



Synthesis and Spectral Properties of Hetaryl Monoazo dyes derived from 2-amino-5-nitrothiazole

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ABSTRACT

Various hetarylazo dyes have been synthesized by coupling reactions between diazotised 2-amino-5-nitrothiazole and 2-chloroaniline, 1,3-dihydroxybenzene and N-phenyl naphthylamine. Spectral measurements were carried out in different solvents. The solvatochromic behaviour of the dyes in various solvents were evaluated. The 2-amino-5-nitrothiazole dye derivatives absorb maximally at longer wavelengths and are tinctorially stronger than the 1-naphthylamine dyes, although the former dyes have higher extinction coefficients. Also, the synthesized dyes exhibit positive solvatochromism so that the absorption bands of the dye, move towards longer wavelengths as the polarity of the solvent increases.

Key words: Absorption maxima, Tautomerism, azo dyes, solvent effects.

INTRODUCTION

The heterocycles are an inescapable and integral feature of many diverse branches of chemistry¹.

Heterocycles have been put to much use in disperse dye Chemistry, which it has been claimed was the first area to foster the industrial exploitation of heteroaromatic amines². 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. In addition, just as new applications have emerged for conventional textile-orientated heterocyclic dyes, such as the utilization in photodynamic therapy and lasers of thiazines and oxazines^{3,4}. Non-textile uses of hetarylazo disperse dye types have increasingly been explored, for example, in reprographic technology, functional dye applications and non-linear optical systems^{5,6}.

Most hetarylazo dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur heteroatom and to which a diazotisable amino group is directly attached, the

ring may also possess one or two nitrogens heteroatoms and be fused to another aromatic ring.

The heterocycle of interest in this study is 2-amino-5-nitrothiazole. Monoazo dyes earlier derived from this amine yielded strong blue shades on acetate fibres from simple aniline and toluidine couplers, and attracted considerable research effort into heterocyclic azo compounds. Among them, are disperse blues 82, 102 and 106^{7,8,9}.

Thus, dyes from this intermediate have achieved significant commercial success for the dyeing of cellulose acetate fibres in which gas fastness is a higher priority than light fastness.

In this present study, the synthesis of monoazo disperse dyes with 2-amino-5-nitrothiazole as the diazo component is reported. Also the absorption characteristics of the disperse dyes and their 1-naphthylamine analogues have been investigated for comparative purposes.

EXPERIMENTAL

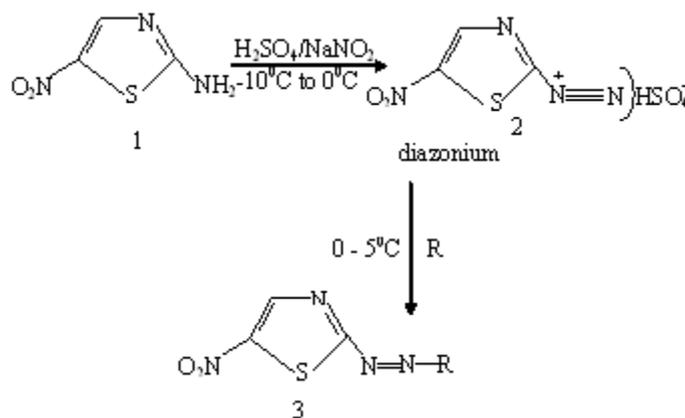
Materials

2-Amino-5-nitrothiazole, 2-chloroaniline, 1;3-dihydrobenzene, N-phenyl-naphthylamine were purchased from Aldrich Chemical Company and used without further purification. All other chemicals used in the synthesis and characterization were of laboratory-reagent grade.

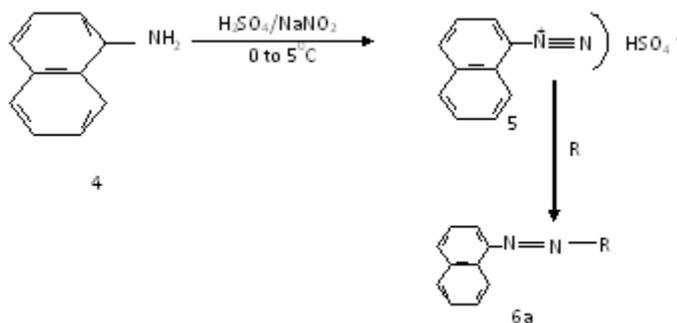
Chemical and Instrumental analysis

The proton nuclear magnetic resonance (¹H NMR) spectra were obtained with a mercury-200BB (200MHz) spectrometer for solutions in an appropriate deuterated solvent. The chemical shifts are reported in ppm using tetramethylsilane (TMS) as the internal reference.

