

Synthesis Of Some Novel Azo Dyes And Their Dyeing, Redox And Antifungal Properties

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Abstract: Azo dyes are widely used colorants in consumer products such as leather, textiles, agriculture, cosmetics and in laboratories as indicators. This paper describes the synthesis of some novel azo dyes starting from 3-nitro salicylic acid. The synthesized dyes were investigated for their redox potentials, evaluated for their dyeing ability on cotton fabrics, resistivity against the fungi growth on jowar seeds. The structure of the products was confirmed by electronic absorption, IR, ¹H NMR, ¹³C NMR spectral studies and elemental analysis.

Key Words: Hazard, aerobic, textile, antifungal, redox, cyclic voltametry.

INTRODUCTION

Synthetic dyes produced in large quantities are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, food, cosmetics and other industries, among them the textile industry is a major consumer. Industrial effluents containing azo dyes are potential health hazards as they may be converted to toxic and/or carcinogenic products under anaerobic conditions. The most importantly these undergo reductive cleavage, leading to the formation of aromatic amines of which have known mutagenic and/or carcinogenic properties.¹ Therefore the use of certain azo dyes is prohibited all over the world. General route for the synthesis of azo dyes involves diazotization of primary aromatic amine followed by coupling with one or more nucleophiles, amino- and hydroxy groups are commonly used coupling components.

Novel mordant and disperse azo dyes prepared by the coupling of various diazo solutions of aromatic amines with 2,4-dihydroxybenzophenone have been studied for their dyeing ability mordanted with chromium salts on wool and polyester textile fibers. These dyes also exhibited fair anti-bacterial properties.² A series of 3-(*p*-substituted phenylazo)-6-pyridone dyes synthesized have been shown to be suitable for the dyeing of polyester fabrics.³ The Schiff base prepared from ninhydrin and 3-amino phenol was coupled with the dizonium solution of various aromatic amines leads to disperse monoazo dyes. These dyes showed excellent dye bath exhaustion and fixation on the polyester fibers and very good light fastness and washing fastness properties.⁴

Copper, cobalt and chromium complex combinations with azo dyes prepared from 1-diazo-2-naphthol-4-sulphonic, and 6-nitro-1-diazo-2-naphthol-4-sulphonic acids by coupling with -naphthol have showed moderate dyeing resistances on wool and polyamides.⁵ 1,2-hydroxy phenyl azo dyes and their metal complex with chromium and cobalt salts synthesized showed dyeing protein and polyamide fibers with excellent light and wash fastness. These dyes are used in electrophotographic or sensor applications for photoconductors, lasers, electro-optical devices and ink-jet printers.⁶

Naphthalimide-based alkali-clearable azo disperse dyes containing a fluorosulfonyl group were synthesized. These dyes were applied to polyester fabric by the HT method and exhibited good leveling, wash and sublimation fastnesses and moderate light fastness.⁷ Thermal analysis plays an important role in the study of the structure and stability of dyes. The resistance to heat at elevated temperatures is one of the main properties required of dyes used in high temperature processes such as dyeing, printing and photocopying and in high technology areas such as lasers and electro optical devices. Thermal behaviour of azo dyes containing steric hindered groups were investigated by thermogravimetry (TG) and the pyrolysis products were determined.⁸

