International Journal of Materials Chemistry and Physics
Vol. 6, No. 1, 2020, pp. 7-13
http://www.aiscience.org/journal/ijmcp
ISSN: 2471-9609 (Print); ISSN: 2471-9617 (Online)

Synthesis of Diazo Dye from Sulpanilic Acid Using 3-Aminophenol and N,N-Dimethylaniline as Couplers and It Application on Linen Fibre

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Abstract

4-[(*E*)-(4-amino-2-hydroxyphenyl)diazenyl]benzene-1-sulfonic acid (monoazo dye) and 4-[(*E*)-(4-{(*Z*)-[4-(dimethylamino)phenyl]diazenyl}-2-hydroxyphenyl)diazenyl]benzene-1-sulfonic acid (Diazo dye) were described, synthesized from sulphanilic acid by diazotization and coupled with 3-aminophenol and further coupled with N,N dimethylaniline with 75.03 and% 80.02% yield respectively. The monoazo dye gave λ_{max} of 435 nm in DMSO, melting point of 222-224°C and the diazo also gave λ_{max} of 450 nm in DMSO, melting point of 118-120°C. The chemical structures of synthesized compounds were studied using UV-Visible spectrophotometer, FTIR, ^{1}H-NMR and ^{13}C-NMR. The synthesized dyes were applied on linen fibre which has been previously modified by acetylation, methylation and benzoylation. The fastness property afforded very good light fastness, excellent washing and rub fastness.

Keywords

Synthesize, Diazotization, UV-visible Spectrophotometer, FTIR, ^{1}H-NMR and ^{13}C-NMR

Received: February 1, 2020 / Accepted: March 5, 2020 / Published online: April 7, 2020

1. Introduction

Azo dyes are the largest group of synthetic dyes, constituting about 60-70% of all the commercial dyes produced [1]. They are relatively cheap, easy to produce, very easy to apply and possess a wide range of colour for both synthetic and natural fibre. This range of colour includes yellows, reds, oranges, violets, navy blues and blacks but green shades are limited [2]. The structural features in organic compounds, that commonly produce colour are =C = C=, –N = O, –N=N–, aromatic rings, = C = O and $–NO_2$ [3].

The depth of shades is usually affected by the number of azo groups present in the dye structure, increasing the number of azo groups to two, three or even four in a single dye structure help to increase the depth of the shade. But the greater the depth of shade the duller the brightness [2, 4, 5].

Azo dyes are applied in biological system and as indicator in complexometric titration of analytical chemistry [6]. Most of the dyes available for industrial use today are azo dyes, which are majorly prepared from diazotization-coupling reaction [3]. Aromatic azo compounds are used as acid-base indicators in asnalytical chemistry, also used in pharmaceutical industries and commercial colourants for clothing, plastics, cosmetics and food beverages. Colour

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changes when used as indicators are caused by change in extent of delocalization of electrons [7]. The greater the delocalization the more the shifts of the absorption max to longer wavelength and causes the light absorbed redder (i.e duller and of more hue), while less delocalization shifts the absorption max to shorter wavelengths [8].

Among other industries such as food, cosmetic, paper and printing industries consuming dye, textile industries remain the largest consumers of commercial dyes produced [9]. Out of the different classes of dyes, azo dyes constitute the largest group of colourant and the most versatile class of dyes used in the industry [10, 11, 12].

Our area of interest in this research is the synthesis of diszo dye from Sulpanilic acid using 3-aminophenol and N, N-dimethylaniline as couplers and it application on linen fibre.

2. Experimentals

2.1. Materials/Equipment

The chemicals used in this work were of analytical grade purchased from Eddyson Nigeria Plc, these include sulphanilic acid, 3-amino phenol, N-N dimethylaniline, and the fibre use was linen material from France. Gallenkamp melting point apparatus, electronic balance (JA2003), UV-visible spectrophotometer (Jenway 6405), FTIR (Cary 630 Agilent technologies USA series), SEM (Phenom Pro X), Tensile Strength Machine (Instron Universal tensile machine) ^{1}H-NMR and ^{13}C-NMR (Bruker Avance DPX 250 NMR spectrophotometer) were used in this research.

2.2. Pre-treatment of Materials

The glasswares were soaked with a mixture of detergent and dilute HNO_3, washed and rinsed with distilled water then dried at 105°C to prevent contamination while the experiment was being carried out.

