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Synthesis of Disperse Azo Dyes from 2-Amino-4- and 6-*N*,*N*-dialkylaminobenzothiazoles and their Application

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ABSTRACT

*2-Amino-6-*N,N*-dialkylaminobenzothiazole and 2-amino-4-*N,N*-dialkylamino-6-thiocyanatobenzothiazoles were prepared by condensation of 4-*N,N*-dialkylaminoanilines and 2-*N,N*-dialkylaminoanilines, respectively, with ammonium thiocyanate and bromine in acetic acid. These amines were diazotised and coupled with substituted *N,N*-dialkylanilines to give 2-(substituted-4-*N,N*-dialkylaminophenyl)azo-6-*N,N*-dialkylaminobenzothiazole dyes and 2-(substituted-4-*N,N*-dialkylaminophenyl)azo-6-thiocyanato-4-*N,N*-dialkylaminobenzothiazole dyes. The dyes were applied to polyester and polyamide fibres and their dyeing properties assessed.*

1 INTRODUCTION

Azo disperse dyes derived from 2-aminobenzothiazoles are bright scarlet to red–violet dyes of high tinctorial power and have excellent dischargeability and fastness to sublimation. Whilst lightfastness is generally moderate, it can be improved by the presence of electron-withdrawing groups in the 6-position of the benzothiazole moiety,[1,2] e.g. acyl or aroyl,[3] cyano,[4,5] nitro,[6–8] thiocyanato,[9] sulphonyl[10,11] and sulphonamide[12,13] substituents.

With a view to studying the effect of *N*,*N*-dialkylamino substituents in the 6-position of the benzothiazole moiety of azo disperse dyes of this type, 2-arylazo-6-*N*,*N*-dialkylaminobenzothiazole dyes were synthesised (Scheme 1). Since the thiocyanato group in the 6-position improves the lightfastness,

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some representative 2-arylazo-4-*N*,*N*-dialkylamino-6-thiocyanatobenzothiazole dyes were also synthesised. These dyes were applied to polyester and polyamide fibres and their fastness properties were studied.

