrics was carried out within the range 280–700 nm. The results of measurements are given in Table 3 and Fig. 2. The reflectance spectral characteristics of the dyes under investigation are relatively flat with a broad maxima dropping steeply within the longer wave range, and showing a bathochromic shift in relation to the spectra in solutions. In addition, changes in the relative intensities of the absorption band are apparent, indicating a change in the state of internal equilibrium of the dye molecule. Probably, this is related to the existence of azo-hydrazone tautomerism. The standardisation of absorption of the examined dyes was carried out at wavelength $\lambda_{max} = 503$ nm (monoazo dyes) and 528 nm (disazo dyes).

Similarly, as in the case of the analysis of spectra in solution, the best agreement of the spectral characteristics is shown between **DR23** and dye **8o** obtained by the coupling of diazotised orthanilic acid. In addition, owing to the replacement of the amino group by the acylamino group, the disazo dyes show a hypsochromic effect in relation to their monoazo analogues (**6**). Evaluation of dyeings on wool is only of relative value, since the disazo dyes are direct dyes. The polarity of the fibre results in a bathochromic effect, which is higher for the monoazo dyes and lower for the disazo dyes. The monoazo dye is polarised to a greater extent, while the urea system facilitates more uniform charge distribution and a higher share of non-ionic interactions in the dyeing process. Only in the *meta*-derivatives should the molecule polarisation effect be very low. This means that the role of the sulphonic acid group consists not only in improving solubility, but, at the same time this group also affects the dye spectral characteristics due to its interaction with the dye chromophore.

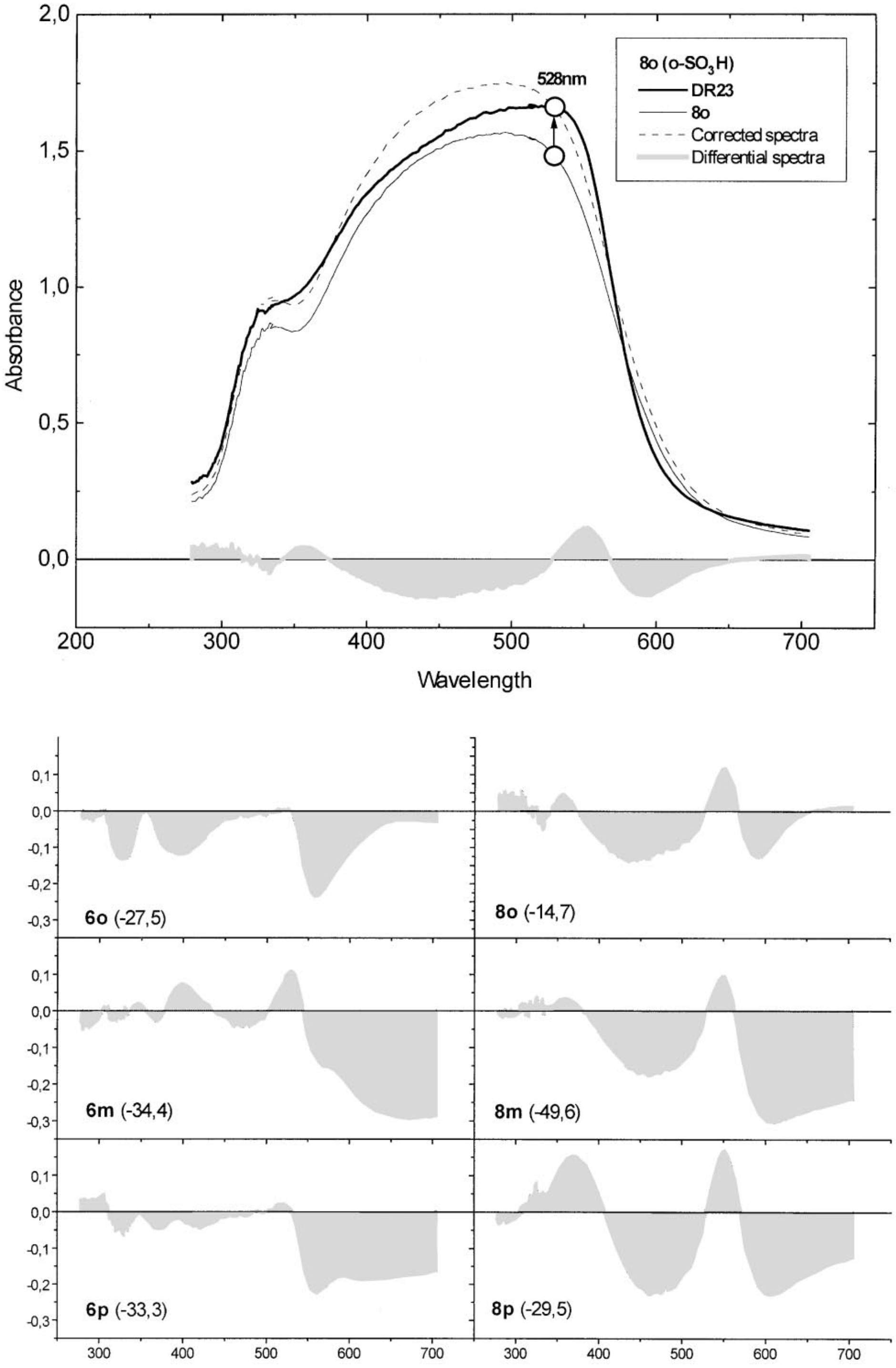


Fig. 2. Differential spectra and areas under the differential curves of monoazo dyes **6o**, **6m**, **6p** and disazo dyes **8o**, **8m**, **8p** on wool.

