Asian Journal of
Materials
Science

Synthesis and Absorption Spectra of Monoazo Dyes derived from 2-Methoxy-5-Nitroaniline

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ABSTRACT

A series of monoazo disperse dyes have been synthesised from 2-methoxy-5-nitroaniline and their spectral properties were investigated. Six monoazo disperse dyes were synthesised by diazotisation of 2-methoxy-5-nitroaniline using sulphuric acid and sodium nitrite and coupling with 1-hydroxynaphthalene, 2-hydroxynaphthalene, N-phenylnaphthylamine, 1,3-diaminobenzene, 1,3-dihydroxybenzene and 3-aminophenol. The results of the study show that the dyes have the potential to act as disperse dyes for application to polyester and nylon fibres. The dyes were characterized by spectral methods. The solvatochromic behaviour of these monoazo disperse dyes in various solvents was evaluated.

Key words: Azo dyes, diazotisation, synthesis, solvent, effect, visible spectroscopy

INTRODUCTION

Azo dyes are by far the largest group of disperse dyes and constitute about 60-70% of all commercial dyes in both number and amount produced. They are characterized by the typical nitrogen to nitrogen (-N = N-) bonds; which is the most common chromophore of azo dyes. They are fairly cheap, easy to apply and have a wide range of colours for both synthetic and natural fibres. The azo group is attached to two radicals (organic residues) of which at least one but, more usually, both are aromatic (carboxylic or heterocyclic). They exist in the trans form with a bond angle of ca. 120° and the nitrogen atoms are Sp^2 hybridized (Venkataranman, 1970; Abrahart, 1977; Otutu, 2008). The range of shades that could be obtained from azo dyes includes yellows, reds, oranges, violets, navy blues and blacks but green shades are limited. The depth of shades is usually influenced by the number of azo groups contained in the dye structure. Thus, the more the number of azo groups in the dye structure, the greater the depth of shade but the duller the brightness (Waring and Hallas, 1990; Otutu *et al.*, 2008; Venkataranman, 1970).

The 2-Methoxy-5-nitroaniline is an aromatic base and could be a useful source of diazonium ions for dye synthesis. This intermediate has been used in the preparation of some organic compounds such as (2-Methoxy-5-nitrophenyl) piperidin-2-ylme thylamine by heating under reflux a mixture of 2-bromomethyl piperidine hydrobromide and 2-methoxy-5-nitroaniline for 17 h.

Another compound that has been prepared from 2-methoxy-5-nitroaniline is 2-[(2-Methoxy-5-nitrophenyl amino) methylpiperidin-1-y1] acetic acid ethyl ester. This was done by heating a mixture of 2-methoxy-5-nitrophenyl piperidin-2-yl-methylamine, ethyl bromoacetate and triethylamine in dry ethanol under reflux for 4 h (El-Kholy *et al.*, 1998). Hence, in this present

study, we report the synthesis and spectral properties of some monoazo disperse dyes of general structure I derived from 2-Methoxy-5-nitroaniline. Also the solvatochromic behaviour of the dyes in various solvents was evaluated (R is given Table 2).
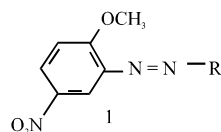
MATERIALS AND METHODS

Materials: The 2-Methoxy-5-nitroaniline, 1-hydroxynaphthalene, 2-hydroxynaphthalene, N-phenylnaphthylamine, 1,3-diaminobenzene, 1,3-dihydroxybenzene and 3-aminophenol were purchased from Aldrich chemical company and Fluka 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 ('H NMR) spectra were obtained with a mercury-200BB spectrometer equipped with an Oxford wide bore magnet, sun 3/160 MHz based computer with an array processor and GE Omega 6.0 software for solutions in a deuterated chloroform as solvent. The chemical shifts were reported in ppm using tetramethylsilane (TMS) as the internal reference.

Melting points were determined using the Thumbnail melting point instrument. Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet Averser 330 series spectrophotometer. The UV-visible spectra were recorded in 1 cm quartz cells on a Genesys 10s VL 200 series spectrophotometer. Dye purity was assessed by Thin Layer Chromatography (TLC) using Whatman 250 m silica gel 60AMK 6F plates as the stationary phase and ether/acetone (5:1 by volume) mixture as developing solvent. Characterisation data are shown in Table 1 and 2.

