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Synthesis and Properties of Disazo Dyes Derived from Water-Soluble Derivatives of Benzidine and 4,4′-Diaminodiphenylurea

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ABSTRACT

From benzidine and 4,4′-diaminodiphenylurea derivatives containing sulpho or carboxyl groups, a series of disazo dyes have been synthesized. The effects of the structure of the dyes on their colour, affinity for cellulose and the fastness of the dyeings, compared with analogous unsubstituted benzidine and diphenylurea dyes, have been studied. It was found that in all sulpho- or carboxyl-substituted dyes a hypsochromic effect, a decrease in affinity for cellulose fibres and a slight increase in fastness is observed. These results can be explained in terms of deformation of the structure of dyes containing sulpho or carboxyl groups.

1 INTRODUCTION

The production and use of benzidine-based dyes has been largely discontinued in view of the toxicological hazards associated with them. The problem of replacing benzidine dyes has not been fully resolved, although a number of approaches have been made, based on two concepts. The first consists in the use of other classes of dye for dyeing cellulose fibres, and the second approach involves the use of other diamines in the dye synthesis. The first solution does not usually ensure obtaining all the hues possible from benzidine dyes; it is more expensive, and often requires alternative dyeing technology. The second concept is of interest, since it could yield new, harmless dyes having the same colour and application properties as the

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benzidine dyes. 4,4′-Diaminocarbanilide,[1] diaminostilbenedisulphonic acid[2] and diaminodiphenylaminesulphonic acid[3] have been investigated in this context, and more recently further suggestions for replacing benzidine with other diamines have been described.[4-8] We have presented some suggestions, involving the use of cyclic derivatives of benzidine.[9]

Most of the above diamines are not readily available and none of them fully satisfies all the requirements for a satisfactory benzidine replacement, namely:

(1) The diamines and derived dyes should not show mutagenity or carcinogenicity.
(2) Disazo and polyazo dyes obtained from the diamines should have a high affinity for cellulose.
(3) The structure of diamine should ensure conjugation throughout the dye molecule thus enabling a range of colours to be obtained similar to those of the corresponding benzidine dyes.
(4) The structure of the diamine should be such that coupling its bisdiazonium salts with two different coupling components is possible, i.e. with formation of asymmetrical disazo and polyazo dyes. This is necessary in order to obtain black, green, brown and navy-blue dyes.

The effect of the dye structure on specific properties of the dyes is generally well established, but in practice unexpected deviations from the generally accepted rules can be encountered. Continuation of studies on establishing the relationship between the structure of amines and their properties is thus necessary.

The causes of carcinogenicity of benzidine have not been fully rationalised, but it has been noted that lack of carcinogenicity is likely to occur in diamines (and derived dyes) whose metabolic decomposition results in the formation of water-soluble products.[10,11] Thus, benzidine derivatives containing carboxyl[12] and sulphonic as well as alkyl and alkoxyl groups[7,8] at 3,3′-positions have been described, these compounds being likely to undergo oxidation or hydrolysis to soluble products.

