Dyes and Pigments **17** (1991) 297–302

Sulphonated Diaminobenzanilides as Substitutes for Benzidine in the Synthesis of Direct Dyes

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(Received 9 April 1991, accepted 23 May 1991)

ABSTRACT

Four isomeric diaminobenzanilidosulphonic acids were used as substitutes of benzidine in the synthesis of black direct azo dyes. These products, analogues of C.I. Direct Black 38, and also some model dyes, were applied to cotton fabric. Application, colouristic and fastness properties of the dyes were determined and the results discussed.

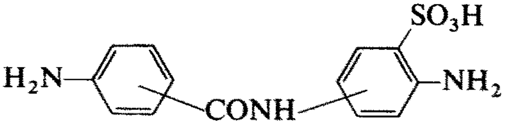
1 INTRODUCTION

The carcinogenic properties of benzidine have resulted in considerable interest in novel diamines which also produce bisdiazo components and which could replace benzidine in the synthesis of direct dyes. One such amine is 4,4′-diaminobenzanilide, which has already been used in the production of some direct azo dyes (e.g. C.I. Direct Green 3, C.I. 32030). However, large-scale production of this intermediate has some inconveniences. The usual method for the preparation of 4,4′-diaminobenzanilide involves condensation of 4-nitrobenzoyl chloride with 4-nitroaniline, followed by reduction of the bis-nitro compound. Variations of the method include the use of 1,4-phenylenediamine instead of 4-nitroaniline. One of the main problems is the use of organic solvents both during the condensation and in some methods of reduction. Alternative reduction methods, e.g. the use of alkali sulphides or of catalytic reduction, can also cause technical, economic and environmental troubles. As a result, there appears to have been a decreasing interest in the use of 4,4′-diaminobenzanilide in synthesis of dyes.

Dyes and Pigments 0143-7208/91/$03.50

The purpose of the present work was to examine the properties of direct dyes prepared using some sulphonated derivatives of diaminobenzanilide. Such substances (formula **1**) may be derived on a technical scale more easily, because both condensation and reduction processes can be carried out in aqueous medium.

It was anticipated that sufficient dye affinity for cellulose fibres would be provided by the use of carbanilides in which the amino groups are located in *para* or *meta* positions to the carbamide bond.



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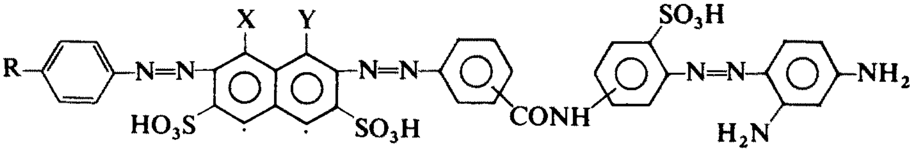
This assumption has been already confirmed by the application of 2-amino-5-[(4′-aminobenzoyl)amino]benzenesulphonic acid (sulphonated 4,4′-diaminocarbanilide) in the synthesis of direct dyes for the colouration of paper.[1] On the other hand, diaminocarbanilides with amino groups *ortho* to the carbamide bond have been used, because of their lower substantivity, in the syntheses of reactive dyes for cellulose fibres.[2]

In this present investigation, the synthesis of analogues of C.I. Direct Black 38 (C.I. 30235), one of the most popular black direct benzidine dyes, is described.

2 EXPERIMENTAL

All sulphonated diaminobenzanilides used in this work were prepared by monoacylation of 2,4-diaminobenzenesulphonic acid (RH acid) and 2,5-diaminobenzenesulphonic acid with 3-nitrobenzoyl chloride or 4-nitrobenzoyl chloride. This process was carried out in aqueous media at pH 7·5–8 and monitored by TLC. The resultant nitroaminobenzanilides were then reduced with iron powder by the conventional method. Details of a similar procedure for diaminobenzenesulphanilides have been described previously.[3,4] Four isomeric sulphonated diaminobenzanilides, viz. 2-amino-5-[(4′-aminobenzoyl)amino]benzenesulphonic acid (abbreviated as diamine *p,p′*), 2-amino-4-[(4′-aminobenzoyl)amino]benzenesulphonic acid (diamine *p,m′*), 2-amino-5-[(3′-aminobenzoyl)amino]benzenesulphonic acid (diamine *m,p′*) and 2-amino-4-[(3′-aminobenzoyl)amino]benzenesulphonic acid (diamine *m,m′*) were used to synthesize C.I. Direct Black 38 analogues of formula **2**. This process was carried out by the method described by Fierz-David and Blangley[5] slightly modified in the case of some isomeric dyes Type II.[6]



2: Type I, X = OH, Y = NH_2
Type II, X = NH_2, Y = OH

Additionally, in order to compare the colour and substantivity of dyes based on benzidine, 4,4′-diaminobenzanilide and its sulphonated derivatives, six model dyes of the type E←D→E were synthesized by the conventional method. In these dyes, D indicates the diamine (benzidine, 4,4′-diaminobenzanilide, and diamine *p,p*′) and E the end coupling component (in this work, naphthionic acid and alkaline-coupled J-acid). Dyeing and fastness properties of all dyes were determined according to Polish Standards, which correspond with British Standards.[7] A commercial sample of C.I. Direct Black 38 (Organika-Boruta Works, Poland) was used as a standard in the latter work.

