

Synthesis of monoazo disperse dyes based on 2-aminoheterocycles and their dyeing performance on nylon fabrics

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(Received 16 May 2000)

Novel monoazo disperse dyes based on various 2-aminoheterocycles were prepared using *N*-methyl-*N*-(2-hydroxyethyl)aniline as the coupling component. All the dyes were applied as disperse dyes on nylon fabric. These dyes have been found to give a wide range of colour shades with very good depth, brightness and levelness on nylon fabric. The visible absorption spectra, elemental analysis and R_f values were investigated. The percentage dye bath exhaustion on fabric was found to be very good. The dyed fabric showed very good to excellent fastness to light, washing, rubbing and perspiration. The sublimation fastness was found to be excellent.

Keywords: nylon fabric, disperse dyes, exhaustion, fastness, 2-aminoheterocycles, *N*-methyl-*N*-(2-hydroxyethyl)aniline.

INTRODUCTION

In the early days of dyestuffs, the majority of dyes were prepared from benzene and naphthalene derived intermediates, including heterocyclic dyestuffs such as Mauveine and Indigo. However, a recent trend has seen the introduction of an increasing number of heterocycles as dye precursors and nowhere has the impact been felt more than in azo dyes.^{1–5} Numerous heterocyclic dyes are now marketed to the extent that no manufacturer can profess to produce a full range of disperse dyestuffs without handling colorants based on heteroaromatic diazo or coupling components. Thus, hitherto unobtainable shades, especially blues and greens, and properties such as high tinctorial power and excellent brightness have become attainable and are commercially competitive with the more expensive anthraquinone dyes.

Most heterarylazo dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur

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heteroatom and to which a diazotisable amino group is directly attached; the ring may also possess one or more nitrogen heteroatom and be fused to another aromatic ring. These diazo components are capable of providing red to blue disperse dyes that meet the rigorous technical and economic requirements demanded of them by both manufacturer and user. Hence, it was thought to synthesise a series of dyes, prepared from various heterocyclic amines, including derivatives of thiazole, thiadiazole and benzothiazole, and to examine the dyeing performance of these dyes on nylon fabric.

EXPERIMENTAL

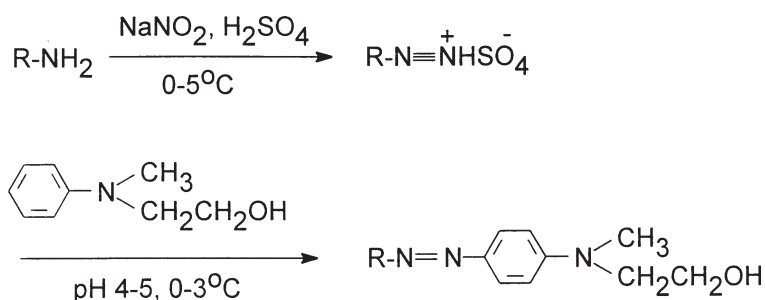
Materials

All the chemicals and coupling component *N*-methyl-*N*-(2-hydroxyethyl)aniline used were of commercial grade. They were further purified by crystallisation and distillation. The solvents used were spectroscopic grade.

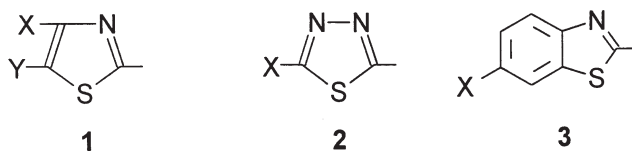
Methods

Preparation of various 2-aminoheterocycles. Various 2-aminoheterocycles, 2-aminothiazole,⁶ 2-amino-5-nitrothiazole,⁷ 2-amino-5-thiocyanothiazole,⁸ 2-amino-4-phenylthiazole,⁹ 2-amino-5-bromo-4-phenylthiazole,¹⁰ 2-amino-5-acetyl-4-methylthiazole,¹¹ 2-amino-5-mercapto-1,3,4-thiadiazole,¹² 2-aminobenzothiazole¹³ and 2-amino-6-methoxybenzothiazole,¹⁴ were prepared by the methods reported in the literature.

Diazotisation of various 2-aminoheterocycles. Diazotisation of the various 2-aminoheterocycles was effected with nitrosylsulphuric acid. The general procedure is described below.



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Scheme 1.