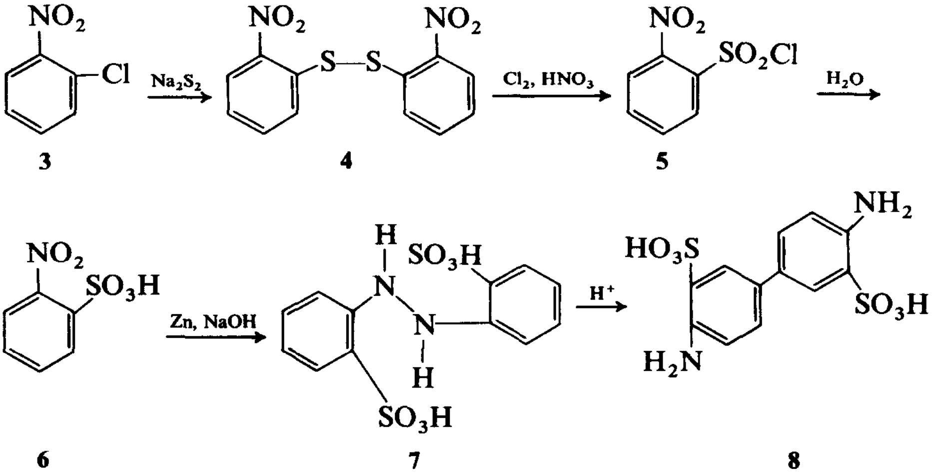
We report here on the possibility of obtaining and using simple water-soluble derivatives of benzidine and 4,4′-diaminodiphenylurea. The lack of mutagenity in benzidine-3.3′-disulphonic acid has been demonstrated (Mikucki, J. & Szarapińska-Kwaszewska, J., Department of Pharmaceutical Microbiology, Medical School, Łódź, unpublished). Benzidine-3,3′-dicarboxylic acid can be considered to be relatively harmless and, in the case of the sulphonated derivatives of diaminodiphenylurea, lack of carcinogenicity could be expected in view of the solubility of its degradation products.

2 RESULTS AND DISCUSSION

Only relatively simple disazo dyes were evaluated in the investigations, since it was easy to determine accurately their standard affinity and spectral properties. For the synthesis of symmetrical disazo dyes, benzidine (**1**) and 4,4′-diaminodiphenylurea (**2**) and their derivatives substituted at the 3,3′-positions by sulphonic or carboxyl groups were used. Benzidine-3,3′-disulphonic acid (**8**) and benzidine-3,3′-dicarboxylic acid (**10**) were readily synthesised, but in the case of diaminodiphenylurea (**2**) derivatives, only 3,3′-disulpho-4,4′-diaminodiphenylurea (**2a**) could be obtained; the corresponding dicarboxylic acid could not be obtained in a simple manner.

The method for obtaining benzidine-3,3′-disulphonic acid (**8**) described previously consists in 'baking' benzidine sulphate.[13] Such a method is not practicable in view of the necessity of using benzidine as starting material. To obtain this compound, the reaction sequence shown in Scheme 1 was used. This involves the synthesis of 2-nitrobenzenesulphonic acid (**6**), its reduction and subsequent benzidine rearrangement.

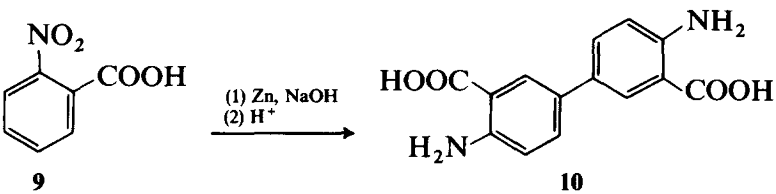
The first three stages of the synthesis, leading to 2-nitrobenzenesulphonic acid (**6**), are well documented in processes for the synthesis of orthanilic acid.[14-16] The formation of the disulphide (**4**) proceeded readily using the previously reported method,[14] and both oxidation of this to the sulphochloride (**5**) and subsequent hydrolysis were found to proceed almost quantitatively. The only difficulty encountered was due to the high solubility of 2-nitrobenzenesulphonic acid (**6**), which inhibited its facile isolation in a crystalline state. The further stages of reduction and benzidine rearrangement were therefore carried out using a solution of acid (**6**), or of a crude



Scheme 1

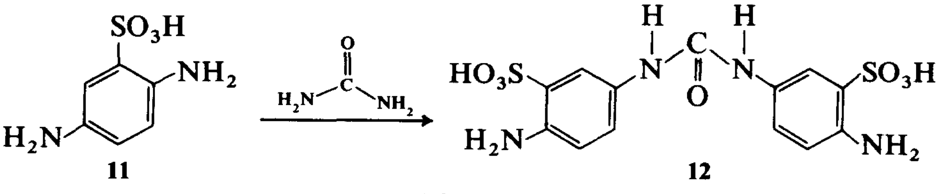
material isolated by concentration of the initial reaction liquor, which contained a large amount of inorganic salts. The final stages of the reaction sequence have not been previously described so far, but the reduction and the rearrangement proceeded well using conditions similar to those used to obtain benzidine-3,3'-dicarboxylic acid.[17] The crude benzidine-3,3'-disulphonic acid (**8**) thus obtained in good yield contained only a small amount of orthanilic acid as by-product, and this was easily removed by crystallisation of the product from water. The purified acid **8** was identical with the product obtained by the conventional method.[13]

