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Azo Disperse Dyes Derived from 3-Amino-7-nitro-2*H*-1,2-benzothiazine 1,1-Dioxide

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ABSTRACT

*3-Amino-7-nitro-2*H*-1,2-benzothiazine 1,1-dioxide was utilised to prepare a range of azo disperse dyes for polyester. These dyes were subjected to methylation, bromination and cyanation reactions and the resultant derivatives were studied with respect to colour–constitution relationships.*

Application properties of the dyes on polyester and their fastness properties were evaluated. The dyes were characterised by IR, PMR and visible absorption spectra.

1 INTRODUCTION

The last decade has seen a significant development in the contribution of heterocyclic compounds to dyestuff chemistry. The design of newer heterocyclic systems free from carcinogenic and mutagenic properties, together with economic routes to such derivatives with due consideration of effluent problems has been a major area in dyestuff research.

In the course of the authors' work, to identify potential non-toxic heterocyclic diazo compounds it was noted that 3-amino-7-nitro-2*H*-1,2-benzothiazine 1,1-dioxide had been synthesised by Sianesi *et al.*[1] through an elaborate and tedious route. The authors set out to devise a more economical and facile route for this diazo compound from cheaper raw materials and to exploit its utility as a diazo compound in the synthesis of azo disperse dyes.

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A new and economical route[2] to the compound was developed, starting from *p*-nitrotoluene, which was chlorosulphonated, followed by amidation and then urea fusion.

In the present paper the authors report studies on the diazotisation of this amine, the synthesis of azo dyes, and their conversion to methylated, brominated and cyanated dyes, together with colour–constitution relationships in the resultant dyes.

2 RESULTS AND DISCUSSION

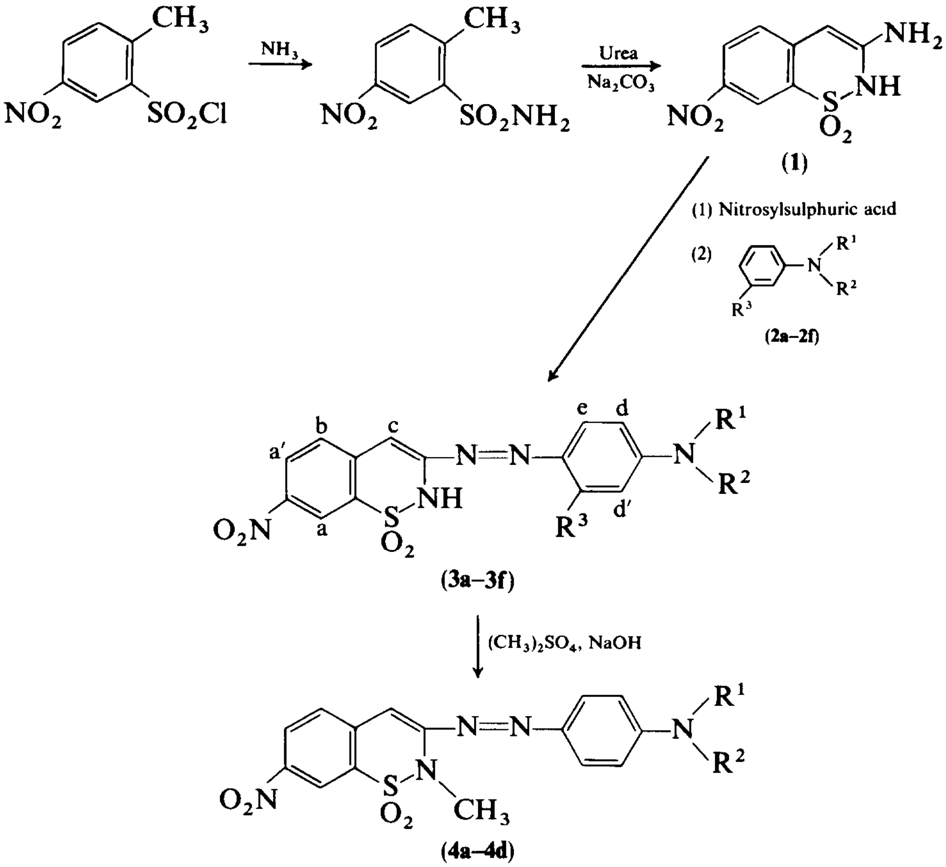
3-Amino-7-nitro-2*H*-1,2-benzothiazine 1,1-dioxide (**1**) was prepared by fusing 4-nitrotoluene 2-sulphonamide with urea at 180°C. The 3-amino derivative, being very weakly basic, could not be diazotised under ordinary conditions. Therefore diazotisation was carried out in aqueous hydrochloric acid in the presence of co-solvents such as polyethylene glycol 400 and 600, but the results were very poor. The best results in terms of the yields of resultant azo dyes were obtained by diazotising with nitrosylsulphuric acid.