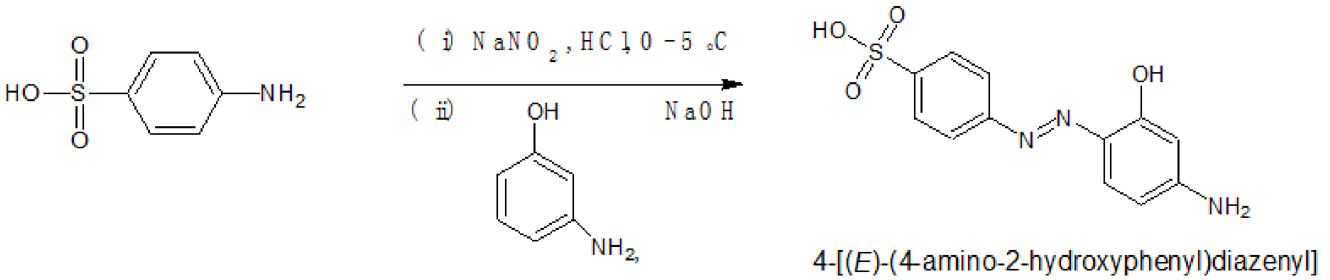
Synthesis of Monoazo dye

Rxn 1:

The synthesis was carried out according to the standard method reported by [13] with some modifications. Sulphanilic acid (4.33 g) was added to conc. HCl (2.5 ml). Distilled H_2O was added to the mixture in 250 ml round bottom flask. Thereafter, crushed ice (12.5 g) was added to conc. HCl (3.75 ml) and the mixture was added to the content of the round bottom flask at 0 – 5°C. Then, $NaNO_2$ (1.8 g) was dissolved in distilled H_2O (3.5 ml) and the solution was gradually added to the mixture in round bottom flask at 0 – 5°C. After that, sulphamic acid (25%) was added in excess. 3-aminophenol (2.73 g) was dissolved in ethanol (20 ml) and added to the resulting mixture and stirred continuously for 1 h. Thereafter, NaOH (5 ml, 20%) was added and continued the stirring intermittently for 1 h. the product (4-[(*E*)-(4-amino-2-hydroxyphenyl) diazenyl]benzene-1-sulfonic acid was filtered under vacuum, washed with distilled H_2O, acetic acid (10%) and cold methanol. It was recrystallized by toluene. The percentage yield was 75.03% and the melting point at 222 – 224°C. The synthetic route of the monoazo dye is shown in Rxn 1

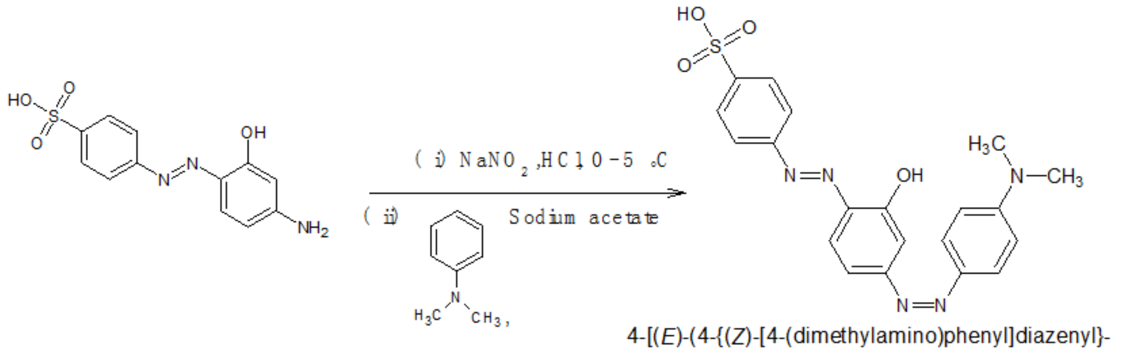
2.3. Synthesis of Diazo Dye

Monoazo dye (3 g) obtained was weighed into a 250 ml beaker containing distilled H_2O (15 ml). Conc. HCl (5 ml) was added to the mixture in the 250 ml beaker. Thereafter $NaNO_2$ (3.6 g) was added to the mixture and stirred for 30 min at 0 – 5°C. The diazonium salt solution formed was slowly added to a solution of N,N-Dimethylaniline (2 ml) in crystallize sodium acetate (3 g) in distilled H_2O (5 ml) with vigorous stirring at 0-5°C for 2 h. The dye product (diazo dye) with chemical name (4-[(*E*)-(4-{(*Z*)-[4-(dimethylamino)phenyl]diazenyl}-2-hydroxyphenyl)diazenyl]benzene-1-sulfonic acid), was filtered, washed with distilled H_2O and recrystallized from carbon tetrachloride. The percentage yield was 80.02% and the melting point at 118 – 120°C. The synthetic route of the diazo dye is shown in Rxn 2.



