

Synthesis and Applications of Heterocyclic Based Dyes Derived From Substituted 1, 3-Benzothiazole on Chrome and Vegetable Tanned Leather

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ABSTRACT

Synthesis and applications of heterocyclic based dyes derived from substituted 1, 3-benzothiazole on chrome and vegetable tanned leather were carried out. The intermediate were diazotized, coupled and the dyes were purified by re-crystallization. The melting points were found to span from 143°C- 186°C and spectroscopic assessment such as FT-IR, GC-MS and NMR spectroscopy were carried out to elucidate their structures. The vibrational frequency obtained for the synthesized dyes shows the characteristics absorption peaks due to stretching frequency of the NH-group in the region 3198.1-3459 cm⁻¹. The IR spectra of the prepared azo dye also showed an absorption peak in the region 1490.9-1543.1 cm⁻¹ attributed to azo chromophoric group (N=N), while the observed peak in the region 1602.8-1695.9. Also the GC-MS analysis of Dye BZT 1, BZT 2, BZT 3 and BZT 4 showed molecular ion peaks at m/z 327.3, 328.3, 328.3 and 329.3 respectively which is consistent with the molecular formula of the dyes. The ¹H and ¹³C- NMR spectra for the synthesized dye showed eight signals with a highly deshielded signal at 10.39 ppm (1H, singlet) which is attributed to the presence of the OH of the carboxylic group, 7.73 – 8.27 ppm due to the presence of amino (-NH₂) protons. Two signals were observed for two pairs of aromatic proton in the (6.84 – 7.81) ppm range with a coupling constant of 8 – 12 Hz. Also a distinct signal was observed up field at 3.06 ppm due to the presence of methyl (CH₃) proton. The ¹³C-NMR spectrum of the Dyes showed the signal at 162.26 ppm for the carbon atom in the COOH group. Thus a signal at 141.41 ppm for carbon atom in the thiazole ring was also observed while the signal at 140.06 -115.56 ppm for aromatic carbon. The heterocyclic dye BZT 1, BZT 2, BZT 3 and BZT 4 were applied at 2 % depth on chrome and vegetable tanned leather. The dyes on application gave pink, dark red, brown and dark brown hues with brighter and deeper shades, tinctorial strength and excellent levelness on the leather. The variation in the shade of dyed fabric results from alteration in the diazo and coupling component. The remarkable degree of levelness and brightness indicate good penetration and excellent affinity of the dyes to the leather. In addition the result obtained showed that the dyed leather have excellent fastness to washing which may be due to the absence of solubilizing group, which affect solubility and washing ability of the dye-out of the leather.

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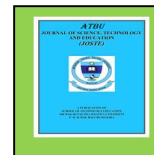
Disperse dyes, 1, 3-benzothiazole, chrome tanned leather and vegetable tanned leather

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INTRODUCTION

Benzothiazole derivatives represent an extensive group of heterocyclic compounds, several of which have already found application in the medical sphere as medicines (Paramashivappa *et al.*, 2003). The compounds encompassing benzothiazole moiety are of great interest and have been extensively used in pharmaceutical chemistry and agriculture division. Heterocyclic bearing a benzothiazole ring residue are reported to show anticancer, anti-inflammatory, analgesic, muscle-relaxant, sedative, antitubercular, diuretic, antimicrobial, anticonvulsant, antiallergic, antimalarial, antiviral, antioxidant, CNS depressant, and plant growth regulatory activity etc Larisa and Nina, (2020). In addition, recently benzothiazole possess derivatives an extended conjugated system and longer fluorescence lifetime forms. 2-amino benzothiazole compounds are considered one of an important type of fused thiazoles which have a wide application. The chemistry of 2-aminobenzothiazole has gained increasing interest in both synthetic organic chemistry and biological fields (Maha, 2012). A number of 2-amino benzothiazole derivatives were prepared by two methods. The first is **Hugersch's** method which concerns the reaction of thiourea derivative with bromine in acetic acid. The second, method concerns the direct reaction of amine derivatives with potassium thiocyanate and bromine in glacial acetic acid. In 1887 **Hoffmann** (5) who first reported the cyclizations of 2-amino thiophenol to 2-amino benzothiazole. Dyes are organic colour compounds which contains groups such as -N=N (azo group), -C=O (carbonyl group), (nitro) -NO₂, etc. and auxochromic group such as amino and substituted amino groups. In other words dyes are organic colored substance that chemically bonds to the substrate to which it is being applied, this distinguish dyes from pigments which do not chemically bind to the material they color (Gupta, 2011). The dye is generally in an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigment are colored, because they absorb only some wavelength of visible light.