Method 1: Synthesis of 2-methoxy-5-nitrophenyl azo-4-hydroxynaphthalene: The 2-Methoxy-5-nitroaniline (4 g, 0.024 mole) was diazotized in 6 mL of concentrated sulphuric acid and 50 mL of water by adding 10 mL of sodium nitrite solution (0.02 mole) dropwise at a temperature of 0-5°C. After 30 min the diazotisation was complete which was verified by using a solution of 4-(N, N-dimethylamino) benzaldehyde which generates colour if undiazotized aromatic amine is still present. The excess nitrous acid was destroyed by adding (0.15 g, 0.003 mole) urea solution.

The prepared diazonium salt solution was added slowly with vigorous stirring to 1-hydroxynaphthalene (3.7 g, 0.03 mole) dissolved in 60 mL of 2 M sodium hydroxide for 5 min. The reaction mixture was further stirred for 1.5 h and the precipitated product was filtered off, washed with water and dried. The crude product was then recrystallized from ethanol-methanol mixture to give 2-methoxy-5-nitrophenylazo-4-hydroxynaphthalene (78% yield). R_f (ether/acetone 5:1) = 0.85. This procedure was also used to synthesise dyes 2b, 2e and 2f.

Method 2: Synthesis of 2-methoxy-5-nitrophenylazo-4-(N-phenylnaphthylamine): The 2-Methoxy-5-nitroaniline (4 g, 0.24 mole) was mixed with 40 mL water and 5 mL of concentrated sulphuric acid. (98%) was added and stirred. The mixture was cooled to 0-5°C. Sodium nitrite
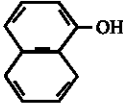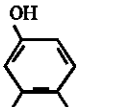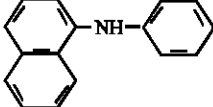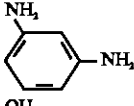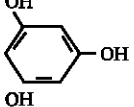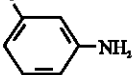
Table 1: FTIR and 'H NMR data of dyes 2a-f

Dye	IR KBr (cm^{-1})	'HNMR, δ(ppm)	Solvent
2a	3448 (OH); 1640 (C = O); 1536 and 1340 (symmetric and antisymmetric NO$_2$ stretch); 761 (Ar-ring)	4.02 (s, 3H, OCH$_3$)	CDCl$_3$
		6.89 (q, IH, naphthalene proton)	
		7.00(d, IH naphthalene proton)	
		7.20(s, IH naphthalene proton)	
		7.30 (m, IH naphthalene proton)	
		7.40 (d, IH naphthalene proton)	
		7.65 (m, IH phenyl proton)	
		7.89 (dd, IH, naphthalene proton)	
		8.00 (dd, IH, phenyl proton)	
		8.20 (d, IH, phenyl proton)	
		9.25 (s, IH, NH)	
2b	3459 (OH); 1623 (C = O); 1523 and 1337; (symmetric and antisymmetric NO$_2$ Stretch); 757 (Ar-ring)	4.02 (s, 3H, OCH$_3$)	CDCl$_3$
		6.42 (d, IH, naphthalene proton)	
		7.02 (t, IH, naphthalene proton)	
		7.25 (s, IH, phenyl proton)	
		7.52 (m, IH, naphthalene proton)	
		7.60 (m, IH, naphthalene proton)	
		7.80 (d, IH, naphthalene proton)	
		8.20 (d, IH, naphthalene proton)	
		8.45 (phenyl proton)	
		8.60 (phenyl proton)	
		9.20 (s, IH, NH)	
2c	3418 (NH$_2$); 1507 and 1333; (symmetric and antisymmetric NO$_2$ stretch); 795 (Ar-ring)	1.8 (t, IH, NHR)	CDCl$_3$
		6.60 (d, IH, phenyl proton)	
		7.00 (dd, IH, phenyl proton)	
		7.35 (d, IH, phenyl proton)	
		7.5 (m, IH, naphthalene proton)	
		7.76 (m, IH, naphthalene proton)	
		7.80 (d, IH, phenyl proton)	
		7.72 (m, IH, naphthalene proton)	
		7.80 (t, IH, phenyl proton)	
		8.02 (s, IH, phenyl proton)	
		8.20 (d, IH, naphthalene proton)	
		8.90 (d, IH, phenyl proton)	
2d	3260 (NH$_2$); 1535 and 1313; (symmetric and antisymmetric NO$_2$ stretch); 755 (Ar-ring)	1.49-1.90 (S, 2H, NH$_2$)	CDCl$_3$
		4.02 (s, 3H, OCH$_3$)	
		6.60 (d, IH, phenyl proton)	
		7.02 (d, IH, phenyl proton)	
		7.40 (d, IH, phenyl proton)	
		7.52 (m, IH, phenyl proton)	
		7.60 (b and m, IH phenyl proton)	
		8.80 (dd, IH, Phenyl proton)	
2e	3454 (OH); 1519 and 1342 (symmetric and antisymmetric NO$_2$ stretch); 744 (Ar-ring)	4.00 (s, 3H, OCH$_3$)	CDCl$_3$
		6.60 (d, IH, phenyl proton)	
		7.10 (d, IH, phenyl proton)	
		7.20 (d, IH, phenyl proton)	
		7.35 (dd, IH, phenyl proton)	
		7.77 (t, IH, phenyl proton)	