4-[(*E*)-(4-amino-2-hydroxyphenyl)diazenyl]
benzene-1-sulfonic acid

Rxn 2:



4-[(*E*)-(4-{(*Z*)-[4-(dimethylamino)phenyl]diazenyl}-2-hydroxyphenyl)diazenyl]benzene-1-sulfonic acid

2.4. Dyeing of Linen Fibre

The dyeing of the linen fibre was carried out according to method reported by [14], using the synthesized dyes of 2% on weight of fibre (Plate 2), usually expressed as percentage. The dyes solutions were obtained by dissolving the dyes in water. To these solutions at temperature 35 - 40°C, 10% sodium sulphate and 4% acetic acid with concentration of 30% were added. The previously wetted linen fibre (1 g) was dipped into the dye bath and dyed for 30 min at this temperature. The temperature was raised to boiling and the material was boiled for 30 min. After dyeing was completed, the fibre (Plate 1) was removed, thoroughly rinsed with cold running water and dried at room temperature. The summary of fastness test result is reported in Table 2.

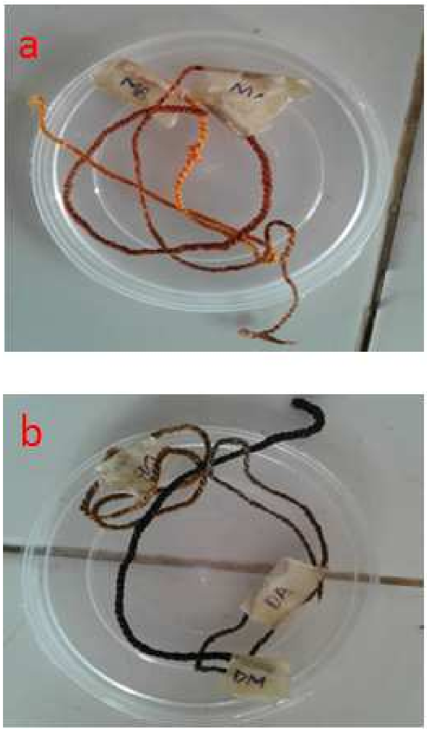


Figure 1. Dyed Linen Fibre (a = Monoazo dyed fibre and b = diazo dyed fibre).

3. Result and Discussion

3.1. Synthesis and Characterization of Monoazo Dye

The Dye 1 melted with decomposition at 222-224°C and yielded 75.03% when recrystallized from toluene. Table 1 gave the summary of the physical property of monoazo and diazo dye. The FTIR spectrum in the Figure 1 revealed the characteristic medium absorption band at 1554.35 cm^{-1} of azo group (-N=N-) stretching vibration [15]. This confirmed the presence of azo group in monoazo dye. The characteristic medium absorption band at 818.78 cm^{-1} confirmed the presence of meta and para di-substituted aromatic ring as shown in the Figure 1 [15, 16]. The absorption band for primary amine group (NH_2) show a duplet band at 3259.00 cm^{-1} and 3097.46 cm^{-1} for stretching vibration confirmed the presence of amino group in the structure [15]. The characteristic absorption band for hydroxyl group at 3452.21 cm^{-1} which was confirmed by absorption band at 1017.27 cm^{-1} for C-O bond established the presence of hydroxyl group. This was not in variance with the work done by Otutu, [15]. Absorption band shown at 1411.25 cm^{-1} possibly indicate the presence of sulfonic group. The ^{1}H NMR spectrum shown in Figure 2 contained eleven peaks, of which peaks at 6.09-8.5 ppm confirmed the presence of an aromatic ring in the structure. Peaks at 2.40 ppm was due to the solvent (DMSO) used. The chemical structure of monoazo dye as shown in 1 revealed 12 aromatic carbon atoms, but two groups of the carbon atoms were in the same chemical environment. Thus, ten (10) aromatic carbon atoms were in different chemical environments. The peaks in the range of 100 – 150 ppm were characteristics of aromatic carbon atoms. The ten (10) peaks in the range of 100 – 150 ppm confirmed the presence of two (2) aromatic rings in the structure of monoazo dye.