Melting points are uncorrected and were determined using a Thumbnail melting point apparatus. The absorption spectra were measured



Scheme 1



Scheme 2

in 1cm quartz cells on a spectrophotometer (Genesys 10S VL. 200 series). The IR spectra were recorded on potassium bromide pellets on Nicolet Averser 330 series spectrophotometer.

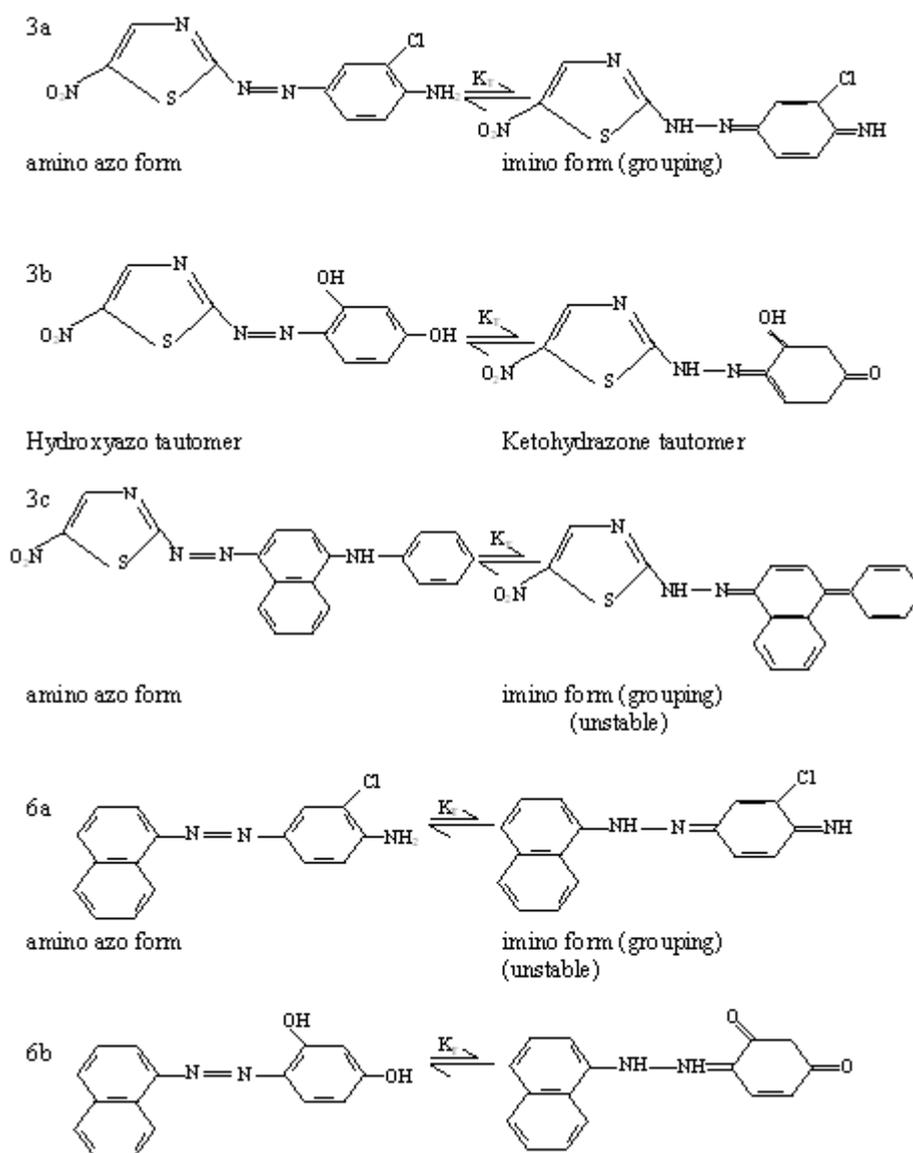
The purity of the dyes was assessed by Thin Layer Chromatography (TLC) using Whatman 250m silica gel 60 AMK 6F plates as the stationary phase and methanol as developing solvent.