Table 1: Continue

Dye	IR KBr (cm^{-1})	'HNMR, δ(ppm)	Solvent
		8.40 (d, IH, phenyl proton)	
		8.72 (s, IH, bonded OH)	
2f	3448 (OH); 1518 and 1342; (symmetric and	1.60 (d, 2H, NH$_2$)	CDCl$_3$
	antisymmetric NO$_2$ stretch)l; 744 (Ar-ring)	4.02 (s, 3H, OCH$_3$)	
		6.90 (d, IH, phenyl proton)	
		7.00 (d, IH, phenyl proton)	
		7.20 (dd, IH, phenyl proton)	
		7.30 (d, IH, phenyl proton)	
		7.50 (m, IH, phenyl proton)	
		8.72 (dd, IH, phenyl proton)	
		9.20 (S, IH, bonded OH)	

Table 2: Yield and melting point of the synthesised dyes 2a-f

Dye	R	Yield (%)	Melting point (°C)	R$_f$	Appearance
2a	naphthalen-OH	78	233-235	0.85	Brown
2b	OH-naphthalene	64	253-255	0.50	Brown
2c	naphthalen-NH-phenyl	58	183-185	0.75	Brown
2d	NH$_2$, NH$_2$ (phenyl)	97	184-186	0.62	Red
2e	OH, OH (phenyl)	98	>280	0.54	Brown
2f	OH, NH$_2$ (phenyl)	96	278-280	0.26	Brown

(3.7 g, 0.03 mole) dissolved in 5 mL of water at a temperature of 0-5°C was added dropwise with stirring to the mixture for 20 min. The resulting diazonium salt solution was added slowly to a solution of N-phenylnaphthylamine (5.2 g, 0.024 mole) with vigorous stirring for 5 min. After further stirring for 2 h, the crude product was collected by filtration, washed with water and dried. Recrystallisation from methanol gave brown solid crystals of dye 2c (4.6 g, 58% yield) R$_f$ (ether/acetone 5:1) = 0.75. This procedure was also used to synthesise dye 2d.

RESULTS AND DISCUSSION

Absorption spectra: The details of the visible absorption spectra of the dyes are summarized in Table 3. The synthesized dyes developed a colour ranging from yellow (λ_{max} 436 nm) to orange (λ_{max} 520 nm) in ethanol.

Table 3: Absorption spectral properties of the synthesised dyes 2a-f

Dye	λ_{max} ETOH (nm)	λ_{max} DMF(nm)	λ_{max} CHCl$_3$ (nm)	$\Delta V_{1/2}$ DMF (cm^{-1})	ϵ_{max} DMF (L mol^{-1} cm^{-1})	f
2a	451	431	460	47000	19000	3.654
2b	490	430, 490 (s)	430, 490(s)	67000	45700	13.314
2c	415, 520 (s)	405, 526 (s)	530	75000	93700	30.456
2d	454	461	439	36000	37900	9.193
2e	436	419, 469 (s)	380	50000	11000	2.376
2f	436	436	392	46000	42900	8.545

s: Shoulder

It is well known that λ_{max} values tend to be related to the strength of the electronic power in the benzenoid system (Karci, 2005). Since, the electronic transition in these compounds involves a general migration of electron density from the donor group towards the azo group, the greatest effect in terms of longer wavelength is achieved by placing the substituent in the positions ortho or para to the azo group for effective conjugation (Griffiths, 1976; Shirai *et al.*, 1998).