Dyes are usually soluble in water whereas pigments are insoluble. The first synthetic dye mauve was discovered serendipitously by William Henry Perkin in 1856. The discovery of Mauveine started a surge in synthetic dyes and in organic chemistry in general. Other aniline dyes followed, such as fuchisine, safranine and induline and many thousands of synthetic dyes have since been prepared. The color of a dye is dependent upon the ability of the ability of the substance to absorb light within the visible region in the electromagnetic spectrum (400-700nm). An earlier theory known as Witt theory states that a colored dye has two components, a chromophore which imparts colour by absorbing light in the visible region (some examples are nitro, azoquinoids groups) and an auxochrome which serves to deepen the color. These theory has been suspended by modern electronic structure theory has been suspended by modern electronic structure theory which states that the colour in dyes is due to excitation of valence-electrons by visible light. (Gupta, 2009). Dyes are aromatic compounds that absorb light of wavelength ranging between 700 – 350 nm. The colors of these dyes are originated by absorbing the light in the visible region of the spectrum due to the delocalization of *n*- and π -electrons throughout their structures (Aziz *et al.*, 2009). The use of heterocyclic diazo components is now becoming a prime area of research by dye chemist and remarkable successes have been recorded. The colour range of these dyes extends to blue and blue green, hitherto the exclusive domain of the anthraquinones (Jitender *et al.*, 2010). Although hydroxyl groups are known to be electron donors, they are less efficient in arylazo phenol versus aryazo naphthol structure. This is because the naphthol system does not lose full aromatization when electron delocalization occurs Chen and Ren, (2018). Therefore 3-amino-2-methylbenzoic acid and 3, 5-diaminobenzoic acid couplers generally give dyes that are more bathochromic than phenol-based dyes. The two main thrusts of dyestuffs research have been improved technical excellence and greater cost effectiveness. One

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long-term aim had been to combine the brightness and high fastness properties of anthraquinone dyes with the strength and economy of azo dyes, (Maradiya and Patel, 2002a).

MATERIALS AND METHODS

Materials

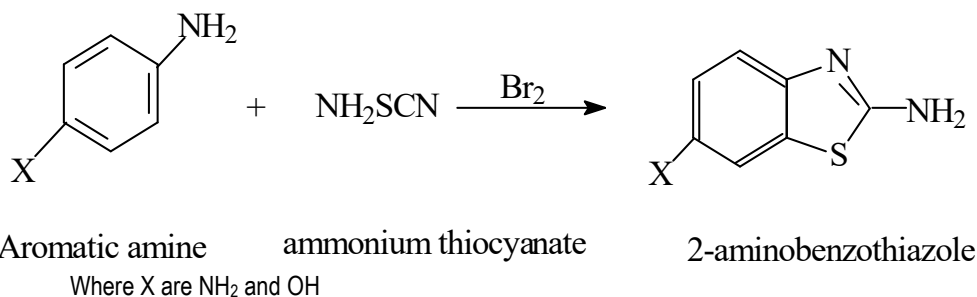
Analytical grade reagents and chemicals from Sigma Aldrich were used for this research work, These include; 4-hydroxyaniline, p-phenylenediamine, 4-methylaniline, N,N-dimethylbenzene-1,4-diamine, N,N-diethylbenzene-1,4-diamine, dimethylformamide (DMF), sodium nitrite, concentrated sulphuric acid, concentrated hydrochloric acid, acetonitrile,

iodine, potassium iodide, absolute ethanol, sodium hydroxide, sodium carbonate, tetrahydrofuran, n-hexane, ethylacetate and ethanol, Gallen-Kemp melting point apparatus, Agilent Uv-visible spectrophotometer, Agilent Fourier transform infra-red spectrophotometer, Agilent GC-MS and ^1H and ^{13}C -NMR spectrometer. These chemicals and reagents were used without further purification

Methods

Synthesis of Intermediates

The aminothiophene intermediate was synthesized by following methods reported in the literature (Alaa and Tarek, 2006).