2 RESULTS AND DISCUSSION

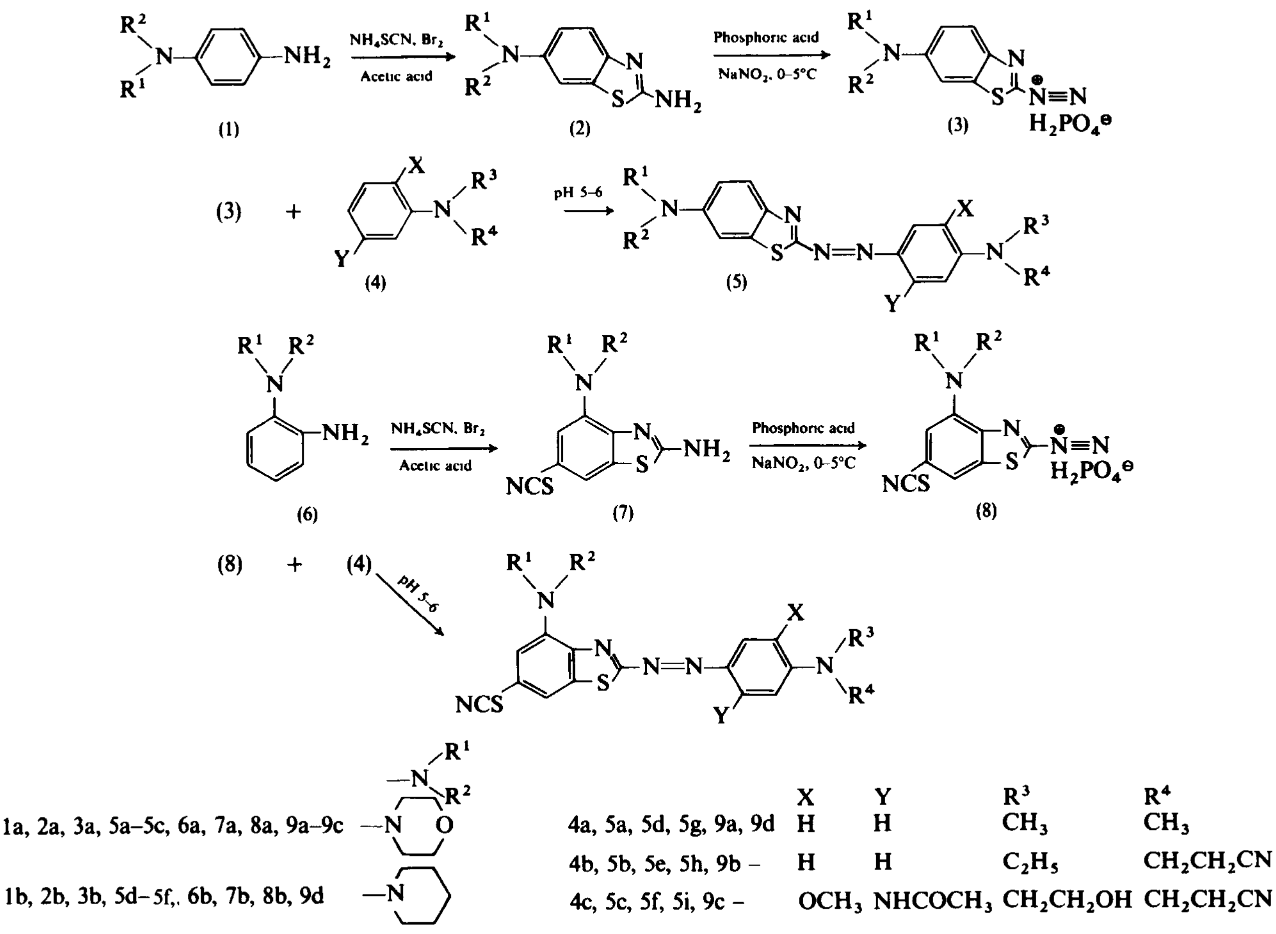
4-*N*,*N*-Dialkylaminoanilines (**1a**–**1c**) and 2-*N*,*N*-dialkylaminoanilines (**6a**–**6c**) were prepared[14,15] from 4-nitrochlorobenzene and 2-nitrochlorobenzene by the condensation with secondary amines such as morpholine, piperidine and *N*,*N*-diethylamine and subsequent reduction of the resulting nitro compounds. The 4-*N*-morpholinoaniline (**2a**), 4-*N*-piperidinoaniline (**2b**), 4-*N*,*N*-diethylaminoaniline (**2c**), 2-*N*-morpholinoaniline (**6a**) and 2-*N*-piperidinoaniline (**6b**) thus obtained were reacted with ammonium thiocyanate and bromine in acetic acid at 30–35°C to give the 2-amino-6-*N*,*N*-dialkylaminobenzothiazoles **2a**–**2c**, and the 2-amino-4-*N*,*N*-dialkylamino-6-thiocyanatobenzothiazoles **7a** and **7b**. These were purified either by crystallisation from toluene or by dissolution in aqueous hydrochloric acid and reprecipitation with dilute sodium carbonate or dilute ammonia. It was found that the rate of addition of alkali during reprecipitation must be slow, otherwise resinous products resulted with consequent lower yields of the 2-aminobenzothiazoles.

The 2-aminobenzothiazoles **2a**–**2c** and **7a**–**7c** were diazotised using orthophosphoric acid (85%) and solid sodium nitrite at 0–5°C and the resulting diazonium salts **3a**–**3c** and **8a**–**8b** were coupled with *N*,*N*-dimethylaniline (**4a**), *N*-ethyl-*N*-β-cyanoethylaniline (**4b**) and 2-methoxy-5-acetamido-*N*-β-hydroxyethyl-*N*-β-cyanoethylaniline (**4c**) at pH 5–6 to give the 2-(substituted-*N*,*N*-dialkylaminophenyl)azo-6-*N*,*N*-dialkylaminobenzothiazole dyes (**5a**–**5i**) and the 2-(substituted-*N*,*N*-dialkylaminophenyl)azo-4-*N*,*N*-dialkylamino-6-thiocyanatobenzothiazole dyes (**9a**–**9d**). The dyes **5a**–**5i** and **9a**–**9d** were obtained in yields 52–80% and were purified by crystallisation from chloroform, by dissolution in acetone and reprecipitation with water, and by column chromatography on neutral alumina using benzene and ethyl acetate as eluent.