Off all the dyes, dye 2c gave the highest λ_{max} value in all the solvents. This result can be attributed to the longer wavelength effect exerted by the N-phenyl group and the naphthalene moiety which has an electron donating property. Half-band widths of the absorption band in DMF were determined (Table 3).
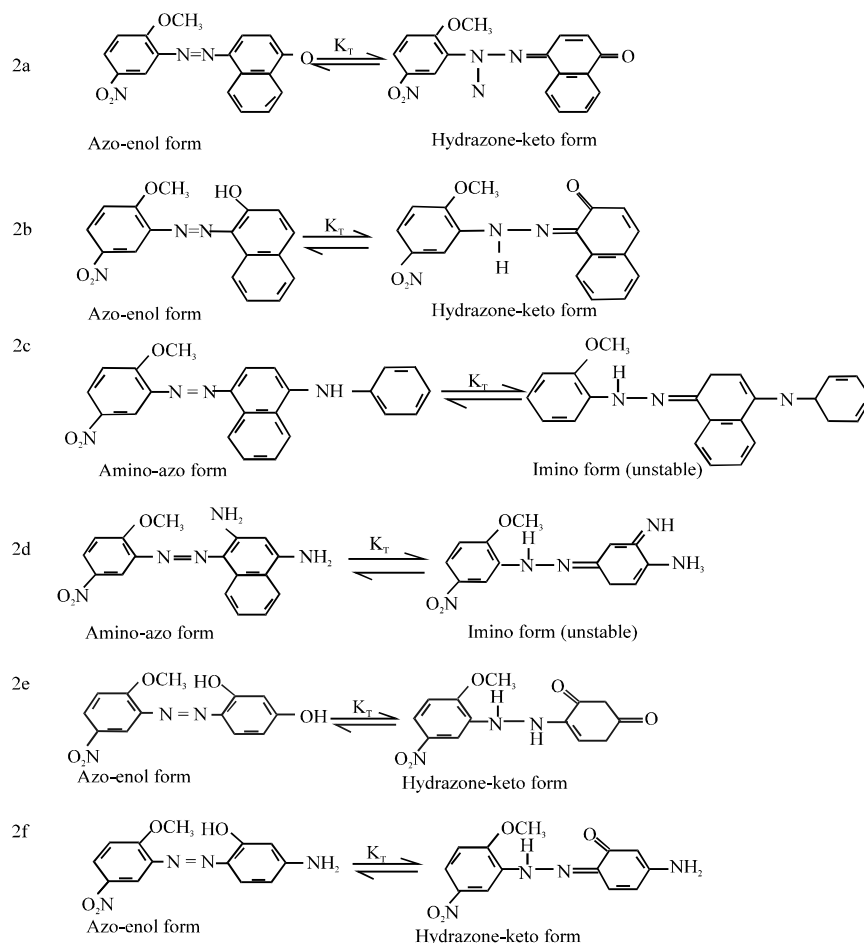
In addition to the effect on λ_{max}, substituents also cause a change in the half-band width values ($\Delta v_{1/2}$). The value of $\Delta v_{1/2}$ is a convenient criterion for the evaluation of the hue brightness of dyes; dyes with low values of $\Delta v_{1/2}$ show bright hues while those with high values of $\Delta v_{1/2}$ show dull hues. Thus, dyes 2a, 2e and 2f showed brighter hues compared to the others. Dye 2f gave the narrowest half-band width and the brightest hue in solvent while dye 2c with half-band width of 75000 cm^{-1} gave the dullest hue in solvent.

In the case of tinctorial strength, from the molar extinction coefficient (ϵ_{max}), the dyes 2b and 2c seem to be more intensely absorbing than dyes 2a, 2d, 2e and 2f. However, it is the oscillator strength (f), rather than ϵ_{max}, that gives a true measure of tinctorial strength since it expresses the area under the absorption curve (Eq. 1). Thus, the dye with a high value but narrow absorption curve (i.e., low $\Delta v_{1/2}$) could be tinctorially weaker than the dye which, although it has a lower ϵ_{max} value, has a broader absorption curve (Gordon and Gregory, 1987).

$$f = 4.32 \times 10^{-9} \times \Delta v_{1/2} \times \epsilon_{max} \tag{1}$$

Indeed, as shown in Table 2, dye 2f with high molar extinction coefficient but narrow absorption curve (i.e., low $\Delta v_{1/2}$) is tinctorially weaker than dye 2d which although has lower molar extinction coefficient, has broader absorption curve.

