SYNTHESIS AND ABSORPTION CHARACTERISTICS OF SOME DISAZO DYES DERIVED FROM 4-AMINO-3-NITROTOLUENE AND 4-AMINOBENZOIC ACID

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ABSTRACT

The synthesis of a series of 4-amino-3-nitrotoluene dye derivatives has been carried out. Diazotization and coupling with 4-aminobenzoic acid gave an intermediate diazo component. Coupling reactions of the diazotized diazo component with 2-methylphenol, 4-hydroxybenzoic acid, chromatropic acid, 4-aminophenol and 4-chloroaniline gave various disazo dyes. The results of the half-band widths showed that although they are disazo dyes they can compete favourably with most monoazo and anthraquinone dyes in terms of hue brightness. The solvatochromism of the dyes was evaluated with respect to spectroscopic properties in various solvents. The dyes were characterized by elemental analysis and spectral methods.

Keywords: Disazo dyes, absorption Characteristics, Tautomerism, Solvatochromic effect.

INTRODUCTION

The use of carbocyclic compounds to prepare disazo dyes for colouring textile and non-textile materials is important due to their increased wash fastness and substantivity (Shuttleworth and Weaver, 1990; James *et al*., 1982). Many non-ionic organic azo pigments such as C.I. (Colour Index) Pigment Yellow 1, Pigment Orange 6 and Pigment red 3 have been prepared from the carbocyclic compound; 4-amino-3-nitrotoluene (Allen, 1971). They are used largely in paints and printing inks. Our research has recently reported some aspects of the preparation and application of certain novel azo disperse dyes involving the use of this intermediate (Otutu, 2008). Dyeing with such disazo disperse dyes of this type gave very good light fastness property on poly (ethylene) terephthalate, using the thermosol process. Also, the disazo dyes containing the 2-aminophenyl group showed excellent levels of fastness (wash and sublimation) on poly (ethylene) terephthalate and nylon fibres. Here we report the synthesis of a new series of disazo dyes from 4-amino-3-nitrotoluene and 4-aminobenzoic acid. We also describe the solvatochromic behaviour of these dyes in various solvents.

MATERIALS AND METHODS

Materials

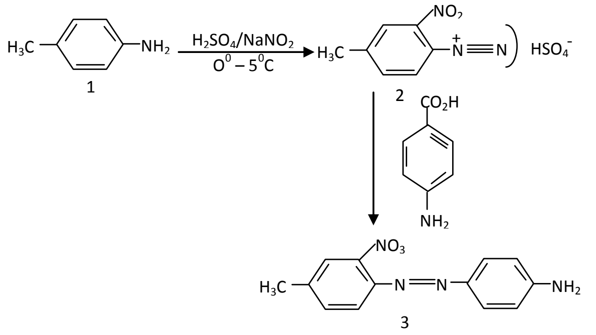
4-Amino-3-nitrotoluene, 4-aminobenzoic acid, 2-methylphenol, 4-hydroxybenzoic acid, chromatropic acid, 4-aminophenol and 4-chloroaniline were obtained from BDH Chemical Company and Aldrich Chemical Company and used without further purification.

Methods

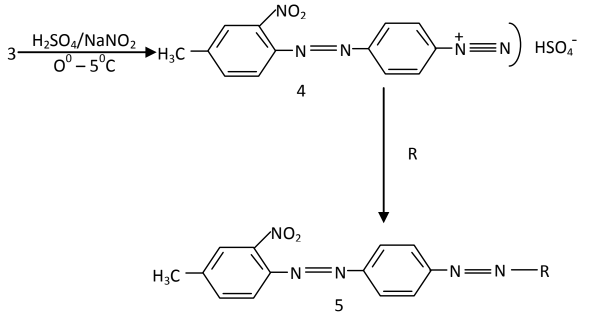
Synthesis of diazo component 3 (Scheme 1)

A finely ground powder of the 0.05mole (8.0 g) 4-amino-3-nitrotoluene was mixed with 50 ml of water and cooled to 0 - 5^0C and diazotized with 5.0 g, 0.0725 mole of $NaNO_2$ at 0^0C in concentrated sulphuric acid (10 ml). The 4-aminobenzoic acid (0.05 mole 7.5 g) which was dissolved in 60 ml acetic acid was coupled with the diazonium salt solution at pH values 4 – 5. The mixture was stirred for a further 2 hours and left to stand overnight at 40^0C in an incubator. The crude product was collected by filtration, washed with water several times and dried. The purity of the dyes was determined by Thin Layer Chromatgraphy (TLC). The yield of the reaction was 75% after the recrystallization of the crude product from carbontetrachloride.