3 RESULTS AND DISCUSSION

Colouristic and application properties of the model dyes are listed in Table 1. As can be seen from the data, the presence of an additional sulphonic group in the diaminobenzanilide residue has no or little influence on the colour of the dyes, although, as has been previously reported, hypsochromic shifts in comparison with benzidine dyes are observed.

Differences in the substantivity of the model dyes are also smaller than expected, especially in the case of dyes with the additional sulphonic group. All dyes based on diaminobenzanilides exhibited similar or slightly lower

TABLE 1
Constitution, Colour and Dyebath Uptake of the Model Dyes of Type E←D→E

D	*E*	*Colour*	λ_{max} *(nm)*	*Percentage uptake on cotton*
Benzidine	Naphthionic acid	Orange-red	495	90
Diaminocarbanilide	Naphthionic acid	Orange	490	85
Diamine *p,p*′	Naphthionic acid	Orange	490	87
Benzidine	J-acid	Violet	535	89
Diaminocarbanilide	J-acid	Red	514	86
Diamine *p,p*′	J-acid	Red	511	90

TABLE 2
Structure and Colouristic Properties of Black Direct Dyes of Formula **2**

Dye number	*Type*	*R*	*Diamine*	λ_{max} *(nm)*	*Colour compared with standard*
C.I. Direct Black 38	I	H	Benzidine	460–590	Standard
I	I	H	*p,p′*	490, 615	Similar
II	II	H	*p,p′*	490, 615	Similar
III	II	NO_2	*p,p′*	490, 635	Close
IV	II	NO_2	*p,m′*	490, 615	Greenish
V	II	NO_2	*m,p′*	490, 615	Close
VI	II	NO_2	*m,m′*	490, 615	Greenish

affinity for cellulose fibres in comparison with benzidine-based dyes, although in previous work[8] the latter were found to be slightly the more substantive (2–3% difference). This may be due to differences in dyeing procedures, dye concentrations, etc.

We additionally synthesized several analogues of C.I. Direct Black 38, mostly of Type II. The latter can be prepared more easily, because all couplings with bis-diazotized diaminobenzanilides are carried out in alkaline medium. This is important from a technical point of view, since it allows the reaction to proceed partially in solution and over a shorter time.

During the synthesis, it was found that the diazo groups in diazotized sulphonated diaminobenzanilides exhibit different coupling power. This phenomenon has already been reported in the case of 4,4′-diaminobenzanilide, in which the diazo group located in benzoic acid residue was found to be more active.[9] Similar results were obtained in this present work. Results of more detailed studies in this area will be described elsewhere.

The structure and colouristic properties of the prepared dyes are listed in Table 2.

All the dyes have colouristic properties similar to each other and to C.I. Direct Black 38, but their spectral characteristics are different. A solution of commercial C.I. Direct Black 38 in water absorbs over a very broad range (460–590 nm) and the absorption curve is flat without any particular maximum. In the case of dyes **I**–**VI** two distinct absorption peaks are observed, a lower-intensity peak at 490–500 nm and a higher intensity peak at 610–615 nm. The latter in dye **III** is bathochromically shifted to 635 nm, probably due to the combined effect of the nitro group in the phenyl ring and the *p,p′*-substitution of the azo groups in the benzanilide residue. The relative intensities of both peaks varies and this results in the hue changes observed on the dyed cotton fabric.

Application properties of the same dyes are listed in Table 3.

It can be observed that despite structural differences in the diamines, all

TABLE 3
Exhaustion Degree, Light- and Wet-Fastness on Dyed Cotton Fabric for Dyes **I–VI** (3% Standard Dyeings)

Dye number	*Exhaustion degree (%)*	*Fastness*			
		Light (Xenotest)	*Water*	*Washing 60°C*	*Perspiration (alkaline)*
Direct Black 38	96	2	3, 3–4	3, 2	4, 4
I	92	2	3, 2	3, 2	4, 3
II	85	2	3, 2–3	3, 3	4, 3
III	93	2	3, 3	2, 2	4, 3
IV	88	2	3, 2	2–3, 2–3	4, 3
V	93	2	3–4, 3–4	2, 2	4, 3–4
VI	88	2	3, 2–3	2–3, 2–3	4, 3

the dyes exhibit a similar affinity for cotton. Lightfastness values are typical of this class of dye and are the same in all cases. The wet-fastness of the new dyes are lower, as was expected, in comparison with C.I. Direct Black 38, probably the result of their increased solubility due to the presence of the additional sulphonic group. Nevertheless, the fastness data are similar to those observed in the case of many commercial direct dyes, and could probably undergo some improvement after appropriate finishing of the dyed fabric.

The results indicate that sulphonated diaminobenzanilides may be considered as possible substitutes for benzidine in the manufacture of some types of direct dyes.

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