



Synthesis and Dyeing properties of Phenyl Azo Moieties of 1,2-dihydroxyanthraquinone

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Abstract

The synthesis of a series of phenyl azo moieties based on the coupler 1,2-dihydroxyanthraquinone (a hitherto anthraquinoid dye) is reported in this paper. Preliminary characterization of the resultant compounds was achieved by means of melting point, thin layer chromatography (TLC), solubility test, ultraviolet visible (UV-VIS) and Infrared (IR) spectroscopy. The dyeing performance of these coloured compounds with both azo as well as anthraquinoid chromophores was also investigated. Hydrophilic fibers (cotton) as well as hydrophobic fibers (nylon and polyester) were employed as test fabrics. Well defined melting points and R_f values reported for these coloured compounds ranged between 267°C - 302°C and 0.59 - 0.75 respectively. Data from UV-VIS ranged between 334 - 348 nm and 460 - 480 nm. The evidence of successful azo coupling as presented in the infrared spectral data range between 1576 - 1582 cm^{-1} . The hues produced on cotton were less bright with wash fastness values of 1 - 2, while brighter shades on polyester and nylon were recorded with washfastness values of 2 - 3% E (exhaustion). % F (fixation) of synthesized dyes on test fabrics gave ranges between 51 - 65, 55 - 70, 65 - 82 and 42 - 50, 40 - 60, 45 - 65 respectively.

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Introduction

Azo compounds, a highly coloured class of synthetic organic compounds have been in use as dyes and pigments for a long time (David and Geoffrey, 1994; Akaranta and Efanga, 1997; Maradiya and Vithal, 2001; Kazaura and Abba, 2002; Karci and Karci, 2008; Kirkan and Gup, 2008; Otutu *et al*, 2008). The renewed spotlight on these compounds is attributed to the need for new members of this class with excellent thermal and optical properties in applications such as toner, inkjet printing (Gregory *et al*, 1990) and oil soluble lightfast dyes (Kandil, 1998). Disperse dyes which encompass azo dyes that are sparingly soluble in water and thus mainly used for dyeing synthetic hydrophobic fibers are clearly the dominant group within the azo dyes used worldwide (Kirk - Othmer, 1992). Before the 1950's almost all the disperse dyes in use were prepared from anthraquinone class and had the limitations of poor dischargeability and sensitivity to oxides of nitrogen (Soliman and El-Shababy, 1994). Additionally, anthraquinone dyes are generally not as cost effective as its azo counterparts owing to their relatively weak tinctorial strength (Vankar, 2000). Recently azo compounds comprised of the basic combinatorial building blocks required for the synthesis of a unique class of disperse dyes that incorporate both azo and anthraquinone chromophores have attracted increasing attention (Hitoshi *et al*, 2003). This is basically due to a need to develop a set of disperse dyes with enhanced compatibility for the versatile textile industry.

Relatively, little research work has been published regarding this class of disperse azo dyes that utilize a coupler with the anthraquinone chromophore. This paper comprises the synthesis of disperse dyes from the coupling component 1,2-dihydroxyanthraquinone, a hitherto anthraquinone mordant dye using various substituted and unsubstituted aromatic amines and their application on polyester and nylon as disperse dyes. In addition to the preliminary characterisation of these dyes, the evaluation of some technical properties was performed.

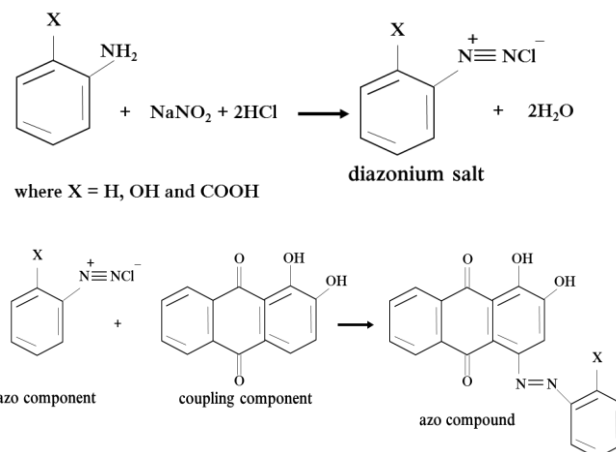
Materials and methods

All the chemicals used in dye synthesis were of analytical grade. Melting points were determined by the open capillary method. The visible spectra were recorded using Pye - Unicam Model Sp500 spectrophotometer. Samples prepared as KBr pellets, were subjected to IR analysis with the spectra recorded in the range 4000 to 400 cm^{-1} using Buck Scientific Spectrophotometer (Model 500). Crude products were purified by

crystallization and characterized by Thin Layer Chromatography (TLC), which was carried out using 1 mm thickness aluminum plates of dimension 20 x 5 cm. The stationary phase was a suspension of silica gel.