Synthesis of 2-aminobenzothiazole

Intermediates

Intermediate 1

4-hydroxyaniline (4.6 g, 0.05 mol) and ammonium thiocyanate (3.8 g, 0.05 mol) were dissolved in absolute ethanol containing 4 ml of conc HCl. To this mixture bromine in glacial acetic acid (6.75 ml, 0.125 mol) was added and the reaction mixture was refluxed for 1 hr. Then it was cooled in ice bath. The precipitate obtained was filtered, washed with cold water and dried. The crude product was recrystallized from ethanol. Maha, (2012).

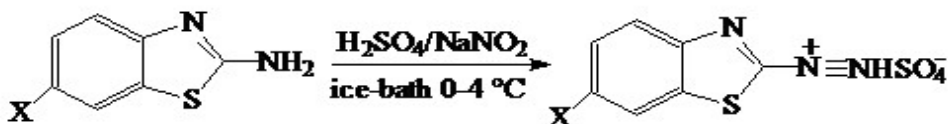
Intermediate 2

P-phenylenediamine (4.6 g, 0.05 mol) and ammonium thiocyanate (3.8 g, 0.05 mol) were dissolved in absolute ethanol containing 4 ml of con. HCl. To this mixture bromine in glacial

acetic acid (6.75 ml, 0.125 mol) was added and the reaction mixture was refluxed for 1 hr. Then it was cooled in ice bath. The precipitate obtained was filtered, washed with cold water and dried. The crude product was recrystallized from ethanol (Maha, 2012).

Diazotizations of 2-aminobenzothiazole Intermediates

A solution of 2-aminobenzothiazole derivatives (0.054 mole) in H_2SO_4 (12 ml) was cooled to 0-4 °C. To this solution was added a cold solution of sodium nitrite (0.54 mole) drop wise with constant stirring. When the addition was complete, the resultant reaction mixture was left in ice-bath for 1hr. It was used as such for further reaction as shown in the reaction below: (Patel *et al.*, 2003).



2-aminobenzothiazole

diazonium salt of 2-aminobenzothiazole

where X is OH, NH₂

Coupling Reaction

The coupling component, 3-amino-2-methylbenzoic acid and 3, 5-diaminobenzoic acid couplers was dissolved separately in acetic acid and cooled to 0°C by adding ice. The diazonium solution of the intermediate 1 and 2 that was prepared was then added for 30-40min with vigorous stirring (Maradiya and Patel, 2010). The resulting product was collected by filtration, wash with water and dried. The crude product was purified by recrystallizing it from ethanol and DMF of ratio 9:1.

Characterization of the Intermediates and the Dyes

The physicochemical properties of the intermediates and synthesized dyes were carried out and spectroscopic properties such as FT-IR, GC-MS and NMR

Dyeing of Fabric with Synthesized Dyes

Chrome and vegetable tanned leather were dyed using the synthesized dyes. The fastness properties of the dyes were examined using standard method.

Application of Dyes

1% stock solution of each dye was prepared, a aliquot ratio of 50:1 was used, 2% shade on weight of fabric (o.w.f) and 1g of fabric each of chrome and vegetable tanned leather. The volume required from each stock solution was calculated based on the formula:

$$V = \frac{P \times W}{C}$$

Where:

P = percentage shade

W = weight of fabric

C = percentage concentration of stock solution.

For the vegetable tanned leather a carrier (phenol) and dispersing agent (anionic detergent) was used to facilitate the dyeing process. The fabric was wetted and thoroughly squeezed to remove excess water. It was then immersed into the bath at 40°C and allowed to reach the boil within 15 minutes. Dyeing was carried out for one hour at a temperature of 60 °C with agitation. At the end of the dyeing process the substrate was removed, squeezed and rinsed thoroughly under running tap and allowed to dry at room temperature (Giles and Rahman, 1992; Nkeoye, 1987; Miah and Ahmed, 2013).