The absorption spectra of the dyes **5a**–**5i** and **9a**–**9d** were recorded in DMF solution and are given in Table 1. The absorption maxima were found to be in the range 520–570 nm.

These dyes were applied to polyester and polyamide fibres, and gave pink to blue hues (see Table 1). Dyeings on polyester fibres were deeper than those on polyamide except in the case of dyes **5c**, **5f**, **5i** and **9c**.

The lightfastness of these dyes was fairly good and varied from 3 to 4, and the sublimation fastness of the dyes on polyester fibres was excellent. The



1a, 2a, 3a, 5a–5c, 6a, 7a, 8a, 9a–9c

1b, 2b, 3b, 5d–5f,. 6b, 7b, 8b, 9d

1c, 2c, 3c, 5g–5i - - - - —$N(C_2H_5)_2$

	X	Y	R^3	R^4
4a, 5a, 5d, 5g, 9a, 9d	H	H	CH_3	CH_3
4b, 5b, 5e, 5h, 9b -	H	H	C_2H_5	CH_2CH_2CN
4c, 5c, 5f, 5i, 9c -	OCH_3	$NHCOCH_3$	CH_2CH_2OH	CH_2CH_2CN

Scheme 1

TABLE 1
Absorption Spectra and Dyeing Properties of Benzothiazole Azo Dyes

Dye	*Absorption λ_{max} in DMF (nm)*	*log E*	*Colour on dyed synthetic fibres*		*Pick-up*	*Lightfastness*	*Sublimation fastness*
			Polyester	*Polyamide*			
5a	520	4·10	Red violet	—	4	4	4
			—	Red violet	4	4	—
5b	520	3·66	Pink	—	3	4	4
			—	Pink	3	4	—
5c	570	3·89	Blue	—	2	4	4–5
			—	Blue	4	4	—
5d	520	3·68	Red violet	—	2	3	4
				Red violet	2	3	—
5e	520	3·95	Pink	—	2	3	4
				Pink	2	3	—
5f	560	3·96	Blue	—	2	3	4
			—	Blue	2	3	—
5g	520	4·06	Red violet	—	3	4	4
			—	Red violet	3	4	—
5h	520	3·94	Pink	—	2	3	4
			—	Pink	2	3	—
5i	560	3·75	Blue	—	2	4	4
			—	Blue	2	4	—
9a	540	3·67	Red violet	—	2	4	4
			—	Red violet	2	4	—
9b	520	3·92	Red violet	—	2	3	4
			—	Red violet	2	3	—
9c	560	3·84	Blue	—	2	4	4–5
			—	Blue	2	4	—
9d	540	3·90	Red violet	—	4	4	4
			—	Red violet	4	4	—

presence of the 6-amino group in the benzothiazole residue, whilst giving dyes of good coloration and sublimation properties, does not give the higher lightfastness which results from the presence of electron-acceptor groups in the 6-position.

3 EXPERIMENTAL

All melting points are uncorrected and in °C. Absorption spectra of the dyes in their DMF solutions were recorded on a Beckman Model 25 spectrophotometer.

3.1 Preparation of starting materials

4-*N*-Morpholinoaniline (**1a**), m.p. 90°C, 4-*N*-piperidinoaniline (**1b**), b.p. 120°C/4 mm, 4-*N*,*N*-diethylaminoaniline (**1c**), b.p. 115–116°C/5 mm, 2-*N*-morpholinoaniline (**6a**), m.p. 98°C, and 2-*N*-piperidinoaniline (**6b**), m.p. 46°C, were prepared following known methods.[14,15]

3.2 2-Amino-6-*N*-morpholinobenzothiazole (2a)

4-*N*-Morpholinoaniline (**1a**) (1·78 g, 0·01 mol) was dissolved in acetic acid (20 ml) and ammonium thiocyanate (2·28 g, 0·03 mol) was added slowly maintaining the temperature at 30–35°C. The mixture was stirred for 30 min and the temperature was adjusted to 25°C. A solution of bromine (1·6 g, 0·01 mol) in acetic acid (5 ml) was added dropwise over 30 min, maintaining a temperature of 25°C. The reaction mixture was then stirred for 12 h at room temperature, before heating to 80–90°C and filtering. The filtrate was cooled and neutralised by the slow addition (over 30 min) of aqueous sodium carbonate solution (5%) to precipitate the product. This was filtered, dried and recrystallised from toluene in colourless crystals (92%), m.p. 210°C. Calculated for $C_{11}H_{13}N_3OS$: N, 17·9; S, 13·6. Found: N, 17·9; S, 13·85%.