The azo dyes **3a**–**3f** were prepared by coupling the diazotised amino derivative with *N*,*N*-dialkylaniline couplers (**2a**–**2f**) in acidic medium at pH 4–5 (Scheme 1). The structure of the dyes was confirmed by IR, PMR and visible absorption spectra. PMR spectra of representative dyes showed the presence of an exchangeable sulphonamide proton indicating the structure **A** as the correct one (Scheme 2). Further evidence of the structure was obtained by the absorption behaviour of the dyes in acid and in alkaline medium. Azo dyes in acidic medium showed a bathochromic shift and in alkaline medium a hypsochromic shift. Such behaviour could be explained only by structure **A**.

Protonation of the azo nitrogen in the conjugated system leads to a bathochromic shift due to an enhanced electron pull between the 7-nitro and the *N*,*N*-dialkylaniline group. In alkali, the ionisation of the sulphonamido —NH to SO_2N^- causes a cross conjugation between the 7-nitro and the ionised SO_2N^- on one hand and the 7-nitro and the *N*,*N*-dialkylaniline group on the other. This cross-conjugation leads to the hypsochromic shift (Scheme 2).

Dyes (**3a**–**3f**) when applied to polyester gave reddish pink to orange shades. Dyes **3a** and **3e** showed average lightfastness with good sublimation fastness whilst the other dyes showed poor lightfastness. The dye **3c** from *m*-chloro-*N*,*N*-dimethylaniline gave very poor results. The physical and spectral data of all the dyes are given in Table 1. Evaluation data of the dyeings are given in Table 4.

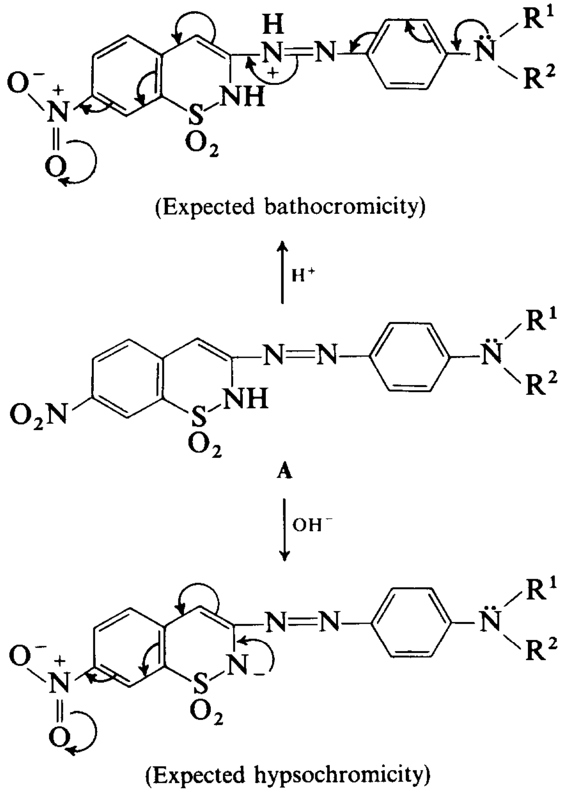
Dyes **3a**–**3d** were methylated with dimethyl sulphate in alkaline medium



a	b	c	d	e	f
$R^1 = C_2H_5$	CH_3	CH_3	C_2H_5	C_2H_5	C_2H_4OH
$R^2 = C_2H_5$	CH_3	CH_3	C_2H_5	CH_2Ph	C_2H_4OH
$R^3 = NHCOCH_3$	H	Cl	H	—	Cl