Measurement of Dye Exhaustion

Dye uptake was determined by measuring the absorbance of diluted dye bath samples at the wavelength of maximum absorption of each dye. The bath was sampled before and after dyeing. A 1ml aliquote was taken from the bath and diluted in 20ml acetone. This is to ensure that the absorbance falls within the readable range of 1.5. The percentage of dyebath exhaustion (%E) was calculated using the equation below, (Jae-Hong Choi *et.al*, 2008; Ozan Avinc *et.al*, 2006).

$$\%E = \frac{A_o - A_i}{A_o} \times 100$$

where A_o and A_i are the absorbance at λ_{max} of the dyebath prior to dyeing and after dyeing respectively.

Wash Fastness Test

The dyed samples were subjected to I.S.O.2 wash fastness test by the following procedures: The specimens were prepared by cutting the dyed fabrics into 5cm x 2cm dimensions; they were then made into composites by stitching the test specimen made of the dyed sample place in between white cotton of dimensions 10cmx4cm. The composite was agitated in solution made up of the following:

Soap solution 5g/l
Liquor ratio 50:1

The washing was maintained at 50°C for 45minutes with continuous agitation in the automated test machine. At the end of the washing test the composite specimen was rinsed in cold water, squeezed to remove excess water and dried. The change in colour of the dyed samples and the staining of adjacent undyed cloths were assessed using the standard grey scale and the results are shown in Table 4.12 and 4.13. (SDC, 1965).

Light Fastness Test (Nunn, 1979)

The dyed samples and blue wool standard were exposed facing due south and inclined at an angle to the horizontal approximately equal to the latitude of the place where the exposure is being made. Adequate ventilation of the samples during exposure was ensured. The partly covered samples were exposed to Ultra-violet radiation. As exposure proceeded for 3days, the samples under test and the blue wool standard were examined at interval and the change in colour of the samples compared visually with the changes that occur in the standards. The light fastness of the sample is the number of the standard that shows a similar visual contrast between the exposed and unexposed part of the samples. The exposure was terminated when the blue wool standard seven fades or when fully exposed and non-exposed test samples is equivalent to grade 3 on the grey scale.

RESULT AND DISCUSSION

Table 1a: Structures with IUPAC Names of the Synthesized Intermediates

Intermediates No	IUPAC Name	Structures of the Synthesized intermediates
1	1,3-benzothiazole-2,6-diamine	
2	2-amino-1,3-benzothiazol-6-ol	

Table 1b: Physical Properties of the Synthesized Intermediates

Intermediate	Molecular formula	Molecular weight g/mol	Melting point °C	% Yield	Colour of the crystal
1	C ₇ H ₇ N ₃ S	165.2	141-142	72	Light brown
2	C ₇ H ₇ N ₂ SO	166.2	160-162	79	Dark brown

The colour of the diazo compounds ranges from light brown to dark brown for the

intermediate 1 and 2 respectively. The molecular mass of the intermediate is from 165.2-166.2

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g/mol while the melting point were 141-162 °C as shown in the Table 1b. The yield of the intermediate can also be described as impressive

ranging from 72-79 %. This is not surprising in view of the result from similar works. (Sabnis *et al.*, 1999).

