Dyes and Pigments **13** (1990) 161–166

Azo Acid Dyes Derived from 3-Amino-7-Nitro-2*H*-1,2-benzothiazine-1,1-dioxide

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(Received 23 March 1989; accepted 15 May 1989)

ABSTRACT

*A series of azo acid dyes for wool were prepared from 3-amino-7-nitro-*2H-*1,2-benzothiazine-1,1-dioxide. These dyes were subjected to chroming on the fibre and their colour and fastness properties assessed. Red to black dyeings of good fastness properties were obtained.*

1 INTRODUCTION

We have previously[1] reported the synthesis and properties of azo disperse dyes derived from the heterocyclic diazo compound 3-amino-7-nitro-2*H*-1,2-benzothiazine-1,1-dioxide. In this present paper we report the synthesis of some azo acid dyes derived from this diazo compound and the chroming of these dyes to obtain metal complex dyes of high light- and wash-fastness and possessing high tinctorial power.

2 RESULTS AND DISCUSSION

The investigation involved the synthesis of monoazo acid dyes by diazotisation of 3-amino-7-nitro-2*H*-1,2-benzothiazine-1,1-dioxide and

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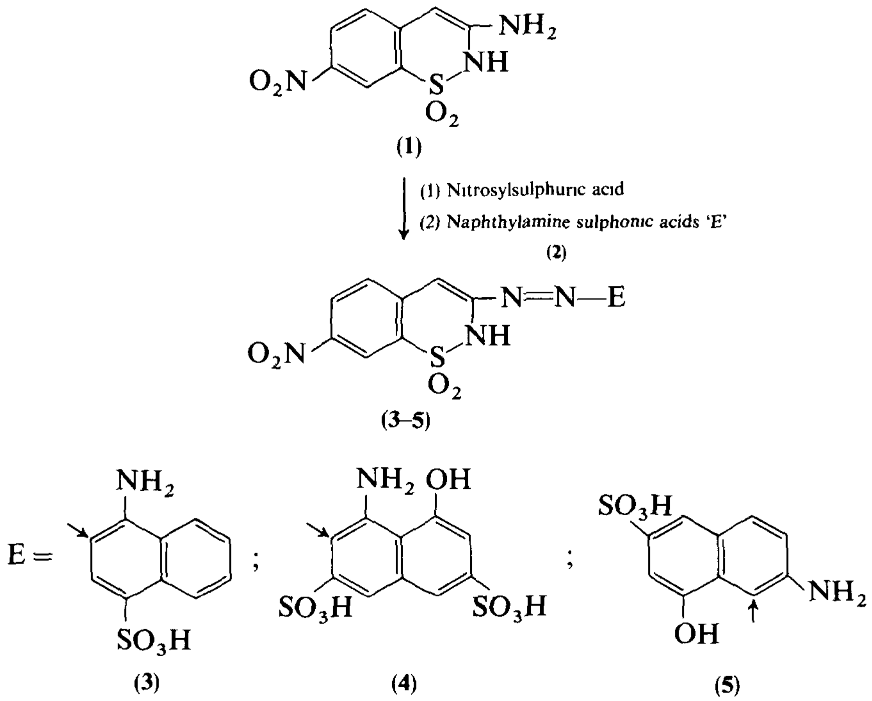
Dyes and Pigments 0143-7208/90/$03·50

coupling with suitable naphthylamine sulphonic acid derivatives, the conversion of these to disazo dyes and the formation of metal complexes of the dyes, the latter being expected to result in dyes of deeper shades and good fastness properties.

3-Amino-7-nitro-2*H*-1,2-benzothiazine-1,1-dioxide (**1**) was diazotised using nitrosylsulphuric acid and coupled at pH 4 with naphthylamine sulphonic acid derivatives such as sodium naphthionate (**2a**), H-acid (**2b**) and Gamma acid (**2c**). These dyes were purified by resalting and their purity checked by TLC. The monoazo dyes gave good dyeings on wool and showed very high exhaustion and tinctorial power. Dye **4** from H-acid, dye **3** from sodium naphthionate dye **5** from Gamma acid gave reddish violet, bright red and violet shades respectively on wool, all dyeings being characterised by high lightfastness.