Synthesis of phenyl azo moieties of 1,2-dihydroxyanthraquinone using the standard methods of diazotization and coupling

Two grams of dry sodium nitrite (NaNO_2) was dissolved in 20 ml deionised water and cooled to 0 - 5°C in an ice bath. The resultant solution was added drop wise to an ice cold solution of acidified aniline (2.45 ml). The cold diazonium salt solution obtained was subsequently coupled to a slightly alkaline solution of 1,2-dihydroxyanthraquinone (6.4801 g). The reaction mixture was stirred over a period of 1 hour at a temperature of < 5°C. The coloured crystals obtained were filtered, washed three times with cold distilled water and dried at 40°C. The crude crystals thus obtained were recrystallized from a minimum amount of glacial acetic acid. Its percentage yield was calculated and melting point was determined. The same standard procedure was repeated for the preparation of the designated aromatic amines and 1,2-dihydroxyanthraquinone (Vogel, 1979 and Carey, 2003). Scheme 1 gives the general reaction equations for these syntheses.



Scheme 1: General reaction equations for synthesis of azo dyes (AAD₁-AAD₃)

Developed dyeing method for cotton test fabrics (Akaranta and Efanga, 1997)

One gram piece of cotton test fabrics were initially treated with hot distilled water for 20 minutes to get rid of lingering filters. Each sample was then saturated with alkaline solution of the coupling component (1,2-dihydroxyanthraquinone), squeezed and dried to shun patchy shades. The dry fabrics were then placed in a beaker containing cold aniline diazonium salt thereby permitting the azo coupling to take place in-situ. This process was repeated with diazonium salts synthesized from 2-aminophenol and 2-aminobenzoic acid. Unreacted coupler and surface colours were then washed off using alkaline soap solution. The cotton fabrics were finally spread out to dry at room temperature.

Disperse dyeing method for polyester and nylon

A paste of finely divided powdered dye (10 mg) was prepared with 3 mg of the dispersing agent ("Omo"), and dispersed in 100 ml of hot water and strained. The dye bath was regulated to 95°C and the pH adjusted to 5 with acetic acid. 1 g of test fabric (Polyester and Nylon) was dyed for 1 hour in a liquor ratio of 100:1. The dyed fabrics were washed and rinsed following standard methods (Burkinshaw, 1994), and finally dried at room temperature. Wash fastness properties were assessed according to the ISO CO6/C2S), wash test using soap solution (5 g/l, liquor ratio 50: 1) for 50 min at 60°C.

The alteration observed in shade and discolorations of adjoining fabrics were assessed according to international standards (ISO, 1994).

Determination of percentage exhaustion and fixation of the synthesized dyes

The dyebath exhaustion percentage (%E) and fixation percentage (%F) of the fibers were determined according to the standard procedures described in literature (Maradiya and Vithal, 2001).

Results and Discussion

Diazotization and coupling

Three phenyl azo compounds based on the coupler 1,2-dihydroxyanthraquinone were successfully prepared following the standard synthetic pathway (David and Geoffrey, 1994; Carey, E. A., 2003) for diazotization and subsequent coupling as shown in Scheme 1.

The high yields (73% - 86%) shown in Table 1 are consistent with related studies and depict the satisfactory nature of the synthesis (Maradiya and Vithal, 2001; Patel *et al*, 2013). The recrystallized azo compounds all exhibited well defined melting points characteristic of relatively pure compounds. The melting temperatures recorded in Table 1 indicate that they are rather high melting azo compounds as compared with related studies (Otutu, 2013).

Table 1: Physical properties and percentage yields of Dyes AAD₁, AAD₂ and AAD₃

Azo compounds	Designation	Colour	Melting point °C	R _f value	% yield
4 (phenylazo) 1,2-dihydroxyanthraquinone	AAD ₁	Greenish Yellow	265 - 266	0.59	73
4 (2 hydroxyphenylazo) 1,2-dihydroxyanthraquinone	AAD ₂	Dark Yellow	300 - 301	0.64	84
4 (2-carboxyphenylazo) 1,2-dihydroxyanthraquinone	AAD ₃	Reddish - brown	301 - 302	0.75	86
1,2-dihydroxyanthraquinone	A	Ruby red	290 - 291	0.79	-

Table 2: Electronic spectra data and solubility survey of Dyes AAD₁, AAD₂ and AAD₃

Compound	λ_{max} (nm)	Log ϵ	Solubility
A	430	4.12	+ Ethyl acetate + Dimethyl sulfoxide (DMSO) + Ethanol * Distilled water
AAD ₁	460	3.94	+ Ethyl acetate + Dimethyl sulfoxide (DMSO) - Distilled water + Ethanol
AAD ₂	473	3.92	+ Ethyl acetate + Dimethyl sulfoxide (DMSO) * Distilled water + Ethanol
AAD ₃	480	3.90	+ Ethyl acetate + Dimethyl sulfoxide (DMSO) * Distilled water + Ethanol

Legend: (+) Soluble; (*) Sparingly soluble; (-) Insoluble

Solubility and spectral properties of synthesized azo compounds

The shear sizes of these azo compounds probably account for the insolubility in certain solvents such as water but they are soluble in organic solvents such as ethanol, ethyl acetate and DMSO as shown in Table 2 (Tiedemann and Yang, 1995).