The analysis was carried out over the range 280–700 nm. The lower polarity of cellulose fibre affects the dye polarisation to a lesser extent. Thus, a greater part of the dye polarisation may be ascribed to the sulphonic acid group acting as a polarising substituent, which becomes apparent in the form of changes in the $\lambda_{\max}$ position in comparison to reflectance spectra performed on wool. (Table 4 and Fig. 3).

Similarly to the wool dyeings, in the case of cotton dyeings the lowest deviation from the reference due is shown by dye **8o**, in which ΔS is −7.8, and by dye **8p** in which the value of ΔS is exceptionally positive. This is due to the equalisation of band intensities within various absorption ranges. The lower polarity of cotton fibre brings about a bathochromic effect in relation to the spectra in solution as well as to those of wool dyeings. Simultaneously, one can observe diversified effects of the -SO_3H group in an *ortho*- position to azo bond in dyes **St**, **DR23**, **6o** and **8o** on spectral properties.

6. Experimental

Tobias acid (**2**) [17], 2-aminonaphthalene-5-sulphonic acid (**3**) [17] and 6-amino-1-naphthol (**4**) [21,22] were prepared according to the procedures described in the literature.

6.1. Bis-ureido-6-(naphthol-1) (5)

Diphenyl carbonate, (2.14 g), 4.04 g of **4** and 0.1 g of *p*-*N*,*N*-dimethylaminopyridine as catalyst in 25 cm^3 of *o*-dichlorobenzene were refluxed for 2 h; solvent was then removed by steam distillation and the residue was filtered, washed with 5% HCl and water. The reaction yield is given in Table 1. TLC: on Silufol 254 UV, eluent: pyridine: toluene (1:3), R_f (**5**) = 0.0.

6.2. Dye synthesis: typified by 8o

Diazotisation of orthanilic acid was carried out according to the usual procedure. 1.72 g of **5** was dissolved in 10 cm^3 of ethanol and 5 cm^3 of 30% NaOH and 100 cm^3 of hot water. The diazo liquor was added dropwise to the solution of a coupling component at of 5–10°C. The dye was precipitated by adding 20% by vol. of NaCl at 70°C. The yield was 76.6% and the purity of **8o** was 82.0%. Chromatography: Whatman 3 paper, eluent: methanol: DMF: water (3:1:1); R_f = 0.89 (**8o**).

6.3. Dye analysis

The dye purity, including the content of chloride ions, was determined by potentiometry. The results are given in Table 5.

6.4. Dyeing procedure

Dyeings of wool and cotton fabrics were performed according to standards BN-85/6041-40 and BN-88/6041-42; these methods are much the same as those used in the other European countries.

Spectral analysis was carried out using of a Perkin–Elmer Lambda 40 and a Specord M40 (Zeiss Jena) spectrophotometer with a reflectance attachment.

Differential analysis was performed using an Microcal® Origin® v3.5 (Microcal Software, Inc.) program for statistical analysis.

Table 4
Differential analysis of reflectance spectra on cotton

	Monoazo dyes			Disazo dyes		
		$\lambda_{\max}$	ΔS		$\lambda_{\max}$	ΔS
o-SO_3H	**6o**	469	−28.3	**8o**	456	−7.8
m-SO_3H	**6m**	484	−52.3	**8m**	490	−11.4
p-SO_3H	**6p**	475	−23.3	**8p**	482	+2.8
	St	**499**		**DR23**	**487**	