Methods

Synthesis

4-nitrothiazole-3-chloro-2-aminobenzene (3a)

2-Amino-5-nitrothiazole (4.0 g, 0.3 mole) was diazotised with (3.00 g, 0.04 mole) of NaNO_2 at -10°C to 0°C in (1.47 ml, 0.03 mole) sulphuric acid[10,11]. Then, 0.03 mol, 2.90 ml of 2-chloroaniline, solution which was dissolved in acetic



Scheme 3

acid (0.03 mole, 1.58 ml) was coupled with the obtained diazonium salt at pH values between 4 and 5. The mixture was stirred for a further 2 hours at room temperature. The crude product was separated by filtration, washed with water and dried. The purity of the dye was determined by Thin Layer Chromatography (TLC). The yield of the reaction was 5.32 g (68%) and its colour was brown solid. It is soluble in CHCl_3 and DMF m.p. = 198 - 200°C. The molecular structure of the compound was elucidated by UV-visible, FTIR and ^1H NMR.

This procedure was also used to synthesise dye 3c.

Synthesis of 4-nitrothiazole-2,4-dihydroxybenzene (3b)

2-Amino-5-nitrothiazole (7.25 g, 0.05 mole) was dissolved in a mixture of 33g conc. H_2SO_4 and 33 g ice at 25°C. A solution of 3.5 g NaNO_2 (0.0507 mole) dissolved in 45g conc. H_2SO_4 was added dropwise to the aminonitrothiazole solution at -10°C to 0°C with stirring [10,11]. After 30 mins of stirring at -10°C to 0°C, the resulting diazonium salt was slowly added to the cooled solution of (5.5 g, 0.05 mole) of 1,3-dihydroxybenzene dissolved in 0.05 mole of sodium hydroxide. The mixture was stirred at 0°C for 1 hour and the product obtained was collected by filtration, washed with water and dried. The purity of the dye was determined by TLC. The yield of the reaction was 74.4% and its colour was yellow-brown. It is soluble in DMF, acetone and ethanol m.p = 178.180°C. The molecular structure of the compound was elucidated by spectroscopic methods such as UV-visible, FTIR and ^1H NMR.

In order to synthesis the 1-naphthylamine disperse dye analogues, the same procedure was repeated except that in place of 2-amino-5-nitrothiazole, 1-naphthylamine was used as the diazo component (scheme 2).

RESULTS AND DISCUSSION

Thermal Properties

Although, it would be unwise to explain in detail the relative values of the melting points of the dyes, because of the complex dependence of melting points on a number of factors, a few general trends can be used to explain the melting points of

the compounds. For example, the dyes that were prepared from low melting point coupling component (N-phenyl-naphthylamine) tended to have low thermal stability: dyes 3c and 6c have low melting point coupling components hence the low thermal stability. It is also presumed that, the more polar dyes which contain more powerful electron-withdrawing group tend to have better thermal properties: the nitrothiazole substituted dyes 3a – c generally showed higher thermal properties than the 1-naphthylamine analogues.

Absorption Spectra

The visible absorption spectra of the heteroarylazo dyes and the 1-naphthylamine analogues are summarized in Table 3. The prepared dyes developed a colour ranging from pink (λ_{max} 415 nm) to orange (λ_{max} 490 nm) (in ethanol).

It is a known fact that the wavelength values tend to be related to the strength of the electronic power in the aromatic ring system [12]. As a result of the fact that the electronic transition in these compounds involves a general migration of electron density from the donor group towards the azo group, bathochromic effect is usually achieved by placing substituents in the positions ortho or para to the azo group for effective conjugation [13,14].

The nitrothiazole dye derivatives absorbed maximally at longer wavelengths, ranging from 40–785 nm in ethanol and 7–24 nm in dimethylformamide (DMF), compared to the visible absorption spectra of the 1-naphthylamine analogues. This is due to the longer conjugation effect exerted by the nitro group which has a more powerful electron-withdrawing property.