Scheme 1



Scheme 2



Synthesis of dye 5a

2-Nitro-4-methylphenylazo-4^1-aminobenzene was suspended in 45 ml of water and diazotized with (0.04 mole, 3.0 g) of sodium nitrite (in 10 ml water) at 0 - 5^0C in 6 ml concentrated sulphuric acid. Excess of nitrous acid was destroyed using (0.003 mol, 0.15 g) urea solution. The coupling component, 2-methylphenol (3 ml) which was dissolved in 2 molar sodium hydroxide (60 ml) was cooled to 0 – 5^0C.

The diazo solution prepared above was slowly added into the coupler solution with stirring for 10 min. After 2 hours of further stirring, the precipitated product was collected by filtration, washed with water and dried. Recrystallization from ethanol-methanol mixture gave compound 5a in 51% yield. The purity of the dye was assessed by TLC (ether/acetone 5:1 by volume). This procedure was also used to prepare dye 5b, 5c and 5d.

Synthesis of dye 5e

A finely ground powder of 2-nitro-4-methylphenylazo-4^1-aminobenzene (0.006 mole 1.50 g) was mixed with 50 ml of water, cooled to 0 - 5^0C and diazotized with (0.0536 mole 3.7 g) of $NaNO_2$ at 0^0C in concentrated sulphuric acid (6 ml). The 0.04 mole, (0.5 g) 4-chloroaniline which was dissolved in (20 ml) acetic acid was coupled with the diazonium salt above at pH values 4 – 5. After stirring for 2 hours, the crude product was collected by filtration, washed with water and dried. Recrystallization from hot ethanol-methanol mixture gave compound 5e in 50% yield. Dye purity was determined by TLC (ether/acetone 5:1 by volume).

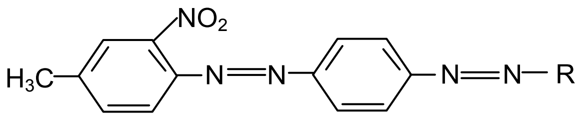
Chemical and Instrumental Analysis

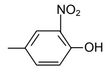
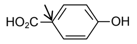
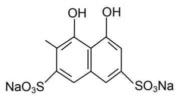
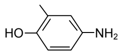
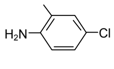
Melting points were determined without correction using the Thumbnail melting point apparatus. The 'H NMR spectra were taken with a mercury – 200BB (200 MHz) spectrometers using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are expressed as δ units (ppm). Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet Averser 330 series spectrophotometer. The UV-visible spectra were recorded in 1cm quartz cells on a Genesys 10S VL 200 series spectrophotometer. Elemental analysis was determined using Perkin Elmer 2400 series for CHN. Dye purity was assessed by Thin Layer Chromatography (TLC) using Whatman 250m silica gel 60AMK 6F plates as the stationary phase and ether/acetone (5:1 by volume) mixture as developing solvent. The characterization data are shown in Tables 1 and 2.

