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Direct urea-based dyes derived from diamines with increased solubilities

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Abstract

Sulphonic acid derivatives of diaminediphenylureas were used to synthesise disazo urea dyes. The properties of the dyes were compared with those of their analogues containing no sulphonic groups in the diazo component. It was found that the properties of the dyes were affected by both the position of the urea group as well as the number and position of sulphonic acid groups. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Urea dyes; Solubilised diamines; Standard affinity; Dyeing fastness; Direct dyes

1. Introduction

Among direct dyes used for dyeing cellulose fibres, benzidine dyes constituted a numerous group and were distinguishable by their high colour intensity, good shade purity and low price.

The production of benzidine dyes was abandoned when benzidine (used for their manufacture) was found to be carcinogenic. It then became necessary to fill the resultant gap in the production of direct dyes. One solution was to use benzidine-free direct dyes obtained by replacing benzidine with other harmless diamines, including urea derivatives. As a concequence, interest in urea-based direct dyes has increased in recent years.

Direct dyes containing urea group have long been known. Most were prepared by acylation of appropriate amine monoazo dyes with phosgene. However, as the use of this strongly toxic agent creates a hazard to dye manufacturers, for many years studies have been made of direct dyes obtainable without the use of phosgene and which contained various urea systems [1–4].

2. Investigations

This paper concerns sulphonated diamines containing a diaminediphenylurea system, such as 3,3′-disulpho-4,4′-diaminediphenylurea (**PS**) and 4,4′-disulfo-3,3′-diaminediphenylurea (**MS**).

In accordance with literature data, these compounds and their decomposition products should be expected to be non-carcinogenic like benzidinedisulphonic acid [2].

As has been previously found [2], **PS** can be easily prepared, analogously to the synthesis of 4,4′-diaminediphenylurea [1], by heating 2,5-

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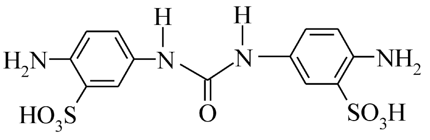
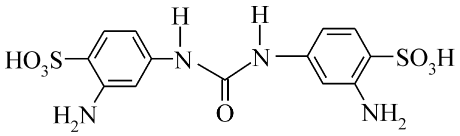


PS



MS

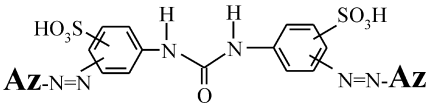
diaminephenyl-1-sulfonic acid and urea in an aqueous medium [2]. This procedure is considerably simpler than that proposed by the German patent [5] which consists of the phosgene treatment of 5-amine-2-nitrobenzene-1-sulfonic acid followed by reduction of the resultant dinitrocompounds.

In this way **MS** was obtained by the same procedure as that proposed by Peng [6], by condensation of 2,4-diaminephenylene-1-sulfonic acid (RH acid) with bis(trichloromethyl) carbonate (known as triphosgene) in an aqueous medium.

The bisdiazotisation of the synthesised diamines **MS** and **PS** followed by coupling with selected components resulted in two series of disazo direct dyes of general formula **1**.

The physical and chemical characteristics of the dyes as well as their application characteristics and colour fastness were examined and compared with those of analogous dyes 2 prepared from 4,4′-diaminediphenylurea (**P**) and 3,3′-diaminediphenylurea (**M**).

The results are given in Tables 1 and 2.



1

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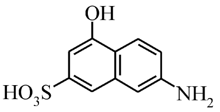
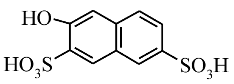


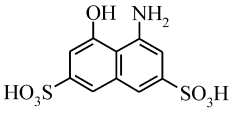
I

(J-acid)



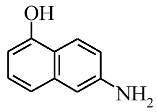
R

(R-acid)



H

(H-acid)



N

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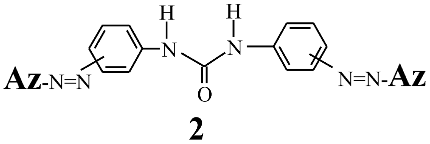
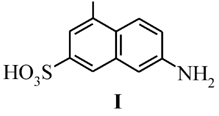


