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Synthesis and Application of Triphenylamine Dyes on Chrome and Vegetable Tanned Leather

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ABSTRACT

P-phenylenediamine, H-acid, and 3-aminobenzoic acid were used to create a triphenylamine dye that was labeled AD1. AD2. and AD3. The intermediate, p-phenylenediamine, H-acid, and 3-aminobenzoic acid melting points of the synthesized dyes were found to be 250°C, 295°C, 342.6°C, and 155°C, respectively. The greatest absorption wavelength fell between 380 and 500 nm. The IR spectra of the synthesized dyes also revealed an absorption peak in the range of 1690-1590 cm-1 for the intermediate, 1650-1550 cm-1 for the NH bent in AD1, 1420–1370 cm-1 for organic sulphates in AD2, and 1680–1630 cm-1 for the C=O amide in AD3. Additionally, the GC-MS analysis of the dyes revealed molecular ion peaks for ADI, AD1, AD2, and AD3 at m/z of 273.1, 344.0, 563.0, and 340.5, respectively, which are consistent with the molecular formula of the dyes. The 1H NMR spectra of the synthesized dve displayed splitting patterns that indicate the existence of protons with aromatic, methanolic, methylene, sulfide, and phenolic functions. On leather that had been vegetable and chrome tanned, the synthetic dves were used. When applied to the leather, the dyes produced pink, dark red, brown, and dark brown hues with brighter and deeper tints, outstanding levelness, and tinctorial strength. Additionally, they provided good to excellent rub and light fastness on both chrome and vegetable tanned leather. Based on the findings, it can be said that both chrome and vegetable-tanned leather can be dyed using AD1, AD2 and AD3 dye.

INTRODUCTION

Dyes are coloring agents, either natural or artificial, soluble or insoluble, that provide color to material by staining or ingesting it. They are made from a solution of fine dispersion and are occasionally used in conjunction with a mordant. There are many different kinds of direct, reactive, acid, and basic dyes used in the textile industry. These dyes are, however, always left in industrial waste. They are frequently used to color products in the textile, paper, leather, and mineral processing sectors. Dyes have color due to their ability to absorb light in the visible spectrum (400-700 nm), the presence of at least one chromophore (color-bearing group), the presence of a conjugated system, or a structure with ARTICLE INFO

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alternate double and single bonds, and the resonance of electrons that it exhibits. This resonance of electrons acts as a stabilizing force in organic compounds. (Aghazada et al., 2017). The color is lost when one of these characteristics is missing from the molecular structure. The majority of dyes also contain molecules referred to as auxochromes (color helpers), such as carboxylic acid, sulfonic acid, amino, and hydroxyl groups, in addition to chromophores. Dyes are used to color surfaces that they have an affinity for because they are soluble in water and/or an organic solvent. (Dizit et al., 2007). The sources of dyes might be either natural or manufactured. In contrast to paints, they are made chemically or from plants and are

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absorbed into the pores of the materials rather than building up on the surface of the fiber or hide. Because the dye molecules' size is less than the pores in the fiber, this is made possible. The dye molecules resemble strips of paper folded into arrows. When the fiber yarn or cloth is placed into the dye bath, its planar shape helps them glide into the polymer system. According to research, dyes are created chemically in a lab or by plants, which are found in many types of plant material. They can be obtained from either natural or manufactured sources (Jitenda *et al.*, 2007).

METHODOLOGY

Synthesis of 4-formyltriphenylamine Intermediate (1a)

Compound 1a was prepared according to the reported literature. Freshly distilled POCI3 (21 eq.) was added drop-wise to DMF (25 eq.) under an atmosphere of nitrogen at 0°C, and then it was stirred for 1 hour. TPA (2g, 8.16 mmol) was added to the above solution and the resulting mixture was stirred for 18 hours at 95 °C. After cooling to room temperature, the mixture was poured into a beaker containing icecube and basified with 0.5 M NaOH. The solid was filtered and extracted with ethyl acetate. After evaporating the organic solvent, the crude product was purified by recrystallization to give a pale-yellow solid. ¹H NMR (400 MHz, dmso) δ 6.23 (dd, J = 17.3, 10.0 Hz, 1H, Ar-H), 6.01 (dd, J = 35.0, 27.2 Hz, 2H, Ar-H), 1.30 (s, 9H, CH₃OH), 1.30 (s, 9H, CH₃OH).

Synthesis of Dye 1

Dye 1 was prepared according to the reported literature. The compound 1a was added to a 100 ml single neck round bottom flask containing 15 ml freshly distilled methanol and then stirred for 2 hours at 65 °C. P-Phenylenediamine (2 eq.) was added to the reaction mixture was refluxed for 2 hours. The yellow color solid was filtered by sing methanol as washing solvent. It was recrystallized in dichloromethane to give the product. ¹H NMR (400 MHz, dmso) δ 5.75 (s, 3H Ar-NH₂), 5.49 (d, J = 8.0 Hz, 5H Ar-NH₂), 5.36 – 5.27 (m, 7H, Ar-

NH₂), 4.88 (s, 5H, CH₂-CH₂), 4.80 (d, *J* = 7.4 Hz, 8H, CH₂-CH₂).