Table 1: FTIR and 'H NMR data of dyes 5a-e

	FTIR (KBr, v cm^{-1})	'HNMR, δ(ppm)	Solvent
5a	3497(OH) 2730(Aromatic C-H) 1570 (Ar-ring) 1524 & 1349 (NO_2) 1275 (C – O)	3.65 (S, 3H, $0CH_3$) 3.87 (Septet, 3H, CH_3) 6.20(d, IH phenyl proton) 6.65(S, IH phenyl proton) 7.30 (m, IH phenyl proton) 7.40 (d, IH phenyl proton) 8.02 (d, 4H phenyl proton) 8.20 (dd, IH, phenyl proton) 9.6 (S, IH, phenyl proton) 9.66 (d, 1H, bonded OH) 10.50 (S, 1H bonded OH NH)	$CDCl_3$
5b	3434 (OH) 2645 (Aromatic C-H) 1641 (C = O) 1502 (Ar-ring) 1564 & 1347 (NO_2) 1248 (C – O)	3.92 (S, 3H, OCH_3) 7.80 (m, IH, phenyl proton) 8.10 (dd, 1H, phenyl proton) 8.22 (d, 4H, phenyl proton) 8.46 (d, 1H, phenyl proton) 8.65 (d, 1H, phenyl proton) 9.63(S, 1H, OH)	$CDCl_3$
5c	3456 (OH) 2767 (Aromatic C – H) 1749 (C = O) 1595 (Ar-ring) 1524 & 1377 (NO_2) 1469 (naphthalene ring) 1232 (C – O)	3.96 (Septet, 3H, CH_3) 6.4 (d, 1H, naphthalene proton) 7.22 (m, 2H, naphthalene proton) 7.40 (m, 1H, phenyl proton) 7.40 (m, 1H, phenyl proton) 8.02 (d, 4H, phenyl proton) 8.40 (d, 1H, phenyl proton) 9.62 (s, 1H, bonded OH) 10.65 (s, 1H, NH)	$CDCl_3$
5d	3415 – 3204 (OH, NH) 2724 (Aromatic C - H) 1689 (C = O) 1568 (Ar-ring) 1514 & 1349 (NO_2) 1275 (C – O)	1.75 (q, 2H, NH_2) 3.79 (Septet, 3H, CH_3) 6.82 (d, 1H, phenyl proton) 7.02 (d, 1H, phenyl proton) 7.20 (m, 1H, phenyl proton) 7.46 (m, 1H, phenyl proton) 7.87 (m, 4H, phenyl proton) 9.26 (s, 1H, phenyl proton) 9.60 (s, 1H, bonded OH)	$CDCl_3$
5e	3424 (NH) 2724 (Aromatic C-H) 1552 (Aromatic < ring) 1524 & 1306 (NO_2)	1.85 (q, 2H, NH_2) 3.68 (Septet, 3H, CH_3) 6.02 (d, 1H, phenyl proton) 7.42 (d, 1H, phenyl proton) 7.62 9m, 1H, phenyl proton) 7.72 (m, 1H, phenyl proton) 8.00 (dd, 1H, phenyl proton) 8.20 (m, 4H, phenyl proton) 10.66 (s, 1H, NH)	$CDCl_3$

Table 2: Yields, melting points and Elemental analysis of dyes 5a-e



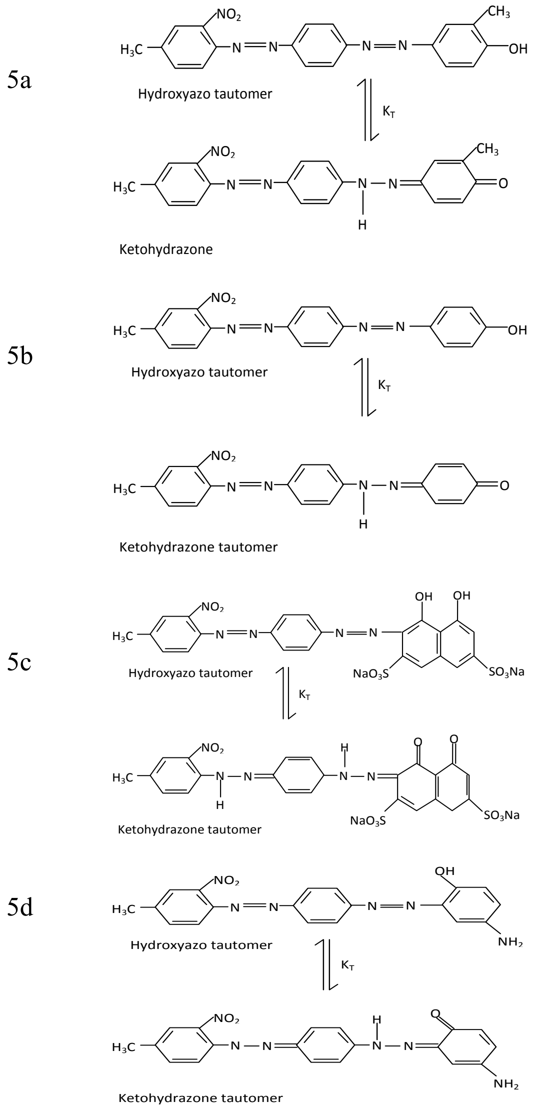
Dye	R	Yield (%)	M.P(^{0}C)	Elemental analysis (%)			
				C	H	N	
5a		51	228 – 230	63.99	4.56	18.66	Calcd
				63.97	4.55	18.65	found
5b		60	168 – 170	63.15	4.18	19.38	Calcd
				63.11	4.17	19.35	found
5c		54	183 – 185	43.74	2.39	11.09	Calcd
				43.71	2.34	11.06	found
5d		56	182 – 184	60.63	4.28	22.33	Calcd
				60.61	4.23	22.30	found
5e		50	193 – 195	57.80	3.83	21.29	Calcd
				57.76	379	21.24	found