Benzidine-3,3'-dicarboxylic acid (**10**) was obtained using the method described by Fierz-David,[17] starting from 2-nitrobenzoic acid (**9**), as shown in Scheme 2.



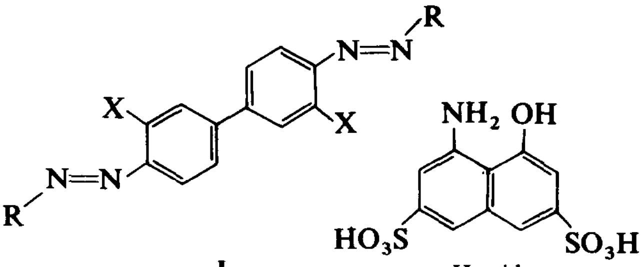
Scheme 2

3,3'-Disulpho-4,4'-diaminodiphenylurea (**12**) was obtained by heating an aqueous solution of 1,4-phenylenediamine-2-sulphonic acid (**11**) for several hours with urea, using conditions similar to those used for preparing 4,4'-diaminodiphenylurea (Scheme 3). Under these conditions, only the amino group at position 4 underwent acylation with urea and no formation of isomeric products was observed.



Scheme 3

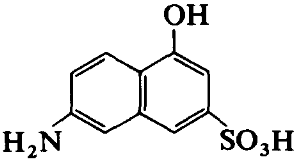
The diamines **8**, **10** and **12** thus obtained were used in the synthesis of disazo dyes and, for comparison, analogous dyes were prepared from benzidine and 4,4'-diaminodiphenylurea. We studied only the symmetrical dyes **I** and **II** from H-acid or J-acid as coupling components, this allowing the facile determination of the standard affinity of the dyes by the chromatographic method,[18] and comparison of the colour of the new compounds with that of the corresponding benzidine or urea dyes.



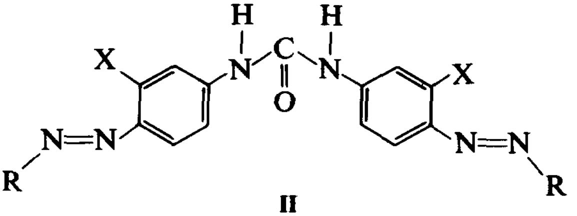
I

H-acid

	R	*X*
Ia	H-acid	H
Ia′	J-acid	H
Ib	H-acid	SO_3H
Ib′	J-acid	SO_3H
Ic	H-acid	COOH
Ic	J-acid	COOH



J-acid



II

	R	*X*
IIa	H-acid	H
IIa′	J-acid	H
IIb	H-acid	SO_3H
IIb′	J-acid	SO_3H

Electronic spectra data (Table 1) show that the dyes containing sulphonic and carboxyl groups *o,o′* to the azo group show a distinct hypsochromic effect in relation to the corresponding derivatives of benzidine or diaminodiphenylurea. The hypsochromic shifts were smaller in the case of substitution with carboxyl groups (**Ic** and **Ic′**) (3·5–4 nm), and greatest in the case of the sulphonated derivatives (6–26·5 nm). In all cases molar absorptivity was similar [(40–56) × 10^3 litre mol^{-1} cm^{-1}], being slightly higher for dyes of higher solubility containing more sulphonic groups.

However, considerable differences in the affinity of the dyes for cellulose fibres were found, the values of standard affinity shown in Table 1 being 2·1–8·5 kJ mol^{-1} lower than values for unsubstituted benzidine or urea dyes. Such a decrease in the standard affinity is reflected in a considerable reduction in the dyebath exhaustion, and hence a considerable decrease in the efficiency of the dyeing process. Such a property renders the dyes unsatisfactory for use as direct dyes.