The absorption bands of these azo compounds AAD₁, AAD₂ and AAD₃ are shown in Table 1. Maximum absorption wavelength (λ_{max}) values are proportional to the electronic power of the substituents in the coupled ring. The Molar extinction (Log ϵ) of the compounds range from 4.12 – 3.90, consistent with their high intensity of absorption

As recorded in Table 2, the bathochromic shift observed was due to the enhanced electron donor properties of the coupled ring. This was achieved through the introduction of auxochromes OH and COOH, ortho to the azo group in AAD₂ and AAD₃ respectively. This gave considerable shifts of 13 nm and 20 nm for AAD₂ and AAD₃ respectively.

The lone pair of electrons of the azo group are not the only interacting non-bonding electrons, since the 1,2-dihydroxyanthraquinone part of the molecules contain oxygen such as C=O and C-O as extra sources of lone pairs of electrons. Thus, other $n \rightarrow \pi^*$ transitions are expected to take place from these non-bonding orbitals to different π^* molecular orbitals extending over such large molecules. The bands at 426 - 480nm are assigned as mixed $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions of

the azo compounds (Tiedemann and Yang, 1995; Masoud *et al* 2004).

Infrared Spectra of Dyes AAD₁, AAD₂ and AAD₃

The infrared spectra of azo compounds AAD₁, AAD₂ and AAD₃ as summarized in Table 3 indicates characteristic bands at 3440 – 3359 cm⁻¹ assigned to the stretching vibrations of the O-H. The strong bands observed at 1646 - 1634 cm⁻¹ in all the azo compounds (AAD₁-AAD₃), indicate stretching vibrations of the C=O group. The azo (N=N) group is confirmed at 1582 - 1576 cm⁻¹. Ortho substitution of the benzene ring appears at 767cm⁻¹ and 772cm⁻¹ for AAD₂ and AAD₃ respectively. These observations are all consistent with recent studies (Masoud, 2004 and Otutu, 2013).

Table 3: Infrared spectral data (cm-1) of Dyes AAD₁ - AAD₃ compared to the coupler A (1,2 dihydroxyanthraquinone).

Compound	O-H	N-H	C=O	C-O	N=N	C=C	C-N	C-H	2adjH	4adjH	5adjH
A	3364	-	1643	1292	-	1579	-	3153	832	765	-
AAD1	3440	-	1646	1282	1582	1436	1174	3073	908	790	708
AAD2	3359	-	1634	1279	1576	1448	1174	3126	-	767	-
AAD3	3364	-	1637	1262	1576	1448	1279	3143	-	772	-

Table 4: Shades and wash fastness properties of azo dyes

Dye designation	Fabric	Shades	% Exhaustion	% Fixation	Wash fastness
AAD1	COF	Orange	51	42	1-2
	PEF	Bright-yellow	56	45	1-2
	NYE	Yellow-green	65	50	1-2
AAD2	COF	Dark-yellow	55	40	1-2
	PEF	Greenish-yellow	60	45	1-2
	NYE	Bright-yellow	70	60	2-3
AAD3	COF	Reddish-orange	65	45	1-2
	PEF	Brown	55	48	1-2
	NYF	Reddish-brown	82	65	2-3

Legend on fabrics: (COF) Cotton; (PEF) Polyester; (NYE) Nylon

Dyeing properties of 1,2-dihydroxyanthraquinone based azo compounds

The azo compounds AAD₁ AAD₂ and AAD₃ gave a range of shades on cotton, polyester and nylon fabrics. The dyes gave yellow to brown hues and brighter and deeper shades with high tinctorial strength and good levelness on Nylon fabrics. This is probably due to the hydrogen bonded dye interaction (Vankar, 2000). Table 4 shows the shades, and wash fastness properties of the azo compounds.

Cotton which was dyed using the developed dyeing method show relatively poor wash fastness indicating that this hydrophilic fiber has little affinity for these hydrophobic disperse dyes AAD₁ - AAD₃. Polyester and Nylon showed moderate to good wash fastness (2 - 3) indicating better affinity due to their hydrophobic nature.

Conclusion

A series of phenyl azo dyes derived from coupler 1,2-dihydroxyanthraquinone were synthesized and tested on cotton, polyester and nylon. The overall properties were satisfactory and compares favourably with related studies previously reported. Several correlations between proposed structures and the physical, spectroscopic and fastness properties were also observed. These dyes possess the added advantage of an azo as well as an

anthraquinone chromophore thereby enhancing their technical properties.

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