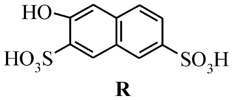
2

where **Az**:



I

(J-acid)



R

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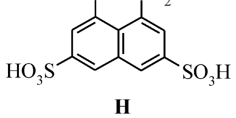

H

(H-acid)

Table 1
Physical, chemical and application properties of dyes

Dye	Purity (%)	λ_{max} (nm)	$\Delta\lambda_{1/2}$ (nm)	Degree of dye exhaustion (%)	R_f [b]	R_M [c]	$-\Delta\mu_o$ [d] (J/mol)
1 MR	99.4	498	84	38.7	0.72	−0.410	−6.20
1 PR	99.5	535	105	66.0	0.50	0.000	−8.06
2 MSR	64.9	493	79	8.3	0.75	−0.477	−5.90
2 PSR	99.4	524	91	16.1	0.67	−0.307	−6.67
1 MI	76.5	480	88	88.2	0.40	0.176	−24.02
1 PI	99.5	524	117	94.6	0.33	0.307	−25.90
2 MSI	89.2	473	92	24.8	0.72	−0.410	−15.61
2 PSI	89.1	509	98	46.3	0.53	−0.052	−20.75
1 MH	99.4	533	91	54.9	0.84	−0.720	−8.36
1 PH	89.8	562	102	57.3	0.59	−0.158	−15.36
2 MSH	59.1	531	91	11.0	0.83	−0.688	−8.76
2 PSH	70.0	552	102	22.2	0.68	−0.327	−13.26
2 MSN	99.5	478[a]	–	15.1	0.77	–	–
2 PSN	99.5	491	113	90.5	0.39	–	–

[a] In 50% DMF/water.

[b] Chromatographic constant.

[c] Log chromatographic constant [Eq. (2)].

[d] Standard affinity [Eq. (2)].

Table 2
Fastness properties of 1% omf dyeings on cotton

	Perspiration								Washing 40°C (staining)	Light fastness (Xenotest)
Dye	Acid		Alkaline		Water 40°C		Rubbing			
	Staining	Alternation	Staining	Alternation	Staining	Alternation	Dry	Wet		
1 MR	3–4	5	3–4	5	3–4	4–5	4	3–4	3–4	1–2
1 PR	3–4	4–5	3	4	3–4	5	4	3	2	3
2 MSR	3–4	4–5	3–4	4–5	3–4	5	5	5	4	1–2
2 PSR	3	4	3	4	3–4	4–5	5	5	3	2
1 MI	3–4	4–5	3–4	4–5	3–4	4–5	4	3–4	4	1
1 PI	3	5	3	5	3	5	4	3	4–5	3
2 MSI	3	5	3	4–5	3	4–5	5	4-5	3–4	1
2 PSI	3	4	3	4–5	3	4	5	4	4	2–3
1 MH	3–4	4–5	3–4	4–5	3	4–5	5	5	4	2
1 PH	3	4–5	3	4	3	4–5	5	5	4–5	2–3
2 MSH	3–4	5	3–4	4–5	3–4	4–5	5	5	4–5	2
2 PSH	3	4	3–4	4–5	3–4	4–5	5	5	4–5	2
2 MSN							4	4–5	5	2–3
2 PSN							5	5	4	3

3. Experimental

3.1. *3,3′-Disulfo-4,4′-diaminediphenylurea (**PS**) and 4,4′-diamineduphenylurea (**P**)*

These were prepared as described previously [1,2]. The diamine content in the separated products was determined by bisdiazotisation with 0.1 M $NaNO_2$. The product homogenecity was examined by chromatography, using Whatman 1 paper and the eluent consisting of propanol + 5% $NaHCO_3$ (2:1); chromatograms were developed with Ehrlich's reagent.