Scheme 1

to give the *N*-methylated azo dyes (**4a**–**4d**) (Scheme 1). These dyes were characterised by IR spectra (showing the absence of sulphonamido —NH) and PMR spectrum (showing absence of the —NH proton of the sulphonamido group) indicating that methylation had occurred at that position. Visible absorption spectra of the *N*-methylated dyes, recorded in neutral and acidic medium, gave further evidence for structure **A**. The increased cross-conjugation between the 7-nitro and the SO_2NCH_3 residue, as compared with the unmethylated dyes **3a**–**3d**, leads to a hypsochromic shift. The dyes gave pink to orange shades on polyester, dyes **4a** and **4b**



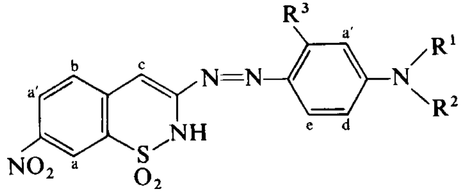
Scheme 2

having average tinctorial power and lightfastness but good sublimation fastness, whilst dyes **4c** and **4d** showed better lightfastness. However, dye **4c** from *m*-chloro-*N*,*N*-dimethylaniline again suffered from very poor sublimation fastness. The physical and spectral data of these dyes are given in Table 2 and evaluation data of the dyeings in Table 4.

It was of interest to study the effect of an electron-withdrawing group at the 4-position of the benzothiazine ring on the colour and properties of the dyes. Dye **4a** was brominated to give the 4-bromo derivative **5**, analysis of which indicated the presence of two bromine groups. This dibromo derivative on subsequent reaction with cuprous cyanide in dimethylformamide gave the 4-cyano derivative **6** (Scheme 3). Compound **6** showed the presence of one bromo group, confirming that dibromination had occurred during the bromination stage. Bromination in the aminated ring of the coupler (Scheme 3) is suggested, since bromination of the diazo intermediate gave only a monobromo derivative (see below). The dibromo compound **5** and monobromo–monocyano compound **6** showed λ_{max} at

TABLE 1

Physical and Spectral Data of Azo Dyes **3a–3f**

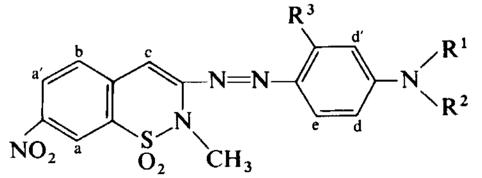


Compd	R^1	R^2	R^3	Molecular formula[a]	M.p. (°C) (DMF)	Yield (%)	Visible absorption data λ_{max} (nm)				PMR spectral data, δ (ppm)
							MeOH	H^+	OH^-	log ε	
3a	C_2H_5	C_2H_5	$NHCOCH_3$	$C_{20}H_{22}N_6SO_5$	235	50	500	508	490	4·5	1·3 (t, 6H, —$N(CH_3)_2$); 3·9 (q, 4H, —$N(CH_2)_2$); 2·7 (s, 3H, —$NHCOCH_3$); 7·0 (d, 1H, proton at d position); 8·1 (m, 3H, protons at c, e, d' positions); 8·5 (d, 2H, protons at a' and b positions); 8·7 (s, 1H, proton at a position); 9·1 (s, 2H, protons of —SO_2NH and —$NHCOCH_3$); (D_2O-exchangeable)
3b	CH_3	CH_3	H	$C_{16}H_{15}N_5SO_4$	270	55	470	504	460	4·4	
3c	CH_3	CH_3	Cl	$C_{16}H_{14}N_5SO_4Cl$	222	55	448	500	440	4·3	—
3d	C_2H_5	C_2H_5	H	$C_{18}H_{19}N_5SO_4$	250	50	480	508	466	4·3	—
3e	C_2H_5	CH_2Ph	H	$C_{23}H_{21}N_5SO_4$	260	58	462	512	420	4·4	—
3f	C_2H_4OH	C_2H_4OH	Cl	$C_{18}H_{18}N_5SO_6Cl$	245	50	460	502	420	4·5	—

Abbreviations: s = singlet; d = doublet; t = triplet; q = quadruplet; m = multiplet.