Synthesis of Dye 2

Dye 2 was prepared according to the reported literature. The compound 1a was added to a 100 ml single neck round bottom flask containing 15 ml freshly distilled methanol and then stirred for 2 hours at 65 °C. H-Acid (2 eq.) was added to the reaction mixture was refluxed for 2 hours. The yellow color solid was filtered by sing methanol as washing solvent. It was recrystallized in dichloromethane to give the product. ¹H NMR (400 MHz, dmso) δ 9.67 (s, 7H, HCOH), 8.54 (s, 6H, HCOH), 7.51 (s, 14H, Ar-OH), 6.52 (s, 54H, Ar-H), 6.49 (s, 84H, Ar-H), 6.36 (dd, J = 64.2, 28.5 Hz, 151H, CH₂-CH₂), 6.14 (d, J = 19.5 Hz, 31H, CH₂-CH₂), 6.11 – 5.51 (m, 128H, Ar-H), 5.80 - 5.51 (m, 41H, Ar-OH), 5.78 – 5.67 (m, 20H, Ar-OH), 4.58 (d, J = 7.8 Hz, 10H, Ar-SH), 2.34 (s, 40H, CH₃OH), 1.45 (s, 12H, Ar-OH).

Synthesis of Dye 3

Dye 3 was prepared according to the reported literature. The compound 1a was added to a 100 ml single neck round bottom flask containing 15 ml freshly distilled methanol and then stirred for 2 hours at 65 °C. 3-Aminobenzoic Acid (2 eq.) was added to the reaction mixture was refluxed for 2 hours. The yellow color solid was filtered by sing methanol as washing solvent. It was recrystallized in dichloromethane to give the product. ¹H NMR (400 MHz, dmso) δ 9.67 (s, 7H, Ar-COOH), 8.54 (s, 6H, Ar-H), 7.51 (s, 14H, Ar-H), 6.52 (s, 54H, Ar-OH), 6.49 (s, 84H, Ar-OH), 4.58 (d, *J* = 7.8 Hz, 10H, CH₂-CH₂), 2.34 (s, 40H, CH₃COOH).

Dyeing of Substrates

The substrates were netted and thoroughly squeezed to remove excess water. It was immersed into a dye bath at 40°C and was carried out for about an hour at a temperature of about 100°C with constant agitation. At the end of the dyeing process, the dyed substrate was removed and squeezed and rinsed thoroughly under running tap water and allowed to dry at room temperature.

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Fastness Properties

The dyed sample was subjected to wash fastness test by the following procedures. The specimens were prepared by cutting the dye substrate 7cm by 2cm into dimensions. It was made into composites by stitching the test specimen made of the dyed sample place between white cotton or dimension of 8cm by 4cm. the composite was agitated in the solution made up of the following;

Soap solution 5g/l

Sodium carbonate 2g/l

Liquor ration 50:1

The washing was maintained at a temperature of 50°C for 45minutes with continuous agitation. At the end of the washing test, the composite

RESULTS AND DISCUSSION

specimen was removed, rinsed in a running tap water and the adjacent fabric was accessed using the appropriate grey scale.

Light Fastness Test

The dyed sample was exposed facing due south and inclined at an angle of the horizontal approximately equal to latitude of the place where the exposure is being made. Adequate ventilation of the sample during exposure to UV radiation for 7 days. The exposed sample was examined at interval and the change in the colour of the sample was compared visually with change that occurs in the standard.



Scheme 2: Synthesis of target dyes (where x = P-phenylenediamine, H-acid and 3-aminobenzoic acid for dye AD1, AD2 and AD3 respectively)

Table 1: Structures with IUPAC names of th synthesized Triphenylamine dyes.				
Dye	IUPAC Name	Dye structure		

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Table 2: Physical properties of the synthesized dyes.

Dye	Empirical formula	Mol. Wt. (g/mol)	Mt. Point (°C)	Methanol (λmax)	Colour Dyes	of
ADI	C ₁₉ H ₁₅ NO	273.1	250.0	380	Violet	
AD1	C ₂₅ H ₂₁ N ₃	341.2	295.0	500	Green	
AD2	C ₂₉ H ₂₃ N ₂ S ₂ O ₇	575.0	342.6	490	Blue	
AD3	C ₂₆ H ₂₀ N ₂ O ₂	392.0	155.8	490	Blue	

 Table 3.0:
 Spectroscopic Properties of the synthesized intermediates and Dyes

Dyes	FT-IR (cm ⁻¹)	GCMS Experimental values of m/z fragment
ADI	1688.5 (open chain imino, Quinone), 1584.1 (C=C, C- N str.), 1423.8 (C=N str.), 1274 (Ar-O str).	43.1, 69.0, 97.1, 117.0, 207.1, 273.1.
AD1	1617 (N-H bend), 1513.3 (C=C-C str.), 1263.6 (C-N str.), 1617.7 (Imino)	43.0, 69.0, 97.0, 207.1, 128.9, 281.0, 344.0.
AD2	1420.1 (org. Sulphates), 1315 (C=O), 1595.3 (C=N str.), 1215 (CO).	73.0, 147.0, 221.0, 281.0, 355.0, 563.0
AD3	1677.3 (C=O str.), 1632 (NH bend), 1379.1 (C-N str.), 1103 (C-O carboxylic acid).	41.0, 73.0, 110.9, 149.8, 208.4, 340.5.