Keto-enol tautomerism: Keto-enol tautomerism is not only of utmost importance to the dyestuff manufacturer but is also important in other areas of Chemistry. Keto-enol tautomers not only have different colours, they also have different tinctorial strengths (and hence economics) and different properties e.g., light fastness (Karci, 2005). Azo dyes 2a-b and 2e-f can exist as a mixture of several tautomeric forms as shown in scheme 1.

2a

Azo-enol form   Hydrazone-keto form

2b

Azo-enol form   Hydrazone-keto form

2c

Amino-azo form   Imino form (unstable)

2d

Amino-azo form   Imino form (unstable)

2e

Azo-enol form   Hydrazone-keto form

2f

Azo-enol form   Hydrazone-keto form

Scheme 1

The infrared spectra of dyes 2e and 2f showed a broad hydroxyl band at 3441-3459 cm^{-1} and C-O band at 1072-1113 cm^{-1}. This suggests that these compounds are predominantly in the azo-enol form as opposed to the hydrazone-keto-form (ketohydrazone form). On the other hand, the infrared spectra of dyes 2c and 2d showed intense NH$_2$ bands at 3418-3260 cm^{-1}. This suggests that these compounds are predominantly in the amino-azo form, since the amino-azo colorants show no evidence of tautomeric behavior (Hallas and Renfrew, 1996). This is true because the imino grouping as shown by the equilibrium equations of 2c and 2d is very unstable. The infrared spectra of dyes 2a and 2b showed intense carbonyl bands at 1620-1680 cm^{-1}. This suggests that these compounds exist exclusively in the hydrazone-keto form as opposed to the azo-enol form, in the solid state (Hallas and Towns, 1997).

'H NMR spectra of dyes 2e and 2f showed no O-H peak at 12.72-13.50 ppm and no N-H peak at 16.00-16.55 ppm. This suggests that these compounds exist predominantly as a single tautomeric form in deuterated chloroform. However, the 'H NMR spectra of dyes 2a and 2b showed an O-H peak at 8.55-9.00 and an N-H peak at 9.20-9.40 ppm. This result suggests that dyes 2a and 2b were present as a mixture of tautomeric forms in deuterated chloroform.

Effect of solvent: The visible absorption spectra of the dyes did not correlate with the polarity of solvent. Each of the dyes gave a single dominant absorption peak without a shoulder in all the

solvents employed with the exception of dyes 2b (in N, N-methylformamide (DMF) and chloroform (CHCl$_3$), 2c (in ethanol (ETOH) and DMF) and 2e (in DMF). The reason for this is probably that dyes 2a, 2d and 2f were present predominantly in a single tautomeric form in each of the solvents. As dyes 2b, 2c and 2e gave a maximum absorption peak with a shoulder in DMF, CHCl$_3$ and ETOH, it suggests that these dyes were present in more than one tautomeric form.

It was observed that although in ETOH, chloroform and N; N-dimethylformamide, the absorption spectra did not change at all for dye 2b. The λ_{max} of dye 2e and 2f shifted hypsochromically in chloroform. For example, for dye 2e, λ_{max} was 380 nm in chloroform, 430 nm in ethanol and 469 nm in N, N-dimethylformamide. On the other hand, it was also observed that λ_{max} values of dye 2c were shifted bathochromically with respect to the λ_{max} in ethanol, N, N-dimethylformamide and chloroform, respectively. Whereas, the λ_{max} value of dye 2a shifted hypsochromically in N, N-dimethylformamide. For example, for dye 2c, λ_{max} was 520 nm in ethanol, 526 nm in N,N-dimethylformamide and 530 nm in chloroform.

CONCLUSIONS

A series of monoazo disperse dyes were prepared from 2-methoxy-5-nitroaniline by diazotization and coupling reactions between it and aryloxy and arylamine couplers and their absorption spectra were investigated.

The dyes developed the colour of yellow to orange. Also the half-band width of the dyes were evaluated and it was found that dye 2a, 2e and 2f showed narrower, half-band widths than dyes 2b, 2c and 2d and hence the former have brighter hues than the later. However, dye 2f with narrow absorption curve was tinctorially weaker than dye 2d which although has lower molar extinction coefficient, has broader absorption curve. The solvent influence on the wavelength of maximum absorption spectra was studied. It was observed that the absorption spectra of dye 2b showed the same λ_{max} in all the solvents and dyes 2a, 2c, 2d, 2e and 2f did not show any correlation with the polarity of the solvents. It was also observed that dyes 2a and 2b may exist as a mixture of tautomeric forms. Dyes 2a-f can be applied to polyester and/or polyamide fibres as disperse dyes.

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