Sulphuric acid (0.01 mol) was cooled to 0 °C and then dry sodium nitrite (0.01 mol) was added to it at 0–5 °C. The reaction mixture was heated to 45 °C for 15 min and then the temperature was raised to 60–65 °C and maintained at this temperature for 1 h. The resulting solution was cooled to 0–5 °C and then treated dropwise at 5–20 °C with a mixture of 17 ml of acetic acid and 3 ml of propionic acid. The resulting nitrosylsulphuric acid was cooled to 0 °C, then the finely ground 2-aminoheterocycle (0.01 mol) was slowly added and the mixture was stirred for a further 1 h at 0–5 °C. The excess nitrous acid was decomposed with the required amount of urea. The resulting clear diazonium solution was used immediately in the coupling reaction (see Scheme 1).

General procedure for coupling. The coupling component *N*-methyl-*N*-(2-hydroxyethyl)aniline (0.01 mol) was dissolved in 10 ml of acetic acid and then cooled to 0 °C. The previously prepared diazonium solution was added dropwise over 1 h with vigorous stirring and with frequent addition of ice flasks. The reaction mixture was stirred for a further 1 h at 3–5 °C and then 10 % sodium acetate solution was dropped in slowly until the pH became 4–5. The product was then filtered off, washed with water until acid-free, and dried at 50 °C in an oven to give the azo dyes. The yields of the dyes ranged from 72–91 %. The dyes thus obtained were recrystallised from ethanol. Total elimination of the contaminants required three recrystallisations.

Dyeing of nylon fabric. Dyeing of nylon fabric was carried out using a procedure reported in the literature.¹⁵

Colour fastness tests. Fastness to light, sublimation and perspiration was assessed in accordance with BS:1006-1978. The wash fastness test was in accordance with IS:765-1979. The rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with AATCC-1961. Detail of the colour fastness tests are described in the literature.¹⁶

General. Melting points were determined by the open capillary method. The visible absorption spectra were measured using a Carl Zeiss UV/VIS Specord Spectrometer. Elemental analysis were carried out on a Carlo Erba Elemental Analyser 1108.

RESULTS AND DISCUSSION

Preparation of various 2-aminoheterocycles

The most convenient synthesis of 2-aminothiazoles is by the condensation of thiourea with an α -chlorocarbonyl compound: for instance, 2-aminothiazole is prepared by condensing thiourea with α -chloroacetaldehyde. Substituents can be introduced into the thiazole ring either by using suitably substituted precursors or by direct introduction *via* electrophilic attack. Thiazoles substituted in the 4-position are prepared by reacting the appropriate ketone with thiourea in presence of bromine. The 2-aminothiazoles, their acyl derivatives, or both, undergo electrophilic substitution in the 5-position and can be nitrated and thiocyanated. Nitration of 2-aminothiazoles is effected in concentrated sulphuric acid below 10 °C. An intermediate 2-nitroamino compound is formed, which rearranges under the reaction conditions to give the 2-amino-5-nitrothiazole. Aminobenzothiazoles are prepared somewhat differently to the thiazoles. Here the thiazole ring is annealed on to a benzene ring, usually *via* an aniline derivative. Thus, 2-amino-6-methoxybenzothiazole is obtained from *para*-anisidine and thiocyanogen. This reaction is usually run by treating *para*-anisidine in acetic acid with ammonium or sodium thiocyanate and bromine to generate 'nascent' thiocyanogen (the Kaufmann reaction), which reacts readily to produce an intermediate *ortho*-thiocyananiline derivative; a spontaneous ring closure then usually occurs un-

der the acidic reaction conditions to produce 2-amino-6-methoxybenzothiazoles. An alternative to the above synthesis is used to prepare 6-unsubstituted benzothiazoles. An aromatic amine is first reacted with potassium thiocyanate to give the *ortho*-arylthiourea which is then cyclised with bromine to the corresponding 2-aminobenzothiazole. Thiosemicarbazide is also used as an intermediate for preparing 2-amino-5-mercapto-1,3,4-thiadiazole by reaction with carbon disulphide, either with or without the presence of a base. Ring closure of the dithiocarboxylate salt occurs on heating under the reaction conditions.

Diazotisation and coupling

Diazotisation in concentrated acid is used for various 2-aminoheterocycles, since hydrolysis of the diazonium salt occurs in dilute acid. Here, the acid of choice is concentrated sulphuric acid, used in an admixture with glacial acetic acid. A particularly important reagent combination is nitrosylsulphuric acid (ONHSO_4) which is used extensively as a nitrosating agent for heterocyclic amines. The various 2-aminoheterocycles were diazotised satisfactorily at 0–5 °C using nitrosylsulphuric acid in acetic acid. In order to determine the end point of diazotisation, it was found useful to check for the presence of unreacted diazo component in samples of the diazotisation mixture by TLC. Thus, when unreacted diazo component was no longer detected by TLC, the diazotisation was ended. The diazonium salt solution was used immediately since it decomposed on standing, even when kept cold. The subsequent coupling reaction occurs readily on adding the resulting diazonium salt continuously to a solution of the coupling component in acetic acid. Frequent addition of ice flakes helped to keep the coupling temperature below 5 °C and facilitated the precipitation of the resulting dye. The coupling was usually accompanied by some decomposition; however, by careful addition of the diazonium salt solution at 0–3 °C to a solution of the coupling component in acetic acid, 72–91 % yields of dye were usually obtained. To complete the coupling, particularly when nitrosylsulphuric acid was used in the previous diazotisation, the pH of the reaction mixture was adjusted to approximately 4–5. Thus, an appropriate amount of 10 % sodium acetate solution was slowly added below 5 °C.

