Dyes and Pigments 9 (1988) 209–215

Azo Acid Dyes Derived from 3,3′-Diaminodiphenylsulphone

A. Rajagopalan, R. Rajagopal and S. Seshadri*

Dyes Research Laboratory, University Department of Chemical Technology, Matunga,
Bombay 400 019, India

(Received 13 May 1987; accepted 19 June 1987)

SUMMARY

*3,3′-Dinitrodiphenylsulphone is a by-product obtained during the manufacture of ludigol (sodium-*m*-nitrobenzenesulphonate). It was reduced to the diamino compound which was then used to prepare various symmetrical and unsymmetrical azo dyes for wool. The fastness properties of the dyes thus prepared were evaluated.*

1 INTRODUCTION

3,3′-Dinitrodiphenylsulphone is a by-product formed during manufacture of ludigol (sodium-*m*-nitrobenzenesulphonate). During the sulphonation of nitrobenzene, two moles of nitrobenzene condense with oleum, resulting in the formation of 3,3′-dinitrodiphenylsulphone. In an attempt to ascertain potential commercial outlets for this compound, it was reduced to the diamine, which was then used to synthesise a series of azo acid dyes.

It is known that non-coplanar dyes from *m*-substituted benzidines[1] give azo dyes with good substantivity and it was anticipated that 3,3′-diaminodiphenylsulphone would similarly yield dyes with good substantivity.

---

* To whom correspondence should be addressed.

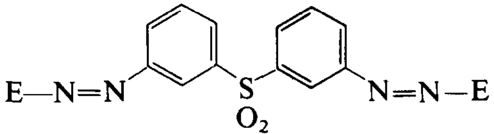
Dyes and Pigments 0143-7208/88/$03·50

2 RESULTS AND DISCUSSION

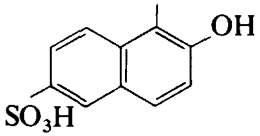
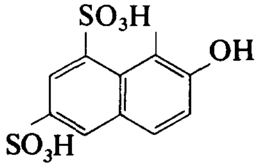
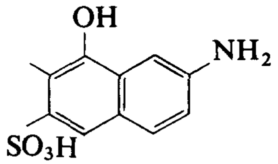
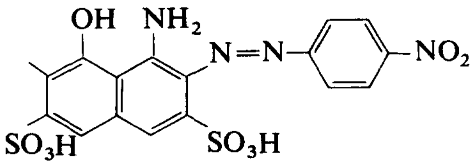
3,3′-Dinitrodiphenylsulphone, obtained as a by-product in the sulphonation of nitrobenzene, was reduced to 3,3′-diaminodiphenylsulphone. One mole of this diamine was tetrazotised and coupled with Schaeffer acid, G-acid and Gamma acid to give dyes typified by structures **I–III.** The dyes from Schaeffer acid and G-acid gave bright orange dyeings of good fastness properties on wool.

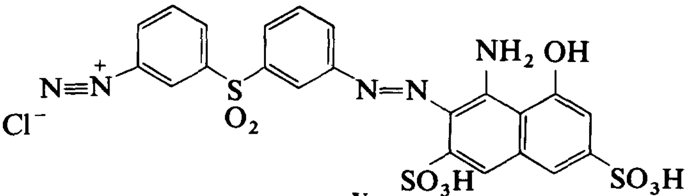
In order to extend the shade range, 1 mol of 3,3′-diaminodiphenylsulphone was tetrazotised and coupled with the monoazo dye *p*-nitroaniline acid $\xrightarrow{\text{acid}}$ H-acid in alkaline medium to obtain the tetrakisazo dye **IV**, which gave blue shades on wool.

When 1 mol of tetrazotised 3,3′-diaminodiphenylsulphone was coupled with 1 mol of H-acid in acidic medium, the monoazo dye typified by structure **V** separated out due to its poor solubility. On addition of this to a

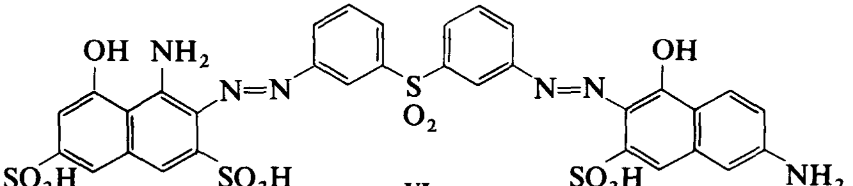


I–IV

Dye	E
I	
II	
III	
IV	



V



VI

solution of a further coupling component, such as J-acid, under alkaline conditions, reaction took place rapidly to yield an unsymmetrical dye represented by structure **VI**. This product gave reddish brown shades on wool.