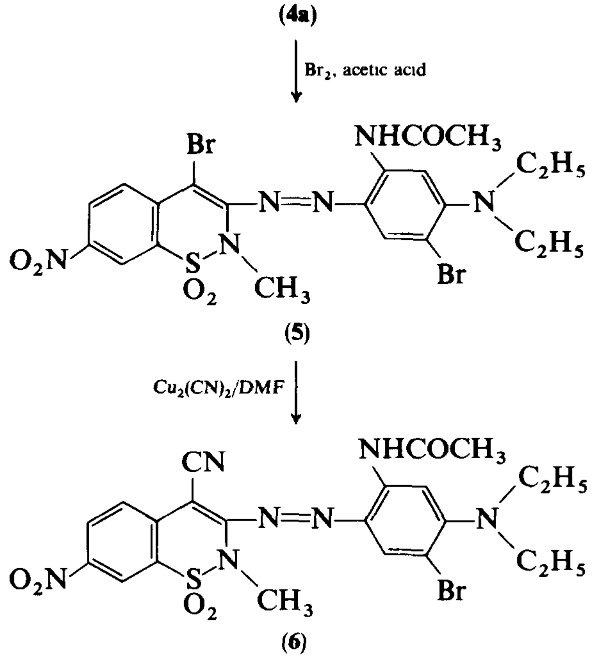
[a] All compounds showed satisfactory elemental analysis, ±0·3%.

TABLE 2
Physical and Spectral Data of the Methylated Azo Dyes **4a–4d**



Compd	*R*^{1}	*R*^{2}	*R*^{3}	*Molecular formula*[a]	*M.p. (°C) (DMF)*	*Yield (%)*	*Visible absorption data* λ_{max} *(nm)*				*PMR spectral data, δ (ppm)*
							MeOH	*H*$^+$	*OH*$^-$	*log ε*	
4a	C_2H_5	C_2H_5	$NHCOCH_3$	$C_{21}H_{24}N_6SO_5$	290	45	482	500	—	3·9	1·3 (t, 6H, —N(CH$_3$)$_2$); 3·8 (q, 4H, —N(CH$_2$)$_2$); 2·7 (s, 3H, —NHCOCH$_3$); 2·5 (s, 3H, —SO$_2$N(CH$_3$)); 8·1 (m, 3H, protons at c, e, d' positions); 8·5 (d, 2H, at a', b positions); 7·0 (d, 1H, at d position); 8·7 (s, 1H, at a position); 9·1 (s, 1H, —NHCOCH$_3$) (D$_2$O-exchangeable)
4b	CH_3	CH_3	H	$C_{17}H_{17}N_5SO_4$	280	40	436	512	—	4·6	—
4c	CH_3	CH_3	Cl	$C_{17}H_{16}N_5SO_4Cl$	300	48	434	504	—	4·3	—
4d	C_2H_5	C_2H_5	H	$C_{19}H_{21}N_5SO_4$	310	50	462	508	—	3·9	—

[a] All compounds showed satisfactory elemental analysis ±0·3%.



Scheme 3

414 nm and 480 nm respectively. However, these compounds gave very weak dyeings on polyester. Physical and spectral data are given in Table 3.