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Table 2: Fastness properties of the dye						
Dye	Dyed sample	Light fastness	Rub fastness			
AD1	Chrome tanned leather	3	4			
	Vegetable tanned leather	4	3			
AD2	Chrome tanned leather	4	4			
	Vegetable tanned leather	3	3			
AD3	Chrome tanned leather	4	4			
	Vegetable tanned leather	4	3			

Gray scale for fastness properties

The synthesized dyes AD1, AD2, and AD3 had absorption maxima between 480 and 500 nm, with AD1 having the largest absorption maxima. The dyes' intermediate showed an absorption maximum at 380 nm. The π-π* electron transfers from the triphenylamine donor to the aromatic amine-derived anchoring groups are responsible for the change in absorbance seen in the produced dyes. The intermediate's FT-IR spectra revealed all the fundamental functional groups related to the formaldehyde derivative of triphenylamine's predicted properties. The following measurements are in cm-1: OH bend at 697, C-H stretch at 823.7, substituted amine at 1159, C=O stretch at 1423.8, and C=C-C aromatic ring stretch at 1584.1. The FT-IR spectrum of dye AD1 showed all the basic functional groups associated with the theoretical characteristics of the dye. From the table showing the functional group assignments, the following vibrations can be detected: N-H bend at 1617.7 cm⁻¹, C-H stretch at 820 cm⁻¹, substituted amine at 1159 cm⁻¹, C=O stretch at 1423.8 cm⁻¹, C=C-C aromatic ring stretch at 1584.1 cm⁻¹, C-N stretch at 1263.6 cm⁻¹ ¹, C-H aromatic bend at 697 cm⁻¹, C-C at 1125 cm⁻¹. The FT-IR spectrum of dye AD2 showed all the basic functional groups associated with the theoretical characteristics of the dye. From the results showing the functional group assignments, the following vibrations can be detected: SO42- at 1088.4 cm-1, C-H stretch at 868 cm⁻¹, C=O stretch at 1423.8 cm⁻¹, C=C-C aromatic ring stretch at 1584.1 cm⁻¹. C-N stretch at 1144 cm⁻¹, C-H aromatic in-plane bend at 1215.1 cm⁻¹, organic Sulphates at 1420.1 cm⁻¹,

open chain -C=N- at 1595.3 cm⁻¹, C-C at 1125 cm⁻¹. The FT-IR spectrum of dye AD3 showed all the basic functional groups associated with the theoretical characteristics of the dye. From the table showing the functional group assignments, the following vibrations can be detected: C=O amide at 1677.3 cm⁻¹, C-H aromatic stretch at 868 cm⁻¹, C=O carboxylate stretch at 1103.3 cm⁻ ¹, C=O amide stretch at 1677.3 cm⁻¹, C-N stretch at 1379.1 cm⁻¹, C-H aromatic out of plane bend at 752.9 cm⁻¹, NH secondary amine at 1551.8 cm⁻¹, NH 1° amine at 1632.6 cm⁻¹, open chain imino -C=N- at 1677.3 cm⁻¹. The GC-MS analysis the of dyes showed molecular ion peaks at m/z of 273.1, 344.0, 563.0 and 340.5 for ADI, AD1, AD2 and AD3 respectively which are consistent with the molecular formula of the dyes. The ¹H and NMR spectra for the synthesized dye showed splitting patterns that signify the presence of aromatic, methanolic, methylene, sulphide and phenolic protons. The fastness properties of the dyed leather ranges from good to very good, the increase in the fastness properties of the dyed leather can be attributed to inter-molecular charge transfer in the chromophore group. It can also be attributed to the hydrophilic nature of the collagen which enhances the penetration of the dye, that there is no absolute value for the light fastness of a dye. The rating obtained for a given colorant for any fading test are; conc. and degree of aggregation of dye within the fabric nature in which the dye is dispersed; molecular structure of the dye substantively, nature of the fabric in which the dye is dispersed. However, the light fastness of dyes on chrome and vegetable tanned leather ranges from 3-4 which could be

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ascribed to coupling component used. The dye solubility was tested and was observed that the dye is soluble in water and methanol.

CONCLUSION

Triphenylamine dyes were synthesized P-phenylenediamine, H-acid and 3using aminobenzoic acid as the condensing components. The FTIR spectroscopy of the dyes show the presence of functional groups that aligned with the structural properties of the dye. The dye gave a good shade on both leather (vegetable and chrome tanned leather) hence both dyes exhibited good fastness property on the substrate. From the properties exhibited by the dye on chrome and vegetable tanned leather, it showed that the dye is excellent in the dyeing of leather.

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