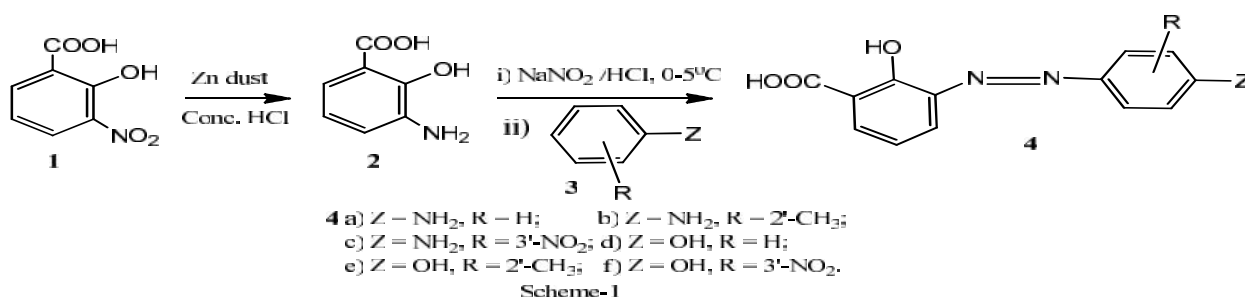
The development of efficient and affordable, eco-friendly methods to completely degrade the carcinogenic aromatic amines produced by the cleavage of the azo dyes in the eco-system still remains the field of interest. For instance, a stab-culture method was developed to screen for azo dyes-decolorizing bacteria from soil and water samples. Decolorized azo dye in the lower portion of the solid media indicates the presence of anaerobic azo dyes-decolorizing bacteria, while aerobic decolorizing bacteria decolorizes the surface portion of the solid media.⁹ The examined H₂O₂/Fe⁰ process was found to be very efficient for discoloration of simulated wastewater containing commercial azo dye. The process has undoubted advantages in comparison with the classical Fenton reaction.¹⁰

In view of the diverse applications associated with azo dyes, we thought of synthesizing new novel azo dyes and study their applications and this project was undertaken.

MATERIALS AND METHODS

The chemicals/reagents used were purchased from Merck Chemicals (India). Electronic absorption studies were carried out by using a solution of the synthesized compounds in dimethyl sulphoxide on UV-Visible spectrometer (UV-160 Shimadzu), the absorption maxima measured in nm and the absorbance values are given in the bracket. IR spectra (KBr pellet) were recorded on Shimadzu 8300 spectrometer. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker supercon 400 MHz spectrophotometer using CDCl₃ as solvent and TMS as an internal standard. The Chemical shifts are expressed in ppm. Elemental analysis was obtained on a Thermo Finnigan Flash EA 1112 CHN analyser. Thin layer chromatography (TLC) were performed on a pre-coated Silica Gel sheets (HF 254, sd-fine) using hexane:ethyl acetate (7:1) eluent and visualization of the spots was done in UV light. Chromatographic separations were carried out on silica gel (70-230 mesh, Merck) column using hexane:ethyl acetate (7:1) as eluent.

In a typical procedure, 3-nitro salicylic acid (**1**) is prepared from salicylic acid, then was reduced to 3-amino salicylic acid (**2**). Then 3-amino salicylic acid was subjected to diazotization reaction, the resulting diazonium chloride was coupled with substituted phenols and amines (**3**) to get the products (**4**) in 52-68% yield (Scheme-1).



Synthesis of 3-nitro salicylic acid: Salicylic acid (0.03 mole) was dissolved in glacial acetic acid (40 ml) in an 250 ml Erlenmeyer flask, to this 1:2 mixture of conc. HNO₃ (0.03 mole) and conc. H₂SO₄ (0.06 mole) was added in cold condition with constant stirring. Then reaction mixture was kept aside for 2 hrs at room temperature. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was transferred into crushed ice, with constant stirring. The solid formed was filtered. Then solid obtained was re-dissolved in water under hot condition and the hot solution was filtered, the filtrate was kept aside to attain the room temperature, the precipitate formed was filtered and was recrystallized by 30% alcohol. The isomeric mixture of 5-nitro salicylic acid was separated. The product (**1**) was obtained in 45% yield, mp 143-145°C.

General procedure for the synthesis of azo dyes:

Typical procedure for the synthesis of 2-Hydroxy-3-[(4-amino-3-methylphenyl)diazenyl]benzoic acid (4a): A mixture of 3-nitro salicylic acid (**1**) (0.01 mole) and zinc powder (0.03 mole) in a 250 ml Erlenmeyer flask fitted with reflux condenser was placed in an ice water bath. To the mixture conc. Hydrochloric acid (18 ml) was added drop wise through condenser and it was refluxed for 4 hrs with occasional shaking. Then the reaction mixture in the flask was cooled to room temperature and filtered. The filtrate was diluted with dil. Hydrochloric acid (15 ml) and with water (25 ml), and then was cooled to 0°C. To this cold solution, a cold solution of NaNO₂ (0.01 mole) in water (8 ml) was added to the flask slowly with constant shaking. After the completion of the reaction, a pale yellow solution of diazonium chloride was obtained, to this yellow solution; a cold solution of freshly distilled aniline (**3a**) (0.01 mole) in dil. Hydrochloric acid was added in small intermittent with constant shaking. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solid separated was filtered and recrystallised from dimethyl sulphoxide. The reaction afforded 2-Hydroxy-3-[(4-amino-3-methylphenyl)diazenyl]benzoic acid (**4a**) in 62% yield, mp : 94°C. The same procedure was used in all cases, however in case of 4d-f, the compounds 3d-f were dissolved in 5% sodium hydroxide.

RESULTS AND DISCUSSION

2-Hydroxy-3-[(4-amino-3-methylphenyl)diazenyl]benzoic acid (4a): Obtained as solid in 62% yield. UV-Vis: max 418 (0.251) nm. IR (KBr): 3434, 3210, 3052, 2910, 1616, 1440 cm⁻¹. ¹H NMR (CDCl₃): 5.15 (s, 1H, OH), 6.21 (s, 2H, NH₂), 6.85 (dd, 2H, Ar-H), 7.56-7.90 (m, 5H, Ar-H), 10.86 (s, 1H, COOH). ¹³C NMR (CDCl₃): 113.1 (2C), 115.0 (1C), 121.3 (1C), 125.4 (3C), 129.1 (1C), 132.0 (1C), 145.6 (1C), 150.6 (1C), 156.5 (1C), 171.3 (1C). Anal. Calcd. for C₁₃H₁₁N₂O₃; MW 257 : C, 60.70, H, 4.31, N, 16.33%; Found: C, 60.59, H, 4.26, N, 16.30%.

3-[(4-Amino-3-methylphenyl)diazenyl]-2-hydroxybenzoic acid (4b): Obtained as solid in 54% yield. UV-Vis: max 426 (0.306) nm. IR (KBr): 3438, 3213, 3051, 2909, 1624, 1455 cm⁻¹. ¹H NMR (CDCl₃): 2.22 (s, 3H, CH₃), 5.22 (s, 1H, OH), 6.12 (s, 2H, NH₂), 6.75 (d, 1H, Ar-H), 7.70-7.94 (m, 5H, Ar-H), 10.80 (s, 1H, COOH). ¹³C NMR (CDCl₃): 17.2 (1C), 112.1 (1C), 121.4 (1C), 122.0 (1C), 122.6 (1C), 125.0 (2C), 128.2 (1C), 129.4 (1C), 140.2 (1C), 155.2 (1C), 170.1 (1C). Anal. Calcd. for C₁₄H₁₃N₃O₃; MW 271 : C, 61.99, H, 4.83, N, 15.49%; Found: C, 61.92, H, 4.80, N, 15.45%.

3-[(4-Amino-2-nitrophenyl)diazenyl]-2-hydroxybenzoic acid (4c): Obtained as solid in 54% yield. UV-Vis: max 449 (0.325), 541 (0.099) nm. IR (KBr): 3446, 3221, 3060, 2919, 1722, 1632, 1431, 1328 cm⁻¹. ¹H NMR (CDCl₃): 5.30 (s, 1H, OH), 6.22 (s, 2H, NH₂), 7.10 (d, 1H, Ar-H), 7.75-7.98 (m, 5H, Ar-H), 10.68 (s, 1H, COOH). ¹³C NMR (CDCl₃): 108.3 (1C), 115.3 (1C), 119.2 (1C), 121.4 (1C), 123.0 (1C), 125.2 (1C), 129.1 (1C), 133.5 (1C), 137.8 (1C), 141.4 (1C), 151.2 (2C), 156.1 (1C), 170.1 (1C). Anal. Calcd. for C₁₃H₁₀N₄O₅; MW 302 : C, 51.66, H, 3.33, N, 18.54%; Found: C, 51.60, H, 3.31, N, 18.48%.