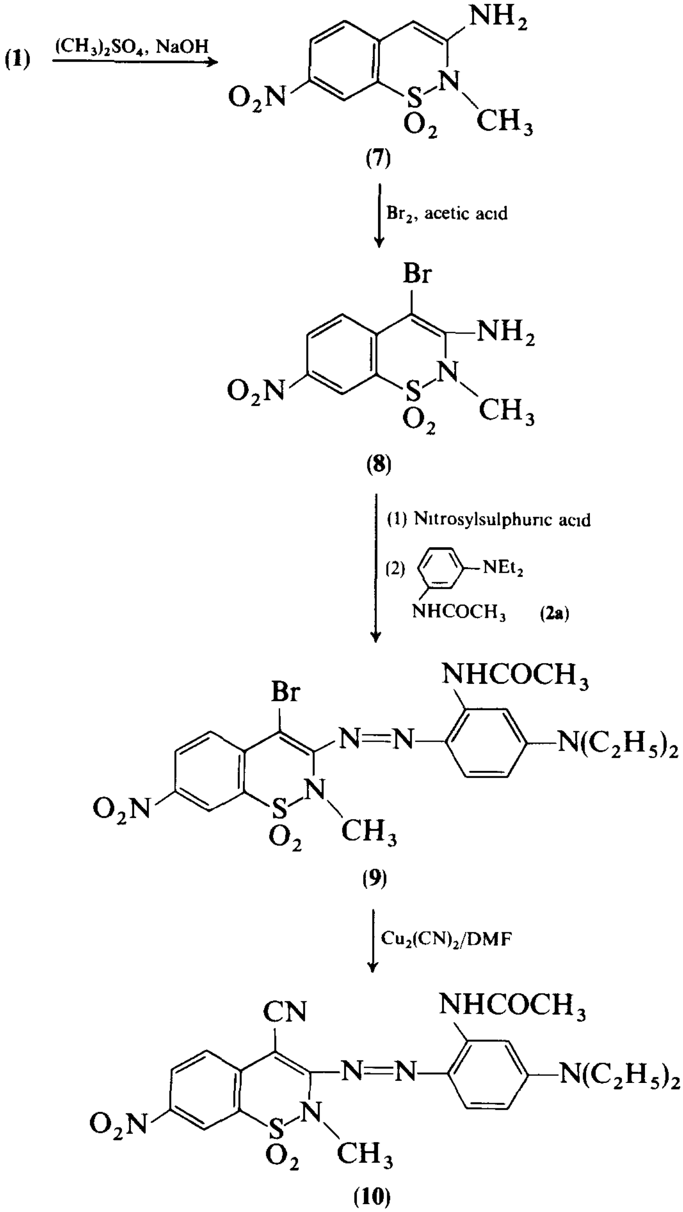
The synthesis of the monobromo azo dye by an alternative route was attempted, starting from 3-amino-7-nitro-4-bromo-*N*-methyl-1,2-benzothiazine 1,1-dioxide (**8**). The 3-amino derivative **1** was methylated to give 3-amino-7-nitro-*N*-methyl-1,2-benzothiazine 1,1-dioxide (**7**), which was

TABLE 3
Physical and Spectral Data of the Brominated and Cyanated Azo Dyes **5**, **6**, **9** and **10**

Compd	*X*	*Y*	*Molecular formula*[a]	*M.p. (°C)*	*Yield (%)*	*Visible absorption spectral data*	
						λ_{max} *(nm)*	*log ε*
5	Br	Br	$C_{21}H_{22}N_6Br_2SO_5$	305[b]	45	414	4·0
6	CN	Br	$C_{22}H_{22}N_7BrSO_5$	325[b]	45	480	3·0
9	Br	H	$C_{21}H_{23}N_6BrSO_5$	330[c]	40	424	4·3
10	CN	H	$C_{22}H_{23}N_7SO_5$	310[c]	42	440	4·4

[a] All compounds showed satisfactory analysis, ±0·3%.
[b] Crystallisation solvent DMF/ethanol (4:1).
[c] Crystallisation solvent DMF.

then brominated to the 4-bromo derivative **8** (Scheme 4). The 4-bromo derivative was diazotised in nitrosylsulphuric acid and coupled at pH 4–5 with *m*-acetamido-*N*,*N*-diethylaniline (**2a**) to give the monobromo azo dye (**9**). This was treated with cuprous cyanide in dimethylformamide to give the monocyano derivative (**10**). Dyes **9** and **10** had λ_{max} at 424 nm and 440 nm