Table 2a: Structures with IUPAC Names of the Synthesized Dyes

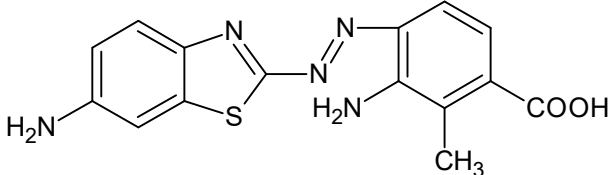
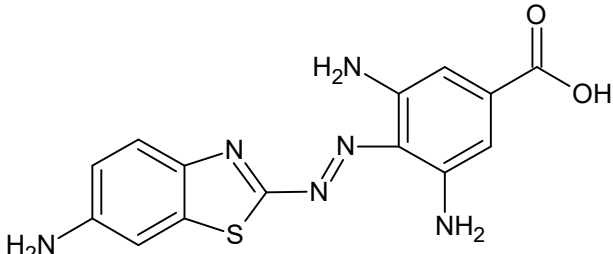
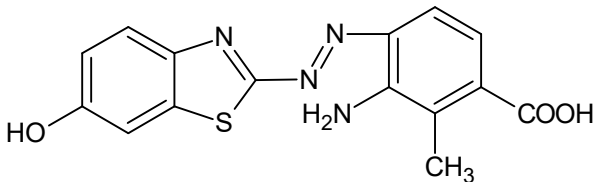
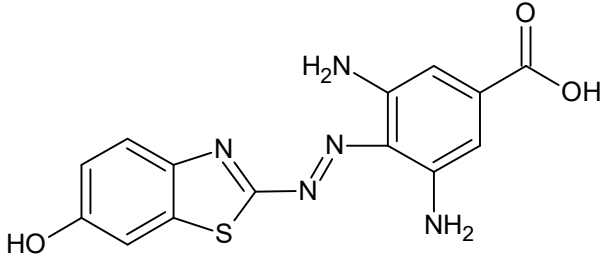
Dyes No	IUPAC Name	Structures of the Synthesized Dyes
1	3-amino-4-[(E)-(6-amino-1,3-benzothiazol-2-yl)diazenyl]-2-methylbenzoic acid	
2	3,5-diamino-4-[(E)-(6-amino-1,3-benzothiazol-2-yl)diazenyl]benzoic acid	
3	3-amino-4-[(E)-(6-hydroxy-1,3-benzothiazol-2-yl)diazenyl]-2-methylbenzoic acid	
4	3,5-diamino-4-[(E)-(6-hydroxy-1,3-benzothiazol-2-yl)diazenyl]benzoic acid	

Table 2b: Physical Properties of the Synthesized Dyes

Dye no	Molecular formula	Theoretical Molecular Weight (g/mol)	Melting point	Yield (%)	Colour of the crystals
BZT 1	C ₁₅ H ₁₃ N ₅ O ₂ S	327.3	177-179	71	Dark brown
BZT 2	C ₁₄ H ₁₂ N ₆ O ₂ S	328.3	164-165	77	Red brown
BZT3	C ₁₅ H ₁₂ N ₄ O ₃ S	328.3	143-144	68	Brown
BZT 4	C ₁₄ H ₁₁ N ₅ O ₃ S	329.3	184-186	75	Dark brown

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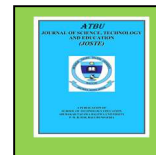


Table 2 shows the physical properties of the synthesized azo dyes. All the purified dyes exhibited fairly well-defined melting points characteristics of a pure compound. Thus, dyes from low-melting diazo components tended to have low melting points themselves and the factors determining high melting points were generally preserved in the dyes from high-melting heteroaryl amine as shown in Table 2 above. Thienyl-2-azo dyes with 3-cyano groups had higher melting points than their analogues with

alkyl esters, which Hallas and Towns (1996a, 1996b) had earlier observed, may be as result of increased polarity and / or the rod like shape of the cyano group being more conducive to efficient packing in the crystal structure. For instance, dye BZT 1, BZT 2, BZT 3 and BZT 4 had melting point of 177-179, 164-165, 143-144, and 184-186 °C respectively. These figures are close in magnitude to that of 1,3- benzothiazole intermediate 1 and intermediate 2 (Robert *et al* 2005).