Table 1. Physical Properties of the Synthesized monoazo and diazo dye.

Properties	**Monoazo dye**	**Diazo dye**
Percentage yield (%)	75.03	80.02
Colour	Burgundy	Burnt brown
Melting point (^{O} C)	222-224	118-120
λ_{max} (nm) in DMSO	435.00	450.60
Colour on dyed linen fibre	Brilliant Orange	Deep/Dark Orange

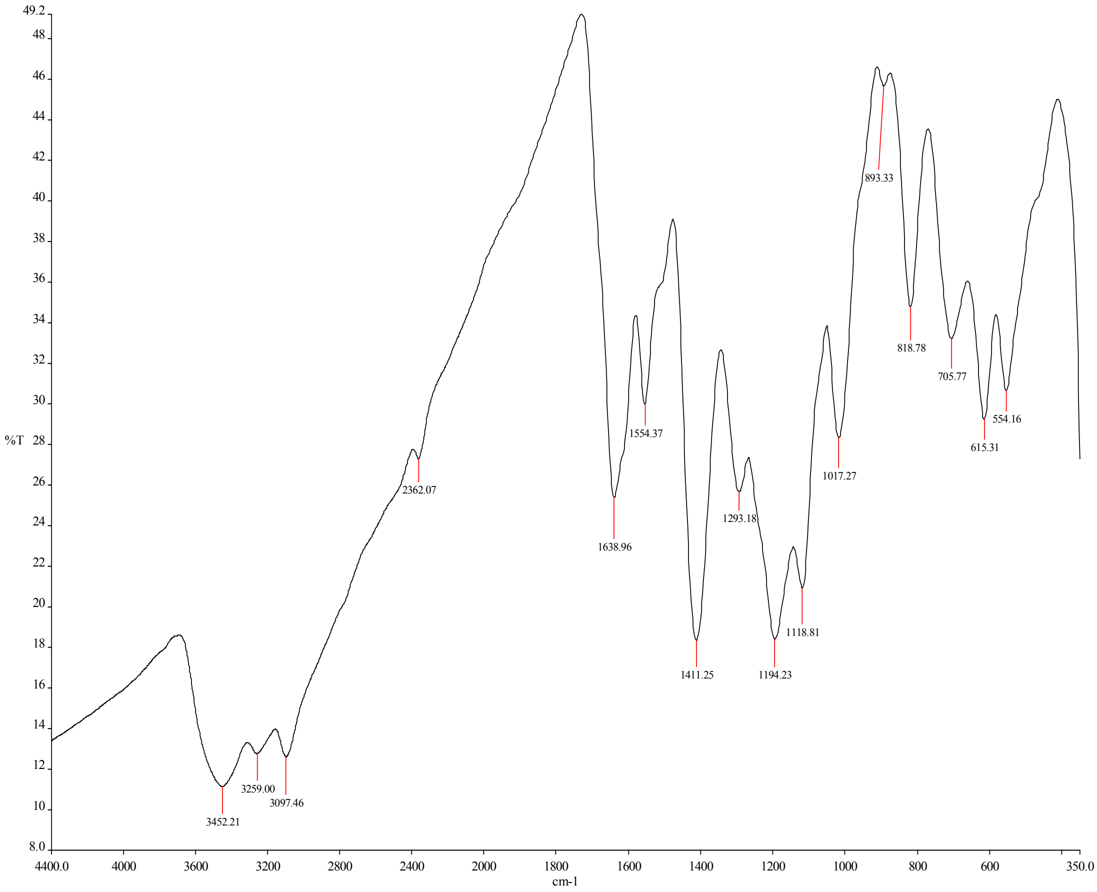
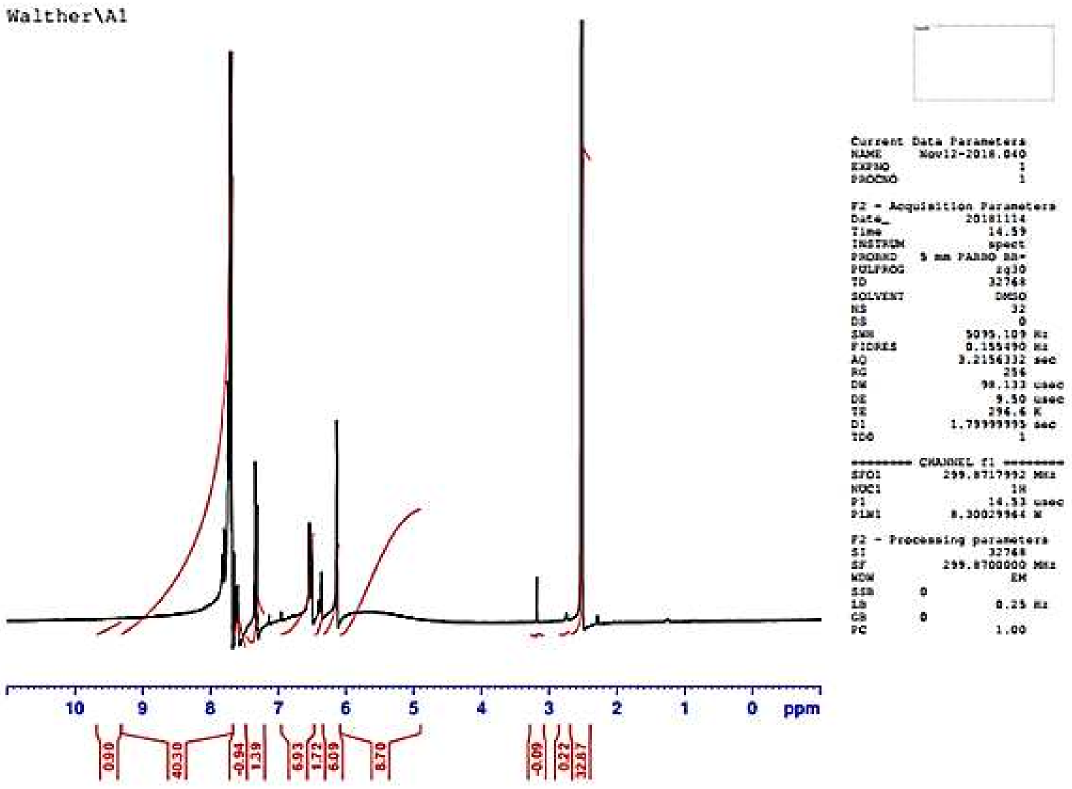