The other 2-amino-6-*N*,*N*-dialkylaminobenzothiazoles (**2b** and **2c**) were prepared in the same manner. 2-Amino-4-*N*,*N*-dialkylamino-6-thiocyanatobenzothiazoles (**6a** and **6b**) were similarly prepared except that the molar proportions of acetic acid, ammonium thiocyanate and bromine were doubled.

3.3 2-Amino-6-*N*-piperidinobenzothiazole (2b)

Obtained from **1b** as a buff-coloured solid (85%), purified by dissolution in hydrochloric acid, filtering and reprecipitation with sodium carbonate solution (5%). Calculated for $C_{12}H_{15}N_3S$: N, 18·0; S, 13·7. Found: N, 17·9; S, 14·1%.

3.4 2-Amino-6-*N*,*N*-diethylaminobenzothiazole (2c)

Obtained from **1c** as a grey-coloured solid (85%), purified as for **2b**. Calculated for $C_{11}H_{15}N_3S$: N, 19·0; S, 14·5. Found: N, 18·4; S, 14·7%.

3.5 2-Amino-4-*N*-morpholino-6-thiocyanatobenzothiazole (7a)

Purified in the manner described for **2b**, as a buff-coloured solid (69%), m.p. 161°C. Calculated for $C_{12}H_{12}N_4OS_2$: N, 19·2; S, 21·9. Found: N, 19·1; S, 21·8%.

3.6 2-Amino-4-*N*-piperidino-6-thiocyanatobenzothiazole (7b)

Purified as given for **2b**, as a yellow-coloured solid (62%), m.p. 91–94°C. Calculated for $C_{13}H_{14}N_4S_2$: N, 19·3; S, 22·1. Found: N, 18·9; S, 21·8%.

3.7 2-(4-*N*,*N*-Dimethylaminophenyl)azo-6-*N*-morpholinobenzothiazole (5a)

2-Amino-6-*N*-morpholinobenzothiazole (**2a**) (2·35 g, 0·01 mol) was dissolved in orthophosphoric acid (85%) (20 ml) with warming and the solution was then cooled externally with stirring to 0°C and to it was added sodium nitrite (0·76 g, 0·011 mol) over 15 min. The mixture was stirred for 1 h at 0–5°C and excess nitrous acid was destroyed by the addition of urea (1 g).

The cold diazo solution was run over 30 min at 0–5°C into a solution of *N*,*N*-dimethylaniline (**4a**) (1·21 g, 0·01 mol) in water (20 ml) and glacial acetic acid (10 ml). Sodium acetate was added in small portions to maintain the pH at 5–6 and the mixture was stirred for 4 h. The intense violet dye which separated was filtered, washed with water and dried. Crystallisation from chloroform yielded dark violet crystals (80%), m.p. 218°C. Calculated for $C_{19}H_{22}N_5OS$: N, 19·1; S, 8·7. Found: N, 18·6; S, 8·3%.

The other dyes **5a**–**5i** and **9a**–**9d** were prepared in a similar manner to that described above for **5a**.

3.8 2-(4-*N*-Ethyl-*N*-*β*-cyanoethylaminophenyl)azo-6-*N*-morpholinobenzothiazole (5b)

Recrystallisation from chloroform yielded deep red crystals (69%), m.p. 270°C. Calculated for $C_{22}H_{24}N_6OS$: N, 20·0; S, 7·6. Found: N, 19·8; S, 7·4%.

3.9 2-(2-Acetamido-5-methoxy-4-*N*-*β*-hydroxyethyl-*N*-*β*-cyanoethylaminophenyl)azo-6-*N*-morpholinobenzothiazole (5c)

Recrystallised from chloroform as bluish violet crystals (60%), m.p. 140–142°C. Calculated for $C_{25}H_{29}N_7O_4S$: N, 18·7; S, 6·1. Found: N, 18·5; S, 6·00%.