3.2. Synthesis of 4,4′-disulfo-3,3′-diaminediphenylurea (**MS**)

To a solution of 0.01 mol of 2,4-diaminephenylene-1-sulfonic acid in 60 cm^3 of water, 0.00166 mol of bis(trichloromethyl) carbonate (triphosgene) was added at 20–60°C for 1 h, maintaining pH at 6–8. The resultant **MS** amine was separated and analysed in the same way as isomer **PS**.

3.3. Synthesis of 3,3′-diaminediphenylurea (**M**)

3,3′-Diaminediphenylurea was prepared as described by Brunner [7], 0.03 mol of urea and 0.05 mol of 1,3-phenylenodiamine were heated in 8.5 cm^3 of 38.5% H_2SO_4 for 32 h at boiling temperature. Then, the reaction mixture was diluted with 60 cm^3 of water and neutralised with 20 cm^3 of 30% NaOH. The filtered off and rinsed product was dried at 60–80°C. The amine content was determined as previously.

4. Dye synthesis

MS or **PS** amine (0.005 mol) was dissolved in 50 cm^3 of water containing 0.025 mol (2.5 cm^3) of 30% HCl and bisdiazotised at 0–5°C with 0.01 mol (2.5 cm^3) of 4 M $NaNO_2$. **M** and **P** diamines were bisdiazotised in the same way, rubbing preliminarily 0.005 mol of amine with 0.03 mol (3 cm^3) of 30% HCl and diluting with 50 cm^3 of water. The bisdiazo suspension was added dropwise at 0–5°C into a solution of 0.01 mol of coupling component in 50 cm^3 of water containing 0.05 mol (50 cm^3) of 10% Na_2CO_3. The resultant dyes were separated from the solution by salting out at 80°C with 20% by vol. NaCl, filtered off at room temperature, rinsed with 10% NaCl and dried at 60–80°C.

5. Dye analysis

The dye homogeneity was determined by chromatography [8,9], using Whatman 1 paper and eluent: MeOH:DMF:water = 3:1:1. The Cl^- ion content (as NaCl) was determined by potentiometry, titrating the dye solutions in an acidic medium (H_2SO_4) with 0.1 M. $AgNO_3$ using calomel and silver electrodes [10].

6. Determination of the degree of dye exhaustion

The degree of dye exhaustion on cellulose fibre (E) was determined by dyeing 2 g samples of a bleached and mercerised woven cotton fabric in a Roaches-Rotec dyeing machine at 1% omf using a liquor ratio of 30:1 and 0.5% omf Na_2SO_4. The fabric sample was heated in the dyebath for 2 h up to 95°C and dyed at this temperature for 1 h. The bath was then cooled over 0.5 h to 60°C, followed by washing and drying in air. The degree of dye exhaustion (E) was determined by colorimetry, measuring the dye concentration before (c_1) and after (c_2) dyeing [Eq. (1)].

$$E = \frac{c_1 - c_2}{c_1} \times 100\% \qquad (1)$$

Spectrophotometric measurements were carried out by diluting dyebath samples, before and after dyeing, to concentrations 10^{-3}–10^{-4} mol/dm^3. Prior to measurement, all solutions were stored in darkness for 24 h. Spectra were recorded within the range 400–700 nm using a Specord M-40 (Zeiss-Jena) spectrophotometer.

7. Determination of the standard affinity

Based on the values of chromatographic constants of dyes R_f, the standard affinity was calculated from the logarithmic chromatographic constants R_M, using linear correlation between R_M and $(-\Delta\mu_o)$ evaluated by Alberti [9] and given by the following equation [9,12,13] [Eq. (2)]

$$-\Delta\mu_o = \frac{b - R_M}{a} \times 4.1868 \ \ [\text{J/mol}] \qquad (2)$$

where:

$$R_M = \lg\left(\frac{1}{R_f} - 1\right),$$

$\Delta\mu_o$ is the standard affinity; b and a are constants for the used coupling components [9] [**R** acid ($a = 0.924$, $b = -1.779$), for **J** acid ($a = 0.292$, $b = -1.499$), and for **H** acid ($a = 0.336$, $b = -1.391$)].