Figure 2. FTIR bands for monoazo dye.



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PROCNO                 1

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PULPROG             zg30
TD                 32768
SOLVENT             DMSO
NS                    32
DS                     0
SWH             5095.109 Hz
FIDRES          0.155490 Hz
AQ             3.2156332 sec
RG                   256
DW                98.133 usec
DE                  9.50 usec
TE                 296.6 K
D1            1.79999995 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         299.8717992 MHz
NUC1                  1H
P1                 14.53 usec
PLW1          8.30029964 W

F2 - Processing parameters
SI                 32768
SF           299.8700000 MHz
WDW                   EM
SSB        0
LB                  0.25 Hz
GB         0
PC                  1.00
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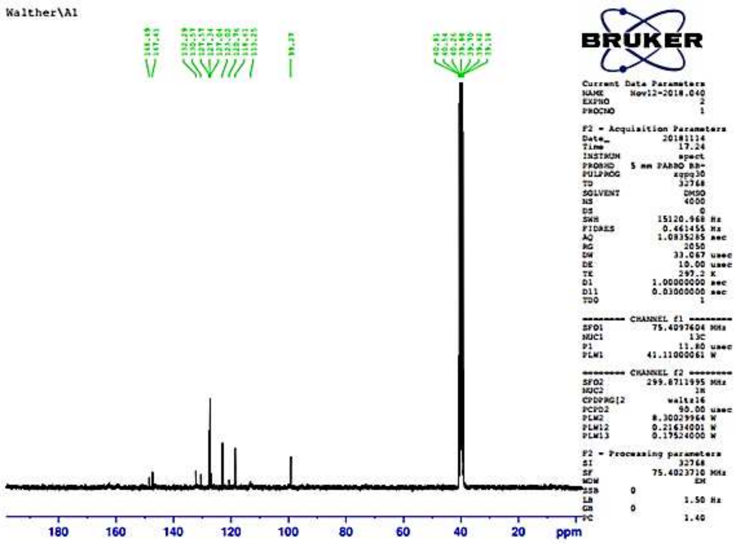
Figure 3. Proton NMR peaks for monoazo dye.