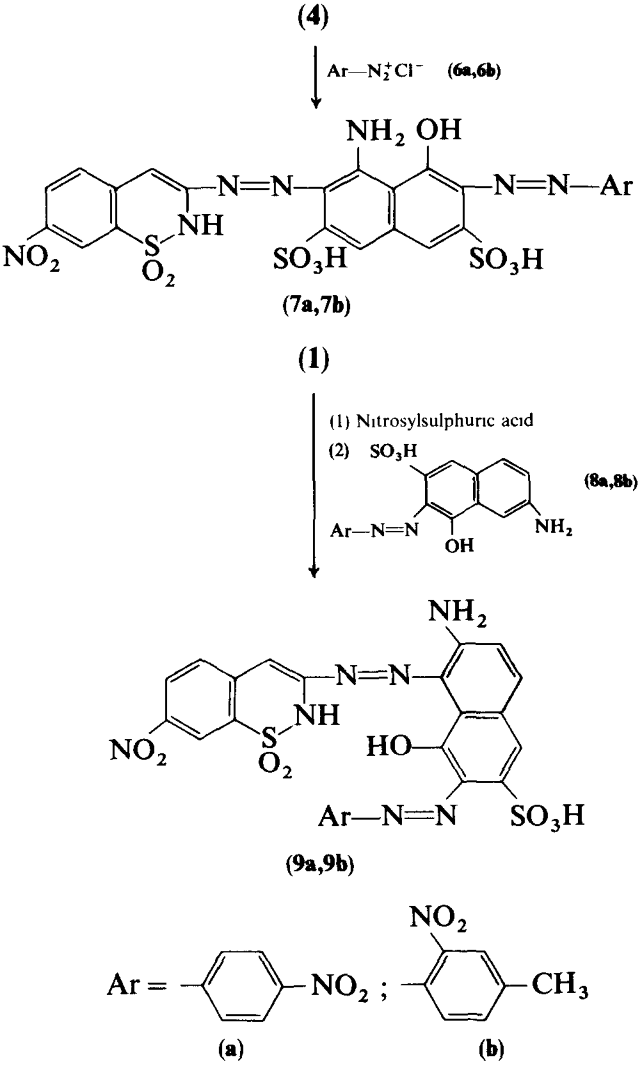


Scheme 1

The dyes were subjected to chroming by the afterchrome process from a dichromate bath. This resulted in a colour shift with dye **3** from red to brownish black, and to deep brown with dyes **4** and **5**. The lightfastness and tinctorial power of the chromed dyes did not alter much and washfastness was improved marginally.

Bisazo dyes (**7a, 7b**) were synthesised by coupling the monoazo dye **4** with diazotised nitroaniline derivatives (**6a, 6b**) at alkaline pH. These dyes were also purified by resalting and their purity confirmed by TLC. Dye **7a** gave a brownish dyeing and dye **7b** gave a yellow shade on wool. These dyes exhibited good tinctorial power and washfastness. Dye **7a** had very high lightfastness (6) whilst the dye **7b** showed a lower fastness (4).

Chroming of dye **7a** yielded a lustrous black shade with high lightfastness (6) and tinctorial power (5) and dye **7b** similarly gave a yellowish brown shade but with lower lightfastness (3–4). The washfastness in both cases was slightly better after chroming.



Scheme 2

TABLE 1

Spectral and Evaluation Data of the Dyes

Dye	λ_{max} *(nm)*[a]	*Dyeing properties (unchromed)*[b]						*Dyeing properties (chromed)*[b]					
		Shade on wool	*PU*	*LF*	*WF*	*SC*	*SW*	*Shade on wool*	*PU*	*LF*	*WF*	*SC*	*SW*
3	520	Red	4	5–6	4	4–5	4–5	Brownish black	4	6	4	4	4–5
4	476	Reddish black	2	3	3	4–5	4	Dark brown	4	3	3–4	4	4
5	524	Violet	4	6	2–3	3–4	4	Dark brown	4–5	6	3–4	4–5	4–5
7a	540	Dark brown	4	5–6	3	3–4	4	Black	4	6	3–4	3	4
7b	448	Yellow	1	4–5	4	4–5	4	Yellowish brown	1	2–3	4	4	4
9a	520	Dark brown	4	6	3	4	5	Black	4	6	3–4	3	4
9b	508	Maroon	4	4	3	4	4	Reddish brown	4	4	3–4	4–5	4