Tautomerism of dyes 3a – c and 6a - c

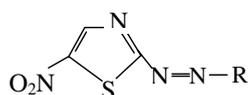
The tautomeric equilibrium position for hydroxyazo-ketohydrazone systems varies according to the chromophore, the nature and position of substituents, the solvent or the substrate, the temperature and various other factors [15]. In general, however, either the hydroxyazo tautomer or the corresponding ketohydrazone form is dominant for a particular structure. Azo dyes 3a – c and 6a – c may exist as a mixture of several tautomeric forms as shown in scheme 3.

Table 1: FTIR and ¹H NMR data of dyes 3a-c and dyes 6a - c

Dye	IR (KBr, v cm ⁻¹)	¹ H NMR, d(ppm)	Solvent
3a	3441 – 3345 (NH) 1596 (Aromatic ring) 1515 & 1384 (NO ₂)	5.82 (2, 2H, NH ₂) 7.22 (m, 1H, Phenyl proton) 7.40 (br & m 1H, phenyl proton) 7.62 (m, 1H, phenyl proton) 7.70 (m, 1H, phenyl proton) 8,60 (br & m, 1H, thiazole proton)	CDCl ₃
3b	3438 (OH) 1629 (C = O) 1560 (Ar-ring) 1522 & 1352 (NO ₂)	6.25 (d, 1H, phenyl proton) 7.02 (d, 1H, phenyl proton) 7.62 (m, 1H, phenyl proton) 8.20 (s, 1H, bonded OH) 8.46 (dd, 1H, thiazole proton) 13, 25 (S, 1H, NH)	CD ₃ OCD ₃
3c	3462 (NHR) 3051 (Ar-CH) 1596 (Ar-ring) 1523 & 1357 (NO ₂)	1.42 (q, 1H, NHR) 6.63 (d, 1H, naphthalene proton) 7.02 (d, 5H, phenyl proton) 7.20 (m, 1H, naphthalene proton) 7.42 (m, 1H, naphthalene proton) 7.65 (q, 1H, naphthalene proton) 8.40 (d, 1H, naphthalene proton) 8.48 (d, 1H, naphthalene proton) 8.82 (d, 1H, thiazole proton)	CDCl ₃
6a	3395 (NH) 3051 (C – H) 1596 (Ar-ring) 1497 (Naphthalene ring)	5.46 (s, 2H, NH ₂) 6.45 (dd, 1H, naphthalene proton) 7.65 (d, 1H, naphthalene proton) 7.40 (br & m, 1H, naphthalene proton) 7.66 (m, 1H, naphthalene proton) 7.87 (dd, 1H, phenyl proton) 8.20 (d, 1H, phenyl proton) 8.65 (dd, 1H, naphthalene proton) 9.20 (dd, 1H, phenyl proton) 9.25 (d, , 1H, naphthalene proton)	CDCl ₃
6b	3446 (OH) 1596 (Aromatic-ring) 1513 (Naphthalene-ring)	6.02 (nd, 1H, naphthalene proton) 6.30 (t, 1H, phenyl proton) 7.00 (d, 1H, naphthalene proton) 7.25 (d, 1H, phenyl proton) 7.40 (m, 1H, phenyl proton) 7.62 (m, 1H, naphthalene proton) 8.02 (d, 1H, naphthalene proton) 8.20 (dd, 1H, naphthalene proton) 8.54 (d, 1H, naphthalene proton) 9.20 (s, 1H bonded off) 13.46(s, 1H, N-H)	CD ₃ OCD ₃
6c	3480 (NHR) 1598 (Aromatic-ring) 1498 (Naphthalene-ring)	1.15 (d, 1H, NHR) 6.40 (d, 1H, naphthalene proton) 6.62 (d, 1H, naphthalene proton) 6.82 (t, 1H, naphthalene proton)	CDCl ₃

7.00 (M, 1H, phenyl proton)
 7.22 (m, 1H, naphthalene proton)
 7.40 (br & m, 1H, naphthalene proton)
 7.54 (m, 1H, naphthalene proton)
 7.85 (br & m, 1H, naphthalene proton)
 8.20 (t, 1H, naphthalene proton)
 8.40 (dd, 1H, naphthalene proton)
 8.86 (d, 1H, naphthalene proton)
 9.22 (q, 1H, naphthalene proton)