Table 3: Spectroscopic Properties of the synthesized intermediates and Dyes

Intermediates/Dyes	FT-IR (cm ⁻¹)	GC-MS Mass (m/z)	¹ H and ¹³ C-NMR (400 MHz, DMSO-d ₆)
Inter 1	3365.8 (N-H str.), 1550.6, 1502.2 (C=C, C-N str.), 1621.4 (C=N str.), 700.7, 745.5 (C-S).	15, 28, 106, 150, 120, 92, 165.0	8.53(S,2H,NH ₂), 7.78(d,1H, J=4Hz), 7.72(d,1H, J=8.0Hz), 7.56(S,1H), 7.39(S,2H,NH ₂); 168.32, 149.22, 131.69, 129.33, 118.43, 117.07, 114.48.
Inter 2	3291.2, 3056.4 (OH, N-H str.), 1505.8, 1599.0 (C=C, C-N str.), 1625.1, 1684.8 (C=N str.), 738.0, 793.1 (C-S)	93, 73, 27, 62, 165.0	10.04(S, 1H, OH), 8.10(S, 2H, NH ₂), 7.76(d, 1H, J=8.0 Hz), 7.68(S,1H), 7.62(d, 1H, J=8.0Hz); 147.40, 145.26, 129.70, 129.39, 124.59, 114.60, 114.28
BZT 1	3354.6, 3317.3, 3198.1 (N-H str.), 2967.0, 2922.2 (C-H str.), 1602.8, 1647.5 (C=N str.), 1490.9, 1543.1 (N=N), 775, 711.9 (C-S).	66, 165, 137, 225, 93.1, 327.3	10.39(S, 1H, COOH), 8.27(S, 2H, NH ₂), 7.93(S, 1H), 7.81(d, 1H, J=8Hz), 7.73(S, 2H, NH ₂), 7.66(S, 1H), 6.84(d, 1H, J=12Hz), 3.06(S, 3H, CH ₃); 162.26, 141.41, 140.06, 139.25, 138.30, 131.90, 130.28, 129.67, 128.99, 128.95, 128.33, 125.70, 124.53, 123.57, 20.56
BZT 2	3421.7, 3267.3 (N-H str.), 1625.1, 1662.4, 1695.9 (C=N), 1505.8, 1539.4 (N=N str.), 797.7, 752.9 (C-S).	57, 207, 253, 119, 91, 328.3	10.37(S,1H,COOH), 8.25(S, 1H), 8.08(S,4H, 2NH ₂), 7.71(S, 2H, NH ₂), 7.78(d, 1H, J=12 Hz), 7.71(S, 1H), 6.82(d, 1H, J=8.0 Hz); 166.31, 151.38, 149.27, 148.79, 145.27, 141.85, 139.27, 138.79, 132.09, 130.19, 130.19, 127.50,

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BZT 3	3459.0, 3309.9 (OH, N-H str.), 2922.2 (C-H str.), 1695.9, 1666.1, 1606.5 (C=N str.), 1528.2 (N=N str.), 745.5 (C-S).	64, 95.9, 195.9, 225.1, 328.3	121.49, 117.98, 117.01, 10.38(S, 1H, COOH), 10.08(S, 1H, OH), 8.31(S,2H, NH ₂),8.23(S, 1H), 8.13(S, 1H), 7.8(d, 1H, J=8Hz), 7.11(d, 1H, J=8Hz), 2.24(S, 3H, CH ₃); 168.30, 142.45, 141.10, 140.30, 139.34, 132.94, 131.32, 130.71, 130.04, 129.99, 129.38, 126.74, 125.57, 21.94
BZT 4	3328.5 (OH, N-H str.), 1602.8, 1662.4 (C=N), 1528.2 (N=N str.), 752.9 (C-S)	55.1, 95.1, 135.1, 163 329.3	10.40(S,1H,COOH),10.04(S, 1H, OH), 8.32(d,1H, J=12 Hz), 8.26(d, 1H, J=12 Hz), 8.14(S, 4H, 2NH ₂), 7.86(S, 1H), 7.60(S, 1H);173.51, 157.29,148.18,145.95, 142.76,141.74,140.47, 139.69, 138.32, 136.69, 136.42, 132.58, 130.53, 129.20, 128.75, 126.88, 122.46, 119.73

Table 3.0 shows the IR-vibrational frequencies, GC-MS and NMR spectroscopy studies of the synthesized dyes and its intermediates and the result obtained indicates that 1, 3-benzothiazole intermediate 1 and 2 show absorption peaks in the range 1550.6-1599.0cm⁻¹ due to the presence of C=C and C=N. The amino group absorption for the two intermediate appeared in the range 3291.2-3365.8 cm⁻¹. However, the vibrational frequency obtained for the synthesized dyes shows the characteristics absorption peaks due to stretching frequency of the NH-group in the region 3198.1-3459 cm⁻¹. The IR spectra of the prepared azo dye also showed an absorption peak in the region 1490.9-1543.1 cm⁻¹ attributed to azo chromophoric group(N=N), while the observed peak in the region 1602.8-1695.9 was due to V_{C=N} as outline in Table 3. Thus intermediate 1 and 2 showed intense molecular ion peaks at m/z 165 and 166±1, consistent with the molecular formulae C₇H₇N₃S and C₇H₇N₂SO respectively. The molecular ion of the