The visible absorption maxima and hues of the above disazo dyes on wool, together with their fastness properties, are given in Table 1.

We have additionally been studying the effect in a dye chromophore of the presence of the residue of an ultraviolet absorber such as 2,4-dihydroxybenzophenone with respect to its influence on the lightfastness of the dyes. On this basis, a series of unsymmetrical azo dyes was prepared by tetrazotising 1 mol of 3,3'-diaminodiphenylsulphone and coupling initially with H-acid, naphthionic acid or Gamma acid in acidic medium and then

TABLE 1
Properties of the Dyes **I**–**IV** and **VI**

Dye	λ_{max}[a] (*nm*)	*Shade on wool*	*Dyeing properties*[b]				
			PU	*LF*	*WF*	*SC*	*SW*
I	466	Reddish orange	1/3	3	3	2	4
II	424	Orange	1/1	4–5	3	3–4	4
III	488	Reddish brown	1/3	3	2–3	3	4
IV	586	Blue	1/3	3	3	2–3	2–3
VI	488	Brown	1/3	3	3–4	3–4	4

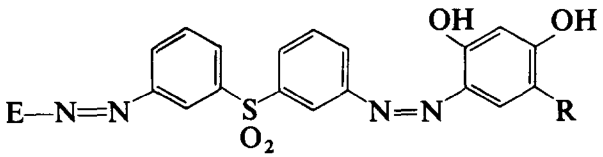
[a] λ_{max}, visible absorption maximum (in 10% aq. sodium carbonate). The dyes used in recording the visible spectra and in dyeing were resalted and the purity was checked by thin layer chromatography using the following solvent system: 4·0 ml *n*-butanol, 1·5 ml ethanol, 2·0 ml 28% aqueous ammonia, 2·0 ml pyridine and 1·5 ml water.

[b] PU, pick-up; LF, lightfastness; WF, washfastness; SC, staining on cotton; SW, staining on wool.

TABLE 2
Properties of the Dyes **VII–IX**

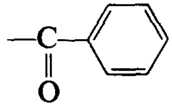
Dye	*E*	*R*	λ_{max}[a] (*nm*)	*Shade on wool*	*Dyeing properties*[b]				
					PU	*LF*	*WF*	*SC*	*SW*
VIIa	H-acid	H	546	Reddish violet	1/12	3	3–4	4–5	4
VIIb	H-acid	$-\underset{\underset{O}{\|}}{C}-Ph$	556	Bluish violet	1/12	4–5	3–4	4	4
VIIIa	Naphthionic acid	H	438	Yellowish orange	1/6	3–4	3	4	4
VIIIb	Naphthionic acid	$-\underset{\underset{O}{\|}}{C}-Ph$	464	Reddish orange	1/6	4–5	3–4	4	4
IXa	J-acid	H	420	Yellowish brown	1/12	3	2–3	4	3
IXb	J-acid	$-\underset{\underset{O}{\|}}{C}-Ph$	492	Light pink	1/12	4–5	2–3	4–5	4

[a,b] Abbreviations as in Table 1.



VII–IX

E = coupling component containing SO_3Na groups

R = (a) H or (b) 

effecting the second coupling with resorcinol or 2,4-dihydroxybenzophenone to give the azo acid dyes typified by structures **VII–IX**, which were then compared with respect to their fastness properties.

The various coupling components used, visible absorption maxima of the resultant dyes, hues of the dyes obtained on wool and the fastness properties of the dyeings are given in the Table 2.

These dyes did not show much substantivity on cotton, but all the dyes gave bright shades on wool and showed good exhaustion properties. Whilst no appreciable change in the washfastness of dyes derived from resorcinol and 2,4-dihydroxybenzophenone was observed, the dyes derived from the latter showed a noticeable improvement in the lightfastness. Further studies will be reported on the use of 2,4-dihydroxybenzophenone as a coupling component in azo acid dyes and to establish whether the lightfastness enhancement apparent in these present dyes has a more widespread applicability.