The fastness properties of the dyeings were generally, similar to those of dyeings with benzidine or urea dyes. Lightfastness was in some cases half a unit lower for dyes containing additional sulphonic groups, but washing fastness was in many cases slightly higher. Fastness to perspiration was

TABLE 1

Properties of Disazo Benzidine (I) and Urea (II) Dyes

Dye no.	Spectral properties λ (nm)	$\varepsilon \times 10^{-3}$ ($l\,mol^{-1}\,cm^{-1}$)	Standard affinity ($kJ\,mol^{-1}$)	Fastness														
				Light	Washing at 40°C[a]			Water[a]			Acid perspiration[a]			Alkaline perspiration[a]			Friction	
					a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*Dry*	*Wet*
Ia	585·5	45	26·3	2	2	4–5	5	2	5	3–4	2	5	4	2–3	5	4–5	4–5	3–4
Ia′	539	46	30·1	3–4	2	4–5	4–5	2	4–5	3–4	2	5	3–4	2–3	5	3–4	4	3
IIa	558	44	28·2	2–3	2	5	5	2	5	4	2	5	4–5	2–3	5	4–5	5	3–4
IIa′	525	42·5	33·0	2	2–3	5	4–5	2–3	5	4–5	2	5	4–5	3	5	4	4	3–4
Ib	578·5	54	23·0	2–3	2–3	5	5	2	5	4	2	5	4	2–3	5	4–5	5	4–5
Ib′	523	56	28·0	2–3	2	5	4–5	2	5	3–4	2	5	4	2–3	5	4	4–5	3–4
Ic	582	52	20·8	2	2–3	4–5	5	2	5	3–4	2	4–5	5	2–3	5	4–5	4–5	4–5
Ic′	534	54	22·7	3–4	2	4	4–5	2	5	3	2	4–5	4	2–3	5	4–5	5	4
IIb	551	45·5	20·7	2	2	5	5	2	5	4	2	5	5	2–3	4–5	5	5	4
IIb′	500	40	25·2	2	2	4	4–5	2	4–5	3–4	2	4–5	4–5	2–3	4–5	4–5	4–5	3–4

[a] *a*, Pollution of cotton; *b*, discoloration; *c*, pollution of wool.

almost identical, and fastness to wet rubbing was generally higher (half a unit).

This combination of low affinity and a distinct hypsochromic effect, together with no significant deterioration of the wetfastness of the dyeings, indicates that the lower substantivity of the dyes containing additional sulphonic or carboxyl groups is not caused solely by an increase in the dye solubility. It is probably also related to deformation of the dye molecule due to the vicinity of the sulphonic or carboxyl groups to the azo bond. A similar hypsochromic shift was observed by Greenwood and co-workers[19] in some similar *o*,*o*′-disubstituted monoazo compounds, and an analogous effect is likely in the case of the *o*-sulpho-*o*′-hydroxyazo dyes which were the subject of this present study.

3 EXPERIMENTAL

3.1 Synthesis and purification of diamines

3.1.1 Benzidine (**1**) *and 4,4′-diaminodiphenylurea* (**2**)

These compounds were purified by crystallisation from water (charcoal) of the diamine hydrochloride.

3.1.2 Benzidine-3,3′-disulphonic acid (**8**)

This was obtained according to Scheme 1. 2-Nitrobenzenesulphonic acid (**6**) was obtained from 2-nitrochlorobenzene (**3**) by the method described by Fierz-David *et al.*[14] Compound **6** (20·3 g, 0·1 mol) was dissolved in water (100 ml) and NaOH (25 g) was added. To this solution, at 50–80°C, zinc dust (25 g) was added portionwise over 30 min. The solution was diluted with boiling water (160 ml) with addition of Na_2SO_3 (5 g); unreacted zinc was filtered off, and the filtrate was acidified with 30% HCl (90 ml). After cooling, the precipitate was filtered, washed with water (100 ml) and recrystallised from water (charcoal) to give benzidine-3,3′-disulphonic acid, **8** (*c.* 12 g). Its purity was determined by titration with 0·1 M $NaNO_2$ and by chromatography on Whatman no. 1 paper, using propanol and 5% aq. $NaHCO_3$ in a ratio of 2 parts propanol to 1 part 5% aq. $NaHCO_3$.