2-Hydroxy-3-[(4-hydroxyphenyl)diazenyl]benzoic acid (4d): Obtained as solid in 54% yield. UV-Vis: max 474 (0.493) nm. IR (KBr): 3448, 3232, 3031, 2924, 1635, 1475 cm⁻¹. ¹H NMR (CDCl₃): 5.30 (s, 2H, OH), 7.12 (dd, 2H, Ar-H), 7.75-8.14 (m, 5H, Ar-H), 10.84 (s, 1H, COOH). ¹³C NMR (CDCl₃): 115.1 (2C), 123.2 (2C), 158.7 (1C), 145.6 (1C), 121.8 (2C), 133.1 (1C), 115.3 (1C), 157.2 (1C), 125.2 (2C), 170.2 (1C). Anal. Calcd. for C₁₃H₁₀N₂O₄; MW 258 : C, 60.47, H, 3.90, N, 10.85%; Found: C, 60.43, H, 3.92, N, 10.81%.

2-Hydroxy-3-[(4-hydroxy-3-methylphenyl)diazenyl]benzoic acid (4e): Obtained as solid in 54% yield. UV-Vis: max 399 (0.062) nm. IR (KBr): 3462, 3233, 3031, 2929, 1634, 1435 cm⁻¹. ¹H NMR (CDCl₃): 2.16 (s, 3H, CH₃), 5.32 (s, 2H, OH), 7.00 (d, 1H, Ar-H), 7.68-8.05 (m, 5H, Ar-H), 10.90 (s, 1H, COOH). Anal. Calcd. for C₁₄H₁₂N₂O₄; MW 272 : C, 61.76, H, 4.44, N, 10.29%; Found: C, 61.70, H, 4.42, N, 10.26%.

2-Hydroxy-3-[(4-hydroxy-2-nitrophenyl)diazenyl]benzoic acid (4f): Obtained as solid in 54% yield. UV-Vis: max 454 (0.062), 569 (0.027) nm. IR (KBr): 3475, 3253, 3061, 2934, 1732, 1620, 1440, 1325 cm⁻¹. ¹H NMR (CDCl₃): 5.28 (s, 2H, OH), 7.50-8.14 (m, 6H, Ar-H), 10.88 (s, 1H, COOH). Anal. Calcd. for C₁₃H₉N₃O₆; MW 304 : C, 51.49, H, 2.99, N, 13.86%; Found: C, 51.43, H, 2.95, N, 13.80%.

The structures of the cycloadducts were provided by UV-Visible, IR, ¹H NMR, ¹³C NMR spectral studies and elemental analysis. For instance, in UV-Visible spectrum, all the compounds showed absorption maxima in the region 418-474 nm. However the compounds **4c** and **4f** showed second absorption maxima peaks at 541 and 569 nm respectively due to the presence of chromophoric (NO₂) group. The results of the electron absorption studies indicating that all synthesized compounds were absorbed in the visible region.

In IR spectra, all the compounds showed a broad band in the range of 3504 cm^{-1} to 3382 cm^{-1} corresponding $-\text{OH}$ (str), however, the observed values are lesser than that of the corresponding free- OH group. This suggests that the compounds possess hydrogen bonding between $\text{C}=\text{O}$ of carboxylic group and OH group ortho to it. The consistent pattern stretching absorption bands due to $-\text{N}=\text{N}-$ observed clearly indicates the formation of the compounds.

In ^1H NMR spectra, all the synthesized compounds **4a-f** showed the peaks due to aromatic and substituent protons at the expected region. In ^{13}C NMR, all products gave the signals due to aromatic and substituent carbons at the expected region. Further, all showed satisfactorily CHN analysis with a deviation of $\pm 0.02\%$ from the theoretically calculated values. All these observations strongly favor the formation of the products.

Redox Potentials: The cyclic voltammetry studies on the synthesized compounds **4a-f** has been carried out at the concentration of 25 mM in DMSO as solvent. Britton Robinson buffer (0.04 M of H_3PO_4 , H_3BO_3 , CH_3COOH) and 0.2 M NaOH solution was used as supporting electrolyte and pH was maintained at 2. A stream of nitrogen was passed into the reaction mixture and then was thermostated. The potential scan rate, current sensitivity, initial potential and final potential were recorded. The resulting current was measured as a function of applied potential. The results were summarized in table-1.