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

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

The bisazo dyes **9a** and **9b** could not be prepared in the same way as dyes **7a** and **7b** because of the less reactive coupling site They were therefore prepared from the diazotised amino derivative **1** by coupling to the monoazo dyes **8a** and **8b** (prepared by coupling Gamma acid with diazotised nitroaniline derivatives) at an acidic pH of 4–5. This coupling reaction was very sluggish and required a long period. The isolated dyes were purified by resalting and their purity confirmed by TLC. Dye **9a** gave a deep brown shade and dye **9b** a maroon shade on wool. Both dyes had high lightfastness and tinctorial power. Chroming of **9a** resulted in a deep black shade on wool having high lightfastness and tinctorial power, and chroming of **9b** gave a reddish brown shade having a lightfastness of 4. The washfastness in both cases was marginally improved (Table 1).

3 EXPERIMENTAL PROCEDURE

3.1 General

The visible absorption spectra were recorded on a Kontron spectrophotometer. 3-Amino-7-nitro-2*H*-1,2-benzothiazine-1,1-dioxide (**1**) was prepared according to the method reported in our earlier communication.[1] The monoazo dyes (**8a,8b**) were prepared by coupling diazotised nitroaniline derivatives (**6a,6b**) (0·01 mol) with Gamma acid (**2c**) (0·011 mol) at pH 8–9. The H-acid, sodium naphthionate, gamma acid and nitroaniline derivatives used were commercial samples.

3.2 Preparation of the monoazo dyes (3–5)

To sulphuric acid (98%, 6 ml) was added at room temperature sodium nitrite (0·8 g, 0·012 mol) and the mixture was digested at 60°C in a water bath for 30 min. The clear solution of nitrosylsulphuric acid was cooled to room temperature (30°C) and then to 20°C. The amino derivative **1** (2·41 g, 0·01 mol) was slowly added to the above mixture and stirred for 2 h at 20°C. The diazotised solution was then run into ice-cold acetic acid (20 ml) and the excess nitrous acid destroyed with urea (1 g).

To the solution of the appropriate coupler E (**2a–2c**) (0·011 mol) dissolved in 5% sodium carbonate solution (10 ml) was added the above diazo solution at 10–15°C in 15 min. The pH of the reaction mixture was then adjusted to 4–5 by the addition of a saturated solution of sodium acetate (25 ml). The coupling mixture was then stirred at 10–15°C for 4–5 h until the reaction mixture showed the absence of diazo compound on spotting with a standard H-acid coupler.

The dyes were isolated by salting and purified by resalting.

3.3 Preparation of the bisazo dyes (7a, 7b)

The monoazo dye **4** (0·01 mol), prepared from the amino derivative and H-acid at acidic pH, was dissolved in 5% sodium carbonate solution (10 ml). To this was added diazotised nitroaniline derivatives **6a**, **6b** (0·01 mol) at 10–15°C. The pH was adjusted to 8–9 by addition of a solution of caustic soda and the reaction mixture stirred at 10–15°C for 3 h.

The dyes were isolated by salting out and purified by resalting.

3.4 Preparation of the bisazo dyes (9a, 9b)

The appropriate monoazo dye **8a**, **8b** (0·011 mol) dissolved in 5% sodium carbonate solution (15 ml) was added to a solution of the diazotised amino derivative **1** (0·01 mol) at 10–15°C over 15 min. The pH of the reaction mixture was adjusted to 4–5 by addition of a saturated solution of sodium acetate (25 ml). The reaction mixture was stirred at 10–15°C for 6 h at pH 4–5 until a test sample showed the absence of the diazo on spotting with a standard coupler. The dyes were isolated by salting and purified by resalting.

3.5 Dyeing

All the dyes were applied on wool from a triethanolamine bath and chroming was done by the afterchrome process from a dichromate bath.

ACKNOWLEDGEMENTS

We thank Indian Dyestuff Industries Ltd, Bombay, for the evaluation of the dyed samples. One of us (R.R.) thanks the University Grants Commission, New Delhi, for the award of a senior research fellowship.

REFERENCE

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