3.1.3 Benzidine-3,3′-dicarboxylic acid (**10**)

This compound was obtained by the method described by Fierz-David & Blangey.[17] The crude product was purified as for **8**.

3.1.4 3,3′-Disulpho-4,4′-diaminodiphenylurea (**12**)

Compound **12** was obtained by boiling a solution of urea (6 g, 0·1 mol) and of 1,4-phenylenediamino-2-sulphonic acid **11** (42 g, 0·22 mol) in water (200 ml) for 60 h. To prevent oxidation of **11**, Na_2SO_3 (0·2 g) was added every few hours. The course of the reaction was checked chromatographically, under the conditions described above. When reaction was complete, activated charcoal (15 g) was added to the boiling solution, and the liquor then filtered. The residue was washed with boiling water (50 ml) and NaCl (60 g) was added to the filtrate. After cooling to 15°C, compound **12** was filtered. The crude product was purified as above to give 3,3'-disulpho-4,4'-diaminodiphenylurea (11 g).

3.2 Synthesis of dyes

The diamines **1**, **2**, **6**, **10** and **12** were diazotised by adding aqueous $NaNO_2$ (0·1 mol) dropwise to a solution or dispersion of the diamine (0·05 mol) in 2% HCl (450 ml) at 0–5°C. On completion of diazotisation (1–3 h), the diazonium liquor was added dropwise to a solution of H-acid or J-acid (0·1 mol) in 5% Na_2CO_3 (600 ml). On completion of coupling (1–2 h), the dye was separated by adding 10–20% NaCl.

Crude dyes were purified by dyeing cotton fabric (20 g) in a boiling solution of dye (5 g) in water (250 ml) for 1 h. After thoroughly rinsing the dyed fabric, the dye was extracted from the cotton with a 50% boiling solution of pyridine in water (5–7 times 150 ml each). The extract was evaporated, giving dyes free from salts.

Homogeneity of the purified dyes was confirmed by chromatography.[18] The content of the disazo compound in the purified dyes was determined vanadometrically.[20]

3.3 Dye properties

Spectra of the azo compounds **I** and **II** were determined in aqueous solutions at a concentration *c.* 2×10^{-2} g litre^{-1} and at pH 7·5 on a Specord UV–VIS spectrophotometer.

Standard affinities of the dyes for cellulose were calculated on the basis of the chromatographic measurements carried out under the conditions described above (Whatman no. 1 paper; methanol/DMF/water, 3:1:1).[18]

Fastness of the dyeings was examined according to Polish Standards; the methods of these determinations are very similar to those used in other European countries.

4 CONCLUSIONS

The results of the investigation indicate that by using non-carcinogenic derivatives of benzidine and diaminodiphenylurea containing sulphonic or carboxyl groups at 3,3′-positions, dyes for cellulose can be obtained. The fastness of dyeings to wet factors with these dyes is slightly better than fastness of dyeings with analogous benzidine or urea dyes, despite the presence of additional sulphonic or carboxyl groups. However, the dyes containing sulphonic or carboxyl groups in the benzidine or 4,4′-diaminodiphenylurea skeleton show a distinct hypsochromic effect and have lower affinity for cellulose fibres compared with the dyes which do not contain such additional sulphonic or carboxyl groups. It is probable that the cause of both these effects is deformation of the structure of the disazo dyes, brought about by the vicinity of the sulphonic or carboxyl groups and azo groups. The hypsochromic effect and low affinity for cellulose fibres renders the dyes unsuitable for the practical coloration of cellulose.

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