Physical properties of the dyes

The purity of the dyes were controlled by TLC using methanol-water-acetic acid (12:3:7) as the solvent system. When adsorbed onto the silica chromatography plates, the dyes produced single colour spot. All the recrystallised dyes exhibited well-defined melting points characteristic of pure compounds. It would be unwise to attempt to explain in detail the relative values of their melting points, because of the complex dependence of the melting points on a number of factors (*e.g.*, polarity, size, geometry, interaction, *etc.*).

Colour and spectral properties of the dyes

The prepared dyes, listed in Table I, are red to blue-violet having adsorptions at 505 to 593 nm. The colour of the dyes is affected by substituents in the thiazole ring. The dye **1d**, derived from 4-substituted 2-aminothiazole, is pink-red with an absorption

at 515 nm. The dyes **1e** and **1f**, derived from 4,5-disubstituted 2-aminothiazole, absorb at 535 and 510 nm, respectively. The parent 2-aminothiazole dyes absorb at 505 nm, hence, the influence of substitution in the 4-position is negligible. The failure of 4-substituents to effect the expected colour shifts in 2-thiazolylazo dyes may result from the inability of the 4-substituent to enter effectively into the resonance of the dye molecule. In contrast to the negligible effect of 4-substituents on colour, 5-substituents cause a marked effect. As would be expected from resonance considerations, the colour of the dyes containing various groups in the 5-position depends in the order of increasing negativity of the substituent; for example, the dye **1c** from 2-amino-5-thiocyanothiazole is red-violet (530 nm), whereas the corresponding dye **1b** from 2-amino-5-nitrothiazole is blue (593 nm). The strong electron attracting capacity of the 5-nitro-2-thiazolyl residue results in the large bathochromic shift and the increase in both λ_{\max} and the extinction coefficient in this dye, which is indicative of delocalisation within an electron rich π -system. In order to bring about a bathochromic shift, a negative group strategically placed in the thiazole ring which allows a greater electronic displacement is necessary. It has been suggested¹⁷ that the increased diene character of the ring may be responsible for the large colour shifts observed. The bathochromicity of thiazolyl dyes is not attributable to a contribution of the 3d atomic orbitals of the sulphur atom of the heterocyclic ring.¹⁸ The parent 2-aminobenzothiazole dye **3a** absorbs at 520 nm but dye **3b** derived from 2-amino-6-methoxybenzothiazole absorbs at 515 nm. Thus, an electron releasing group at 6-position of benzothiazole causes a small hypsochromic shift in the dye.

TABLE I. Characterisation data and % exhaustion for the synthesised dyes

Dye no.	Substituents		Melting point (°C)	Yield (%)	λ_{\max}	log ϵ	Exhaustion (%)	R_f
	X	Y						
1a	H	H	168–169	85	505	4.29	85	0.89
1b	H	NO ₂	202–204	72	593	4.57	83	0.93
1c	H	SCN	215–216	86	530	4.31	92	0.91
1d	Ph	H	130–132	82	515	4.61	76	0.86
1e	Ph	Br	190–192	82	535	4.48	80	0.87
1f	CH ₃	COCH ₃	215–216	85	510	4.80	79	0.90
2a	SH	–	208–209	79	535	4.35	83	0.92
3a	H	–	228–230	78	520	4.15	85	0.82
3b	CH ₃ O	–	242–243	91	515	4.31	83	0.84

Dyeing properties of dyes

All the dyes were applied on nylon fabric at 2 % shade as disperse dyes. Their dyeing properties are given in Tables III. These dyes gave a wide range of shades varying from red to blue with excellent brightness, levelness and depth on fabric. The variation in the shades of the dyed fabric result from both the nature and position of the substituent present on the diazo component. The dyed fabric have good to excellent

light, wash and perspiration fastness and excellent sublimation fastness. A remarkable degree of levelness and brightness after washing indicates good penetration and excellent affinity of these dyes to the fabric.