3 EXPERIMENTAL

Visible spectra were recorded using a Uvikon spectrophotometer. 3,3′-Dinitrodiphenylsulphone was reduced with sodium disulphide according to the modified Zinin method.[2]

3.1 Preparation of 3,3′-diaminodiphenylsulphone

To a solution of sodium disulphide prepared from sodium hydroxide (108 g, 2·7 mol) and powdered S (86·4 g, 2·7 mol) was added 3,3′-dinitrodiphenylsulphone (92·4 g, 0·3 mol) and the resulting mixture heated at 90°C for 2 h. The diamine obtained was filtered, washed free of sodium disulphide and purified by dissolving in hot hydrochloric acid and neutralising with sodium hydroxide. Yield 75%, m.p. 168°C.

3.2 Preparation of the symmetrical disazo dye I

3,3′-Diaminodiphenylsulphone (2·48 g, 0·01 mol) was dissolved in 10% hydrochloric acid (18·3 ml) and water (25 ml) and the solution cooled to 0°C. It was then tetrazotised using sodium nitrite (1·45 g, 0·021 mol) and the excess of nitrous acid was destroyed by adding urea.

Schaeffer acid (90%, 5·22 g, 0·021 mol) dissolved in aqueous sodium hydroxide was added to the tetrazotised solution and the pH adjusted to 9·0 with sodium carbonate. The reaction mixture was stirred for 1 h at 5–10°C and the product isolated by adding salt (15% w/v) at 80°C and cooling the reaction mixture to 40°C. The filtered dye was purified by resalting.

Dyes **II**, **III** and **IV** were similarly prepared from G-acid, Gamma-acid and the monoazo dye *p*-nitroaniline $\xrightarrow{\text{acid}}$ H-acid (Table 1).

3.3 Preparation of the unsymmetrical disazo dye VI

A solution of 80% H-acid (4·0 g, 0·01 mol) in water (40 ml) containing sodium carbonate (0·6 g) was added to a tetrazotised solution of 3,3′-diaminodiphenylsulphone (2·48 g, 0·01 mol) and the liquor stirred at 0–5°C and pH 1–2 for 3 h. A test solution, when spotted against H-acid showed no blue colouration.

The diazo slurry was added to an 80% solution of J-acid (3·3 g, 0·011 mol) in 20% aqueous sodium carbonate (12·0 ml) and stirred for 1 h at 5–15°C and pH 9·0. Reaction was complete in about 2 h and the dye was isolated by adding salt (25 g) at 80°C. The dye was filtered at 40°C and then purified by resalting.

3.4 Preparation of the disazo dye VIIa

To the monoazo diazo slurry prepared as above from 3,3′-diaminodiphenylsulphone (0·01 mol) and H-acid (0·01 mol) was added a solution of resorcinol (1·11 g, 0·011 mol) in 10% sodium hydroxide (4 ml) and the mixture stirred at 8–10°C and pH 9·0 for 1 h. The dye was isolated by salting out and was then purified by resalting.

3.5 Preparation of the dye VIIb

This dye was prepared by the same procedure as described for the dye **VIIa** using 2,4-dihydroxybenzophenone (2·354 g, 0·011 mol) instead of resorcinol as the end coupler.

Dyes **VIII** and **IX** were prepared in the same manner (Table 2).

4 CONCLUSION

3,3′-Diaminodiphenylsulphone was used to prepare symmetrical and unsymmetrical azo acid dyes. The dyes gave dyeings having bright shades, reasonable washfastness and good lightfastness. Tinctorial power of these dyes was only average. Results of the work indicate that 3,3′-diaminodiphenylsulphone has potential as a useful diazo component in the synthesis of acid wool dyes.

ACKNOWLEDGEMENTS

We thank Dr H. S. Desai of Amar-Dye Chem. Ltd, Bombay, Dr N. B. Desai of Indian Dyestuff Industries Ltd, Bombay, and Professor (Miss) M. D. Bhavsar of the Silk and Art Silk Mills Research Association, Bombay, for their help in the evaluation of dyeings. We also thank Sandoz (India) Ltd, Bombay and The University Grants Commission, New Delhi, for financial support.

REFERENCES

1. R. N. Sen and R. Sadasivam, *J. Indian Chem. Soc.*, **9**, 403 (1932).
2. H. K. Porter in *Organic reactions*, ed. W. G. Dauben, vol. 20, pp. 455–81. New York, John Wiley and Sons (1973).