3.10 2-(4-*N*,*N*-Dimethylaminophenyl)azo-6-*N*-piperidinobenzothiazole (5d)

Recrystallised from chloroform as dark violet crystals (71%), m.p. >300°C. Calculated for $C_{20}H_{23}N_5S$: N, 19·2; S, 8·8. Found: N, 19·3; S, 8·8%.

3.11 2-(4-*N*-Ethyl-*N*-*β*-cyanoethylaminophenyl)azo-6-*N*-piperidinobenzothiazole (5e)

Recrystallised from chloroform as deep red crystals (59%), m.p. 228–229°C. Calculated for $C_{23}H_{26}N_6S$: N, 20·1; S, 7·7. Found: N, 20·0; S, 7·5%.

3.12 2-(2-Acetamido-5-methoxy-4-*N*-*β*-hydroxyethyl-*N*-*β*-cyanoethylaminophenyl)azo-6-*N*-morpholinobenzothiazole (5f)

Recrystallised from chloroform as bluish violet crystals (63%), m.p. 231°C. Calculated for $C_{26}H_{32}N_7O_3S$: N, 18·8; S, 6·1. Found: N,18·3; S, 5·9%.

3.13 2-(4-*N*,*N*-Dimethylaminophenyl)azo-6-*N*,*N*-diethylaminobenzothiazole (5g)

Purified by dissolution in acetone and reprecipitation with water, then column chromatographed on neutral alumina using benzene:ethyl acetate as eluent (95:5) to give **5g** as red violet crystals (79%), m.p. 219°C. Calculated for $C_{19}H_{23}N_5S$: N, 19·8; S, 9·1. Found: N, 19·5; S, 9·3%.

Purification of other dyes **5h**, **5i** and **9a**–**9d** was effected in the same manner.

3.14 2-(4-*N*-Ethyl-*N*-*β*-cyanoethylaminophenyl)azo-6-*N*,*N*-diethylaminobenzothiazole (5h)

Dark red crystals (52%), m.p. 120°C. Calculated for $C_{22}H_{26}N_6S$: N, 20·7; S, 7·9. Found: N, 20·45; S, 7·7%.

3.15 2-(2-Acetamido-5-methoxy-4-*N*-*β*-hydroxyethyl-*N*-*β*-cyanoethylaminophenyl)azo-6-*N*,*N*-diethylaminobenzothiazole (5i)

Bluish violet crystals (57%), m.p. 190°C. Calculated for $C_{25}H_{31}N_7O_3S$: N, 19·25; S, 6·3. Found: N, 19·1; S, 6·1%.

3.16 2-(4-*N*,*N*-Dimethylaminophenyl)azo-4-*N*-morpholino-6-thiocyanatobenzothiazole (9a)

Violet crystals (67%), m.p. 239°C. Calculated for $C_{20}H_{20}N_6OS_2$: N, 19·8; S, 15·1. Found: N, 19·7; S, 14·8%.

3.17 2-(4-*N*-Ethyl-*N*-*β*-cyanoethylaminophenyl)azo-4-*N*-morpholino-6-thiocyanatobenzothiazole (9b)

Deep red crystals (71%), m.p. 130°C. Calculated for $C_{23}H_{23}N_7OS_2$: N, 20·55; S, 13·4. Found: N, 21·0; S, 13·9%.

3.18 2-(2-Acetamido-5-methoxy-4-*N*-*β*-hydroxyethyl-*N*-*β*-cyanoethylamino-phenyl)azo-4-*N*-morpholino-6-thiocyanatobenzothiazole (9c)

Bluish violet crystals (73%), m.p. 238°C. Calculated for $C_{26}H_{28}N_8O_4S_2$: N, 19·3; S, 11·0. Found: N, 19·1; S, 11·25%.

3.19 2-(4-*N*,*N*-Dimethylaminophenyl)azo-4-*N*-piperidino-6-thiocyanatobenzothiazole (9d)

Dark violet crystals (68%), m.p. 179°C. Calculated for $C_{21}H_{22}N_6S_2$: N, 19·9; S, 15·2. Found: N, 20·1; S, 14·85%.

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