8. Determination of fastness

The fastness to washing at 40°C, water at 40°C, dry and wet rubbing, acidic and alkaline perspiration and light was carried out according to the ISO standards. Light fastness was evaluated using a Xenotest 150S apparatus (Hanau).

9. Results

From the results listed in Table 1 it is apparent that dyes **1**, obtained from **MS** and **PS** diamines containing additionally sulphonic groups displayed wery low exhaustion due to their high water solubility conferred by the high number of sulphonic groups, compared with dyes **2** obtained from **M** and **P** amines. The lower uptake of dyes **1** are confirmed by their high chromatographic constants (R_f) as compared with the analogous dyes **2** and the calculated standard affinity $-\Delta\mu_o$ (Table 1).

The calculated values of R_M and $-\Delta\mu_o$ [Eq. (2)] are given in Table 1. The highest standard affinity is shown by the **J** acid derivatives, while the lowest affinity belongs to the derivative of **R** salt. These relationships are consistent with previously determined data [9,11,14] for both benzidine and carbazole direct dyes. The reason for the different values of $-\Delta\mu_o$ for the two sets of dyes is the number of sulphonic groups in the coupling component and the type of the diazo component used.

Comparing analogous dyes containing azo bonds in the *para*-position and dyes containing these bonds in the *meta*-position, it is apparent that dyes of the **P** type were characterised by higher affinity then dyes of the **M** type. This is consistent with expectations and is accounted for by the more linear structure of dyes **P**. From the results given in Table 2 it follows that there were no significant differences between the dyes under investigation. Only in some cases were the fastness values of dyeings obtained with dyes **2** higher than those of dyes **1**.

All of the dyes were of moderate fastness. In spite of misgivings, the increase in the number of sulphonic groups in the molecule of dyes **1** brought about no significant deterioration of their fastness to wet treatments.

The colour of the dyes differed significantly, depending mainly on the type of the diazo components. A distinct bathochromic effect was observed with the *para*-derivatives, both sulphonated (**1 PS**) and those without sulphonic groups (**2 P**) in relation to the analogous *meta*- derivatives (**2 MS** and **2 M**). The presence of the sulphonic groups in the diazo component caused a small hypsochromic shift. The maximum difference in $\Delta\lambda_{max}$ was 15 nm (**PI–PSI**) the minimum only 2 nm (**MH–MSH**).

The position of λ_{max} of the dye solutions depends on the type of the coupling component used (**R**, **H**, **I**). The **H** acid derivates absorbed at higher wavelength, then the derivatives of **I** acid. The largest difference in $\Delta\lambda_{max}$ was 58 nm. Dyes with azo bonds in the *para*-position in relation to urea were characterised by a dull shade and broadened half widths of absorption bands ($\Delta\lambda_{1/2}$) when compared to the corresponding *meta*-azo dyes.

For the purposes of comparison, **MSN** and **PSN** dyes were prepared using an analogue of **J** acid without sulphonic groups: 6-amine-1-naphthol as a coupling component. The solubility of these dyes is due to the presence of sulphonic groups exclusively in the diazo component (**MS**, **PS**). Using the example of these dyes one can very clearly see the dependence of dye exhaustion on the linearity of the dye molecule. The extent of exhaustion of dye **PSN** was almost six times higher than that of the **MSN** dye. Dye **2 PSN** showed the same high exhaustion as the isomeric dye **1 PI**.

The light fastness of all the dyes under investigation was rather low, although some differences were observed between the dyes insofar as dyeings obtained with dyes **P** and **PS** amines displayed somewhat higher light fastness than those with analogous **M** and **MS** derivatives.

10. Conclusions

The presence of sulphonic groups in the diazo component and the arrangement of the azo bonds in *meta*-positions effects, adversely, the dyeing properties of the dyes. Thus it seems useful to suggest the use of 3,3′-disufo-4,4′-diaminediphenylurea and sulphonic group-free coupling components.

Acknowledgements

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