Scheme 4

TABLE 4
Evaluation of Dyeings of the Azo Dyes on Polyester

Compd	*PU*[a]	*Xeno*[b]	*Thermo*[c]	*Shade on polyester*[d]
3a	2	3	4–5	Reddish pink
3b	1	2	4–5	Orange
3c	2	2–3	1	Bright orange
3d	1	2	3–4	Reddish orange
3e	2	3	3	Reddish brown
3f	1	2–3	4–5	Light brown
4a	1	2–3	4–5	Light pink
4b	1	2	4	Light brown
4c	4	3–4	1	Yellowish orange
4d	2	4	4	Reddish orange
9	1	2–3	4	Brownish yellow
10	1	3–4	4	Yellowish brown

[a] Pick-up.
[b] Lightfastness.
[c] Sublimation fastness.
[d] Dyed by HTHP (high-temperature, high-pressure) method.

respectively. The hypsochromic shift of these dyes compared with **3a** and **4a** is attributed to the presence of the electron-withdrawing functions at the 4-position enhancing the cross-conjugation. Dye **9** gave a yellow shade and dye **10** a yellowish orange shade on polyester, both with good sublimation fastness but average lightfastness. The tinctorial power of these derivatives was very poor. The physical and spectral data of the azo dyes are given in Table 3. Evaluation data of the dyeings are given in Table 4.

3 EXPERIMENTAL PROCEDURES

3.1 General

All melting points are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 397 spectrophotometer from Nujol mull. Visible absorption spectra were recorded on a Kontron spectrophotometer. PMR spectra were recorded on a Varian EM 360 L spectrophotometer using TMS as external standard.

N,*N*-Dialkylaniline couplers used were commercial samples. 4-Nitrotoluene-2-sulphonyl chloride[3] and 4-nitrotoluene 2-sulphonamide[4] were prepared according to reported methods.

3.2 Preparation of 3-amino-7-nitro-2*H*-1,2-benzothiazine 1,1-dioxide (1)

4-Nitrotoluene 2-sulphonamide (21·6 g, 0·01 mol) was heated with urea (30·0 g, 0·05 mol) at 180°C for 3 h. The reaction mixture was then cooled to 100°C and diluted with ethanol (50 ml) and the product recrystallised from isopropanol.

Yield = 15·0 g (60%); melting point 227°C (Lit.[1] m.p. 228°C).

3.3 Preparation of the azo dyes (3a–3f)

To sulphuric acid (98%, 5 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 and then to 20°C. The amino compound (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 (25 ml) and the excess nitrous acid destroyed with urea (1 g).

To the coupler **2a–2f** (0·011 mol) dissolved in acetic acid (10 ml) was added the above diazo liquor over 30 min. The pH was adjusted to 4–5 using saturated sodium acetate solution (40 ml). When the reaction mixture showed the absence of colour with the test coupler (H-acid) the reaction was stopped and the products filtered, washed with water to remove traces of acid, and repeatedly washed with ethanol to remove any impurities.

Physical and spectral data of the dyes are given in Table 2.

3.4 Preparation of *N*-methylated azo dyes (4a–4d)

Azo dyes **3a–3d** (0·01 mol) were pasted with dimethylformamide (5 ml) and stirred with caustic soda (0·05 mol, 5%). The mixture was cooled to 15°C and dimethylsulphate (0·015 mol) was added slowly over 0·5 h. The pH was adjusted to 8–9 and the reaction mixture stirred at 50°C for 4 h. The products were isolated after neutralisation and were filtered, washed free of alkali and dried. Physical and spectral data of the dyes are given in Table 2.

3.5 Preparation of the dibromo azo dye (5)

To the azo dye **4a** (0·01 mol) stirred in acetic acid (10 ml) was added bromine (0·02 mol) at room temperature. The reaction mixture was heated to 80°C and maintained at that temperature for 5 h. The product was isolated by quenching the reaction mixture into water and filtering. The product was recrystallised from dimethylformamide. Physical and spectral data of the compound are given in Table 3.