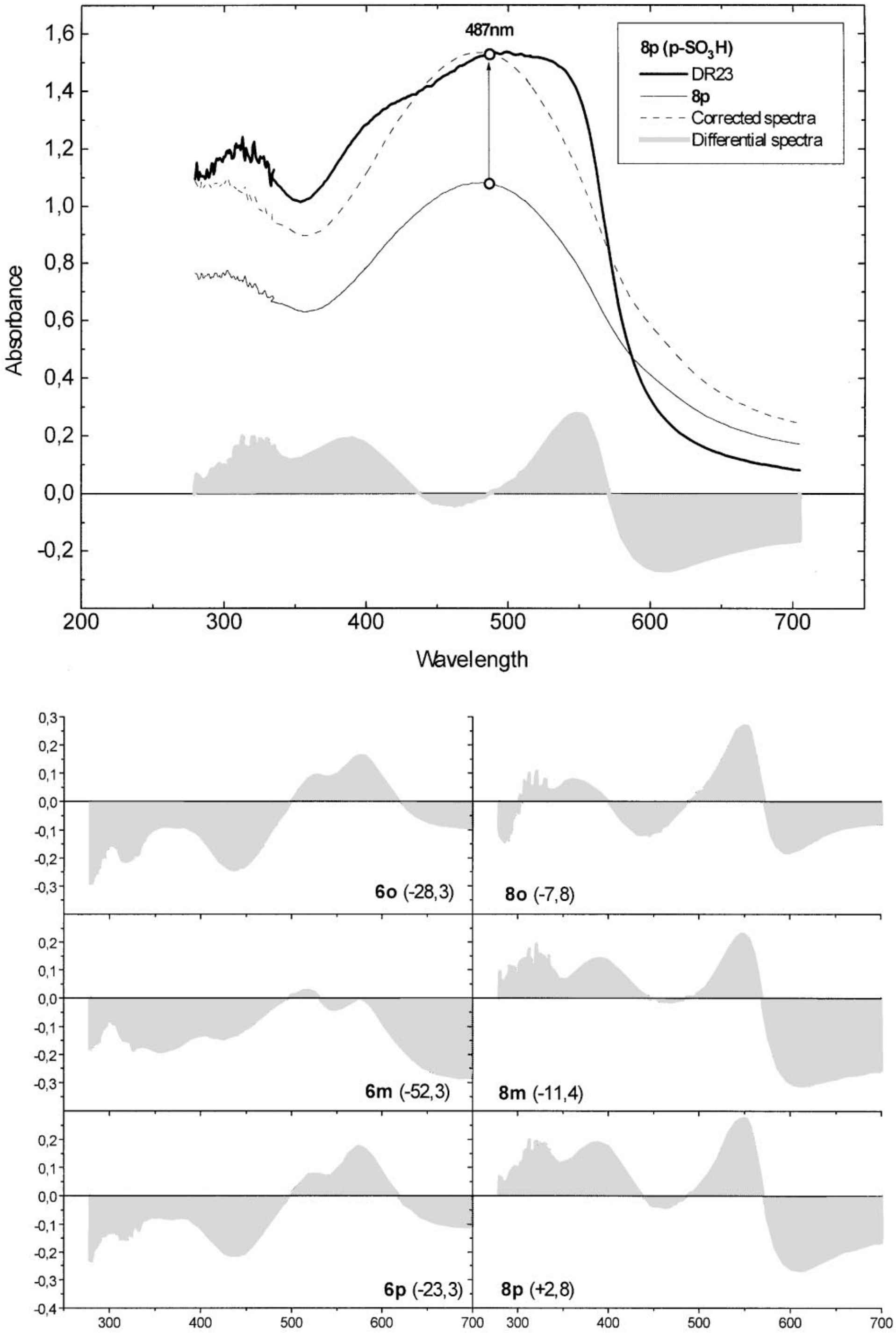


Fig. 3. Differential spectra and areas under the differential curves of monoazo dyes **6o**, **m**, **p** and disazo dyes **8o**, **m**, **p** on cotton.

Table 5
Purity of the monoazo and disazo dyes

Dye	purity [%]	Dye	purity [%]
St	67.1	**DR23**	74.3
6o	95.6	**8o**	82.0
6m	63.5	**8m**	69.0
6p	81.0	**8p**	69.7

7. Conclusions

The presence of a sulphonic acid group in the diazo component brings about a clear effect on the spectral properties of the dyes investigated, a distinct influence of the sulphonic acid group on the dye colour and purity of shade being apparent. A particularly "negative" effect is shown by its presence in *meta*-position in relation to the azo bond, and in such a case, hypso- and hypochromic effects and a strong absorption within the near uv range are observed. The ΔS values of *meta*-derivatives are the highest both in solutions and on fibres. This indicates that sulphonic acid groups play a significant part, affecting the electron density distribution in the dye molecules, despite the fact that according to the generally accepted views they should not take part in electronic interaction with azo systems. However, they may probably affect the spatial structure of the dyes and the stabilisation of the hydrazone form, and consequently they may influence indirectly the electron density distribution of the dye molecules.

In all the examined cases, the *meta*-isomer showed the lowest coincidence with the spectral characteristics of the reference dye C.I. Direct Red 23.

The most important differences were observed in the $\lambda_{\max}$ positions of the dyes as compared to C.I. Direct Red 23. The spectra of **DR23** showed two absorption bands at 495 and 523 nm which are discrete "vibronic" bands of the hydrazone form [23–26]. This phenomenon does not occur in dyes **6** and **8**; the dyes containing a sulphonic acid group in the diazo component have no "vibronic" bands. In the case of dyes **6** and **8**, a clear hypsochromic effect in spectra in solutions and on dyed fabrics in relation to **DR23** was observed.

The presence of a sulphonic acid group in the *ortho*-position to the azo bond in the diazo component results in the (**6o** and **8o**) showing similar shade in comparison to the reference dyes **St** and **DR23**.

The new group of dyes reported herein may constitute an alternative to the currently used conventional urea derivatives, manufactured by reacting appropriate amine derivatives with phosgene, although dullness of their colour must also be considered.

Acknowledgements

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