RESULTS AND DISCUSSION

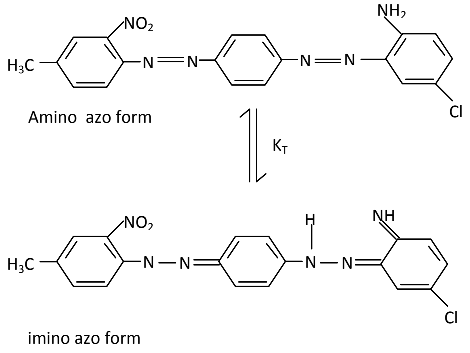
Azo-hydrazone tautomers

The existence of hydroxyazo-keto hydrazone tautomerism is not only of utmost importance to the dyestuff manufacturer but is also important in other areas of Chemistry (Karci, 2005; Koh *et al.,* 2004; Hallas and Renfrew, 1996). The hydroxyazo-ketohydrazone tautomers not only have different colours, they also have different tinctorial strengths (and hence economics) and different properties (Ortega-Luoni *et al*., 2007).

In addition, it has been found that, compared with the hydroxyazo tautomer, the corresponding ketohydrazone tautomer is usually more bathochromic and of higher tinctorial strength. 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 (Zollinger, 2003; Samieh *et al*., 2008; Zeynel, 2009). In general, however, either the hydroxyazo tautomer or the corresponding tautomer or the corresponding ketohydrazone formed is dominant for a particular structure. Azo dyes 5a – e can exist as a mixture of several tautomeric forms as shown in scheme 3



5e



Scheme 3

The infrared spectra of dyes 5a – d showed a broad hydroxyl band at 3467 – 3522 cm^{-1} and a C-O band at 1272 – 1275 cm^{-1}. This suggests that these compounds are predominantly in the hydroxyazo form, as opposed to the hydrazone-keto form in the solid state.

On the other hand, the infrared spectra of dyes 5c and 5d showed intense carboxyl bands at 1680 – 1740 cm^{-1} and an N-H band at 3252 – 3360 cm^{-1}. This suggests that these compounds are predominantly in the keto hydrazone form, as opposed to the hydroxyazo form in the solid state. The infrared spectrum of dye 5e showed intense N-H band at 3424 cm^{-1}. This suggests that this compound is predominantly in the aminoazo form. This supports the fact that amino azo colorants have been found to show no evidence of tautomeric behaviour (Otutu *et al*., 2011; Clark and Hester, 1991).

The 'H NMR spectra of dyes 5a – d showed OH peak at 9.62 – 9.66ppm and an N-H peak at 10.00 – 10.65ppm. These results suggest that dyes 5a – d were present as a mixture of tautomeric forms in $CDCl_3$. On the other hand, 'H NMR spectrum of dye 5e did not show any N – H peak at 13.00 – 14.00 ppm. This result suggests that the single tautomeric form predominates in $CDCl_3$.