3.6 Preparation of the 4-cyano derivative (6)

A mixture of the dibromo derivative **5** (0·001 mol) and cuprous cyanide (0·001 mol) was refluxed in dimethylformamide (5 ml) for 5 h. The reaction mixture was cooled and run into water. The product which separated out was treated with 5% hydrochloric acid containing ferric chloride at 60°C to break up the copper complex. The product was filtered, washed with water and then with alcohol and recrystallised from dimethylformamide. Physical and spectral data of the compound are given in Table 3.

3.7 Preparation of 3-amino-7-nitro-*N*-methyl-1,2-benzothiazine 1,1-dioxide (7)

A mixture of 3-amino-7-nitro-2*H*-1,2-benzothiazine 1,1-dioxide (**1**) (4·9 g, 0·02 mol) and dimethyl sulphate (0·03 mol) in caustic soda (0·06 mol, 5%) was heated at 50°C for 4 h. The pH of the reaction mixture was maintained at 8–9 throughout the reaction. The product was filtered, washed with water to remove traces of alkali, dried, and recrystallised from dimethylformamide.

Yield, 3·8 g (74%); m.p. 274°C IR, 3340–3330 cm^{-1} (—NH_2).

	Elemental analysis %			
	C	*H*	*N*	*S*
$C_9H_9N_3SO_4$ requires	42·3	3·5	16·4	12·5
Found	42·1	3·3	16·2	12·3

3.8 Preparation of 3-amino-7-nitro-4-bromo-*N*-methyl-1,2-benezothiazine 1,1-dioxide (8)

The *N*-methylated derivative **7** (2·55 g, 0·01 mol) was stirred in glacial acetic acid (10 ml) and bromine (0·5 ml, 0·01 mol) was added slowly at room temperature. The reaction mixture was heated to 80°C and maintained at that temperature for 4 h. The product was isolated by running the reaction mixture into water. The compound was crystallised from dimethylformamide/ethanol (4:1) mixture.

Yield, 2·0 g (62%); m.p. 305°C; IR, 3340–3330 cm^{-1} (—NH_2).

	Elemental analysis (%)				
	C	*H*	*N*	*S*	*Br*
$C_9H_8N_3SO_4Br$ requires	32·3	2·3	12·5	9·5	23·9
Found	32·0	2·5	12·4	9·6	23·6

3.9 Preparation of the monobromo azo dye (9)

The 4-bromo derivative **8** (1·7 g, 0·005 mol) was diazotised in nitrosylsulphuric acid (prepared from 0·006 mol sodium nitrite and 6 ml sulphuric acid) at 15–20°C. The diazotised mixture was run into ice-cold acetic acid (10 ml) and the excess of nitrous acid destroyed by urea (1 g).

The above diazo solution was slowly run into a solution of *m*-acetamido-*N*,*N*-diethylaniline (**2a**) (1·0 g, 0·0055 mol) in acetic acid (10 ml) at 15–20°C. The pH was adjusted to 4–5 by addition of a saturated solution of sodium acetate (15 ml) and the coupling mixture stirred for 4 h. The product was isolated after checking for the absence of diazo compound in the reaction mixture by spotting with a test coupler (H-acid). The filtered product was washed with water to remove traces of acid and washed with alcohol. Physical and spectral data of the azo dye are given in Table 3.

3.10 Preparation of the 4-cyano derivative (10)

A mixture of the azo dye **9** (0·55 g, 0·001 mol) and cuprous cyanide (0·08 g, 0·001 mol) was refluxed in dimethylformamide (3 ml) for 6 h. The product was treated with 5% hydrochloric acid containing ferric chloride to break up the copper complex at 60°C. The solid product obtained was filtered, washed free of acid and dried. Physical and spectral data of the compound are given in Table 3.

3.11 Dyeing procedure

All the dyes were applied to polyester using a high-temperature high-pressure dyeing method. The evaluation data of all the dyeings are given in Table 4.

4 CONCLUSION

The present work highlights the potential of a novel heterocyclic diazo component 3-amino-7-nitro-2*H*-1,2-benzothiazine 1,1-dioxide in the synthesis of a new series of azo disperse dyes. Further work is in progress in the authors' laboratory to exploit the synthetic utility of the compound in heterocyclic and dyestuff chemistry.

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