Table-1: Oxidation-reduction potentials of compounds 4a-f measured by cyclic voltammetry.

Compound	Oxidation				Reduction				Scan rate mV/sec
	E_1 (mV)	I_1 (μA)	E_2 (mV)	I_2 (μA)	E_1 (mV)	I_1 (μA)	E_2 (mV)	I_2 (μA)	
4a	474	-9.48	918	-11.72	277	13.26	--	--	10
4b	419	-6.97	895	-11.82	261	13.76	--	--	20
4c	542	-13.14	945	-13.84	282	12.09	--	--	20
4d	595	-11.95	--	--	401	6.75	--	--	50
4e	481	-9.03	--	--	352	4.27	--	--	20
4f	578	-32.6	--	--	543	14.1	303	20.6	20

The result of the study reveals that under specified conditions the synthesized compounds undergoes oxidation and reduction. The redox potentials of the compounds suggest that these may be used as indicators in redox titrations.

Textile applications: The synthesized compounds **4a-f** has been studied for their ability of dyeing to cotton fabrics. Among the compounds **4c** and **4f** have showed good dye absorption properties on cotton fabrics, while the others showed poorer absorption ability. The results of electronic absorption spectra showed that these dyes have high absorption intensity gave bright intense hues on cotton fabrics. The color parameters of the dyed fabrics were measured and the dyes have excellent absorption, intense and of very good fastness properties on cotton fabrics.

Antifungal activity:

Seed coating: The seeds are the bridge between generations, so it is necessary to store them after mixed with melathin powder to prevent fungal growth till the next planting season. The germination percentage may decrease with time and hence the seed stocks are tested from time to time for their viability using either sand bed method or Petri plate method. The fungi on the seed surface or in the seeds greatly affect the seedling viability.

The anti fungal activities of the synthesized compounds have been tested with the seeds of jowar and green gram. In a typical experiment, the blotting discs dipped in distilled water were placed in the Petri plates. On the other side, 20 g of Jowar were taken in polythene bag, to this, 2-3 drops of water was added and then was thoroughly shaken for 30 minute for the proper distribution of water on the surface of the seeds. By doing so the surface of the seed gets expanded. Now a known quantity of the synthesized compounds was mixed with the seeds in the different polythene bags and shaken well till the compounds were coated on the surface of the seeds. Then the seeds were transferred to Petri plates and sufficient water was added and kept in incubation for 72 hours. The various fungi developed were noted, control experiments were carried out under similar conditions. The results of the study were summarized in table-2.

Table-2: Resistance of the compounds 4a-f against fungi formation on jowar seeds.

Fungal Species	Fungi Formation Incidence (%)												
	Control	4a		4b		4c		4d		4e		4f	
		X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
<i>A. niger</i>	28	-	8	-	4	-	-	9	-	-	-	20	8
<i>A. flavous</i>	-	8	4	-	-	-	16	6	-	9	3	-	-
<i>R. nigaricans</i>	-	40	-	-	12	-	-	-	-	6	2	4	-
<i>A. nidulens</i>	4	-	-	22	18	-	-	-	-	-	-	-	-
<i>C. herbarum</i>	-	-	-	-	6	24	13	-	-	2	-	14	4
<i>T. roseum</i>	8	-	8	-	-	-	-	22	10	3	-	5	-
<i>A.alternate</i>	-	-	-	8	3	-	-	-	-	8	5	7	-
X= 0.100 g; Y= 0.250g													

The experimental result indicates that the synthesized compounds possess good antifungal activities against many of the fungi species. It was observed that the variation of the compounds concentration remarkably influences the growth of the fungal organisms.

SUMMARY

Although there was a ban on the use of azo dyes all over the world for their adverse effect on the environment, their enormous applications influencing the researchers to continue in the field. The methodology to make them complete eco friendly remains of interest.

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