Table 2: Coupling components, Yields (%), and melting points



Dye	R	Yield %	MP(°C)	Appearance
3a		68	198 - 200	Yellow-brown
3b		74	178 - 180	Yellow-brown
3c		59	113 - 115	Brown
6a		69	98 - 100	Brown
6b		77	188 - 190	Brown
6c		67	108 - 110	Brown

Table 3: Influence of solvent on the UV – VIS absorption spectra of dyes 3a – c and 6a – c

Dyes	ETOH λ_{\max} (nm)	DMF λ_{\max} (nm)	Chloroform λ_{\max} (nm)	λ_{\max} DMF ($1\text{mol}^{-1}\text{cm}^{-1}$)
3a	490	413,750(s)	385	86,700
3b	470	413,613(s)	392	23,000
3c	490	414,425(s)	450	91,500
6a	439	406,436(s)	392	25,400
6b	415	413	380	17,100
6c	436	420	415,590(s)	31,700

The infrared spectra of dyes 3a, 3c, 6a and 6c showed NH for amine bands at 3395 – 3462 cm^{-1} . This suggests that these dyes are predominantly in the amino azo form as opposed to the imino form which is relatively unstable. On the other hand, the infrared spectra of dyes 3b and 6b showed intense carbonyl bands at 1629 – 1630 cm^{-1} and an N – H band at 3235 – 3250 cm^{-1} . This suggests that these compounds are predominantly in the ketohydrazone tautomer as opposed to the hydroxyazo tautomer in the solid state.

The ^1H NMR spectra of dyes 3b and 6b showed an O – H peak at 9.46 – 9.20 ppm and N – H peak at 13 – 14 ppm. This result suggests that dyes 3b and 6b may be present as a mixture of tautomeric forms.

Effect of Solvent

Generally, in many dye molecules, the ground state is less polar than the excited state so that a polar solvent will tend to stabilize the excited state more than the ground state leading to a bathochromic shift in the absorption maximum, which is termed “positive solvatochromism” $\Delta E_2 < \Delta E_1$ (figure 1). The interaction of a solvent with a dye molecule is greater in polar solvents, for example ethanol, which possess a strong permanent dipole, and is most pronounced with a solute molecule that contains a permanent dipole. As the difference between the polarity of the ground and excited states is increased by the presence of stronger electron-withdrawing group in the diazo component ring of a dye, more marked positive solvatochromism is observed¹⁶.

The visible absorption spectra of the dyes correlated with the polarity of solvent: the absorption of dyes was affected largely by solvent polarity. The

nitrothiazole dye derivatives absorbed at higher wavelengths when compared with the 1-naphthylamine dye analogues. For example, dye 3a – c absorbed at 490, 470 and 400 nm respectively in ethanol, 413, 413 and 425 nm respectively in dimethyl formamide and 385, 392 and 450 nm in chloroform. The absorption spectra of dyes 3a-c of the nitrothiazole derivative and 6a of the 1-naphthylamine analogue showed a shoulder at 750 nm, 613 nm, 425 nm and 436 nm respectively in dimethylformamide. Surprisingly too, dye 6c of the 1-naphthylamine analogue showed a shoulder at 590 nm. These results may suggest a mixture of tautomeric forms in the particular solvents.

CONCLUSIONS

Hetarylazo disperse dyes of 2-amino-5-nitrothiazole derivatives were synthesized and their absorption spectra, and solvent effects were examined.

The 2-amino-5-nitrothiazole dye derivatives developed the colour of orange to pink which is bathochromic compared with 1-naphthylamine analogues. Also, the 2-amino-5-nitrothiazole dyes showed generally better thermal properties than the 1-naphthylamine analogues. In addition, the hetarylazo disperse dyes absorbed maximally at longer wavelengths than the 1-naphthylamine analogues. The synthesized dyes exhibited positive solvatochromism so that the absorption band of the dyes move towards longer wavelengths according to the polarity of solvent. It was also observed that dyes 3a-c of the 2-amino-5-nitrothiazole derivative and 6b of the 1-naphthylamine analogue may exist as a mixture of tautomeric forms. The hetarylazo disperse dyes and their 1-naphthylamine analogues can be applied to polyester and nylon fibres as disperse dyes.

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