Effect of Solvent

The visible absorption spectra of the dyes did not show any correlation with the polarity of solvent. The dyes gave a single dominant absorption peak without a shoulder in all the solvents used, except dye 5a – d in N, N-dimethyl formamide (DMF). The reason for this is probably that dyes 5a – e were present predominantly in a single tautomeric form in ethanol (ETOH) and chloroform ($CHCl_3$). As dyes 5a – d gave maximum absorption peak with a shoulder in DMF, it suggests that these dyes were present in more than one tautomeric form.

It was observed that although, in chloroform and N,N-dimethylformamide the absorption spectra did not change significantly, λ_{max} of dyes 5a – e shifted hypsochromically in ethanol. On the other hand, it was observed generally, that λ_{max} values of the dyes shifted bathochromically with respect to the λ_{max} in chloroform and N, N-di methylformamide.

Table 3: Influence of solvent on UV-visible absorption spectra of dyes 5a–e

Dye	ETOH	$CHCl_3$	DMF	$\Delta v_{½}$ DMF (cm^{-1})	ε_{max} DMF (1 mol^{-1}cm^{-1})	F
5a	433	442	440, 580(s)	87000	21900	8.231
5b	427	442	438, 580(s)	68000	31600	9.282
5c	438	443	448 , 580(s)	81000	93000	32.543
5d	436	445	446, 580(s)	68000	30600	8.989
5e	430	436	440	74000	34700	11.093

S = Shoulder
Oscillator strength (f), = 4.32 x 10^{-9} x $\Delta v_{½}$ x ε_{max}

Half-band widths

The half-band widths of the absorption bands in DMF were determined and the results are shown in Table 3. The value of half-band widths, $\Delta V_{½}$ is a very important criterion for the determination of the hue brightness of dyes; thus, dyes with low values of $\Delta v_{½}$ exhibit bright hues while those with high values of $\Delta v_{½}$ show dull hues. From the results of the $\Delta v_{½}$, dyes 5b, 5d and 5e respectively showed narrower half-band widths than dyes 5a and 5c, which means that the former dyes in solvent are brighter than the latter analogues in solvent. However, the correlation between half -band width and brightness of disperse dyes on polyester is another matter.

From the molar extinction coefficient (ε_{max}) data, dyes 5a and 5c seem to be more intensely absorbing than 5b, 5d and 5e. However, the true measure of tinctorial strength of dyes is obtained from the oscillator strength (f), rather than ε_{max}. Since it expresses the area under the absorption curve (Eqn 1). This means that the dye with a high value but narrow absorption curve (i.e. low $\Delta v_{½}$) could be tinctorially weaker than the dye which although has a lower ε_{max} value, has a broader absorption curve (Karci, 2005).

$f = 4.32 \times 10^{-9} \times \Delta v_{½} \times \varepsilon_{max}$ … (1)

Thus, from Table 3, dye 5c gave high molar extinction coefficient but narrow absorption curve: Low $\Delta v_{½}$, and so it is tinctorially weaker than dyes 5a, 5b, 5d and 5e. These dyes, although have lower molar extinction coefficients, they have broader absorption curves and hence are tinctorially stronger when compared with dye 5c.

CONCLUSION

A series of disazo dyes were synthesized from 2-methylphenol, 4-hydroxbenzoic acid, chromatropic acid, 4-aminophenol and 4-chloroaniline, as the coupling components, and 4-amino-3-nitrotoluene and 4-amino benzoic acid as the carbocylic diazo components. The solvent influence on the wavelength of maximum absorption was studied. It was observed that the absorption spectra of dyes 5a – e generally showed a maximum peak at longer wavelength in N,N-dimethylformamide and chloroform.

When compared with the absorption spectra of the dyes in ethanol, it was also observed that dyes 5a – d may exist as a mixture of tautomeric forms, in N,N-dimethylformamide. Dyes 5a, 5b, 5d and 5e can be applied to polyester and/or polyamide fibres as disperse dyes while dye 5c can only be applied to polyamide fibres due to the presence of acidic group.

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