intermediate 1 shown in Table 3 underwent different fragmentation. Also Dye BZT 1, BZT 2, BZT 3 and BZT 4 showed molecular ion peaks at m/z 327.3, 328.3, 328.3 and 329.3 respectively which is consistent with the molecular formula of the dyes as indicated in Table 2b. The ¹H and ¹³C- NMR spectra for the synthesized dye showed eight signals with a highly deshielded signal at 10.39 ppm (1H, singlet) which is attributed to the presence of the OH of the carboxylic group, 7.73 – 8.27 ppm due to the presence of amino (-NH₂) protons. Two signals were observed for two pairs of aromatic proton in the (6.84 – 7.81) ppm range with a coupling constant of 8 – 12 Hz. Also a distinct signal was observed upfield at 3.06 ppm due to the presence of methyl (CH₃) proton. The ¹³C-NMR spectrum of the Dyes showed the signal at 162.26 ppm for the carbon atom in the COOH group. Thus a signal at 141.41 ppm for carbon atom in the thiazole ring was also observed while the signal at 140.06 -115.56 ppm for aromatic carbon.

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Table 4: Wash Fastness and Light Fastness of the Synthesized Dyes on Chrome Tanned Leather

Dyes	Change	Staining	Light Fastness	% Exhaustion	Colour on Substrate
BZT 1	4-5	4-5	5	78	Red brown
BZT2	5	4	5	74	Dark brown
BZT3	4	4	6	80	Brown
BZT4	4	5	5	70	Pink

Table 5: Wash Fastness and Light Fastness of the Synthesized Dyes on Vegetable Tanned Leather

Dyes	Change	Staining	Light Fastness	% Exhaustion	Colour on Substrate
BZT 1	4	5	6	65	Dark red
BZT2	5	4-5	5	74	Brown
BZT3	5	4-5	6	62	Red
BZT4	5	5	5	82	Dark red

The heterocyclic dye BZT 1, BZT 2, BZT 3 and BZT 4 were applied at 2 % depth on polyester and nylon 6, 6 fabric. Their dyeing properties are given in Table 4 and 5. These dyes gave pink, dark red, brown and dark brown hues with brighter and deeper shades, tinctorial strength and excellent levelness on the fabric. The variation in the shade of dyed fabric results from alteration in the diazo and coupling component. Thus from Table 4 and 5 all the dyes show good to excellent fastness to washing on chrome tanned leather and good to very good fastness to washing in vegetable tanned leather respectively. The remarkable degree of levelness and brightness after washing indicate good penetration and excellent affinity of the dyes to the leather. In addition the result obtained showed that the dyed leather have excellent fastness to washing which may be due to the absence of solubilizing group, which affect solubility and washing ability of the dye-out of the fabric. Also, the fastness properties are interrelated since they depend, among other things such as the rate of diffusion of the dyes on fabric. This rate is a function of the geometry of dye molecule, the concentration of the dye in the fabric which appeared to be the most influential factor in the fastness of dyeing. (Dawson, 1991). However, the light fastness ratings of the dyed chrome and vegetable tanned leather are shown in Table 4-5 showing very good to

excellent light fastness. The intramolecular hydrogen bonding between amine and azo group can also be ascribed to be responsible for higher value of light fastness (Divyesh *et.al* 2014). In a related work by (Evans and Stapleton, 1978). It was also observed by Maradiya, 2010, that there is no absolute value for the light fastness of a dye.

CONCLUSION

Heterocyclic based dyes derived from substituted 1, 3-benzothiazole as diazo components was synthesized and the intermediate was diazotized, coupled with 3-amino-2-methylbenzoic acid and 3, 5-diaminobenzoic acid. The dyes were purified by re-crystallization and was characterized using FT-IR, GC-MS and ¹H and ¹³C-NMR. The dyes gave mostly brown, dark brown, dark red orange and pink shades on the chrome and vegetable tanned leather and exhibited good to excellent washing fastness properties on the substrate and moderate to very good light fastness indicating that the dyes were good on both substrate.

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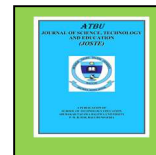
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