TABLE II. Elemental analysis of the dyes

Dye No.	Molecular formula	Molecular mass M_r	C %		H %		N %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
1a	C ₁₂ H ₁₄ N ₄ OS	262	54.96	54.80	5.34	5.20	21.37	21.26
1b	C ₁₂ H ₁₃ N ₅ O ₃ S	307	46.90	46.60	4.23	4.11	22.80	22.65
1c	C ₁₃ H ₁₃ N ₅ O ₃ S ₂	351	44.44	44.32	3.70	3.60	19.94	19.82
1d	C ₁₈ H ₁₈ N ₄ OS	338	63.90	63.78	5.32	5.20	16.56	16.47
1e	C ₁₈ H ₁₇ N ₄ OSBr	417	51.79	51.69	4.07	3.91	13.42	13.38
1f	C ₁₅ H ₁₈ N ₄ O ₂ S	318	56.60	55.42	5.66	5.51	17.61	17.51
2a	C ₁₁ H ₁₃ N ₅ OS ₂	295	44.74	44.62	4.42	4.31	23.72	23.66
3a	C ₁₆ H ₁₆ N ₄ OS	312	61.53	61.41	5.12	5.01	17.91	17.86
3b	C ₁₇ H ₁₈ N ₄ O ₂ S	342	59.64	59.45	5.26	5.17	16.37	16.30

TABLE III. Colour fastness properties of dyes on nylon fabric

Dye No.	Colour shade on nylon	Light fastness	Wash fastness	Rubbing fastness		Perspiration fastness		Sublimation fastness
				dry	wet	acid	alkaline	
1a	Reddish violet	4-3	5	5-4	5-4	5	5	5
1b	Blue	5	5	5	5	5	5	5
1c	Maroon	5	4-5	4-5	5-4	5-4	5-4	5
1d	Dark brown	5-4	5-4	5	5	4-5	4-5	5
1e	Red	5	5-4	5	5	5	5	5
1f	Bright red	4	4-5	4-5	4-5	4	4-5	5
2a	Navy blue	5	5	5	5	5	5	5
3a	Red	5	5-4	5	5	5	5	5
3b	Maroon	5-4	5-4	5	5	5	5	5

CONCLUSION

The various 2-aminoheterocycles possessed sufficiently different basicities to warrant the employment of various conditions for diazotisation. Phenyl and strong electron-attracting substituents reduced the hydrophilicity and basicity, to the extent that nitrosylsulphuric acid was needed for satisfactory diazotisation. Monoazo disperse dyes containing the *N*-methyl-*N*-(2-hydroxyethyl)aniline coupling moiety have been prepared from various 2-amino-heterocyclic compounds. The dyeing and fastness properties of these dyes have been examined. A gamut of colour shades ranging from red to blue was obtained by applying the variously substituted dyes. Bathochromic colours were observed as stronger electron-attracting substituent were introduced at the

5-position of the thiazole ring. The dyes showed that substituents in the 4-position of the aminothiazole have little effect on the colour of the dye.

The 2-aminoheterocyclic diazo components are able to provide a wide range of deep, and bright shades of disperse dyes on nylon. These dyes give good exhaustion and level dyeing and excellent affinity. Their synthesis is generally convenient and economical (as compared to anthraquinones which could only provide up to blue hues). The small size of the heterocycles enable better dyability. The intrinsic conjugation in the heterocyclic structure ensures very good colour strength. The compactness of the structure provides for excellent sublimation fastness. The 2-azo heterocycle structures show excellent dischargeability (an additional dyeing property, not exhibited by the carbocyclic azo and anthraquinone disperse dye structure).

ИЗВОД

СИНТЕЗА МОНОАЗО ДИСПЕРЗНИХ БОЈА БАЗИРАНИХ НА 2-АМИНОХЕТЕРОЦИКЛИМА И ЊИХОВА СПОСОБНОСТ БОЈЕЊА ТКАНИНА ОД НАЈЛОНА

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Добивене су нове моноазо дисперзне боје базиране на различитим 2-аминохетероциклима коришћењем *N*-метил-*N*-(2-хидроксиетил)анилина као куплујуће компоненте. Све боје су наносене на тканину од најлона као дисперзне боје. Нађено је да ове боје дају широк опсег нијанси боја са добром моћи продирања, сјајем и равномерношћу бојења најлонске тканине. Испитани су апсорпциони спектри у видљивој области, елементална анализа и R_f вредности. Нађено је да је процентуално исцрпљивање купатила за бојење тканине врло добро. Обојена тканина показује одличну стабилност на светлост, прање, трење и зној. Стабилност на сублимацију је одлична.

(Примљено 19. маја 2000)

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