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PULPROG          zgpg30
TD                32768
SOLVENT            DMSO
NS                 4000
DS                    0
SWH           15120.968 Hz
FIDRES         0.461455 Hz
AQ            1.0835285 sec
RG                 2050
DW               33.067 usec
DE                10.00 usec
TE                297.2 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.4097604 MHz
NUC1                13C
P1                11.80 usec
PLW1        41.11000061 W

======== CHANNEL f2 ========
SFO2        299.8711995 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         8.30029964 W
PLW12        0.21634001 W
PLW13        0.17524000 W

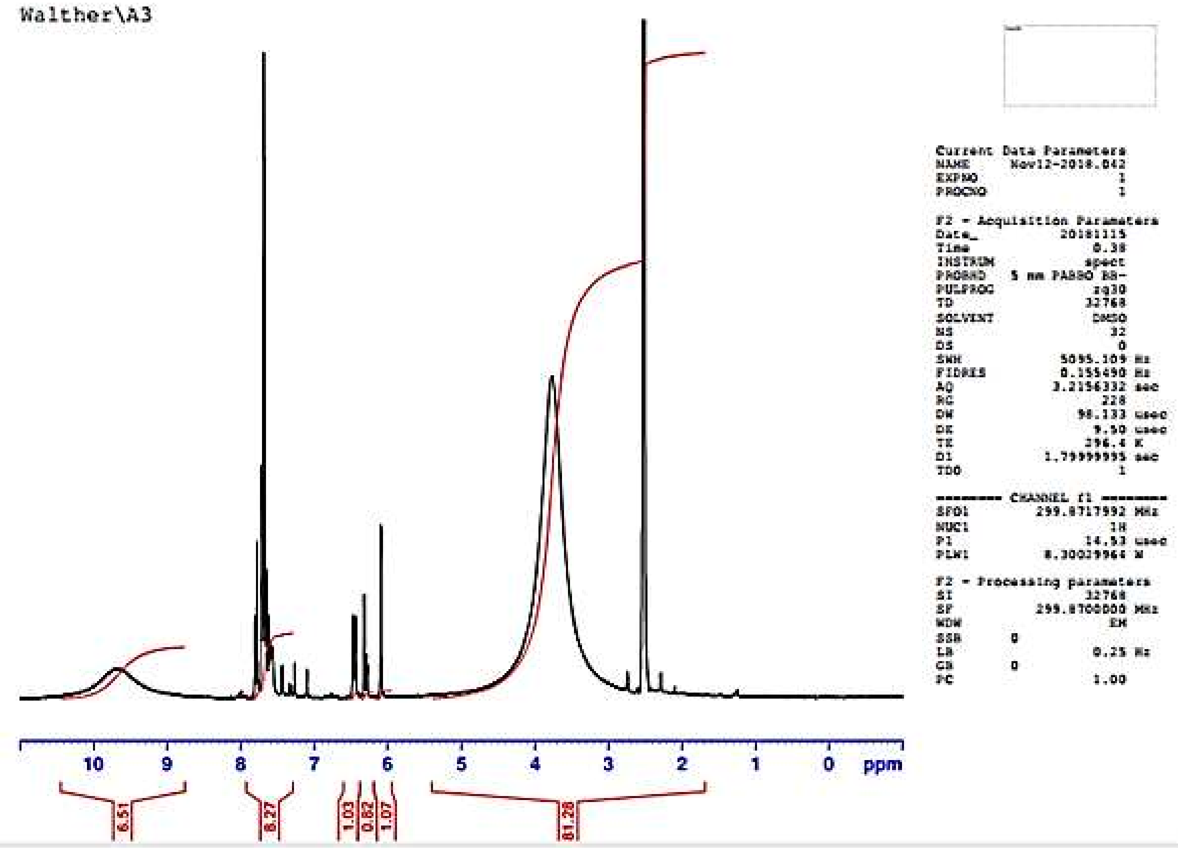
F2 - Processing parameters
SI                32768
SF           75.4023710 MHz
WDW                  EM
SSB        0
LB                 1.50 Hz
GB         0
PC                 1.40
```

Figure 4. ^{13}C NMR peaks for monoazo dye.

3.2. Synthesis and Characterization of Diazo Dye

The diazo dye melted with decomposition at 118-120°C and yielded 80.02% when recrystallized from toluene. The FTIR spectrum in Figure 4 revealed the characteristic absorption band at 1557.86 cm^{-1} of azo group (-N=N-) stretching vibration. This confirmed the presence of azo group in diazo dye. The characteristic medium absorption band at 812.70 cm^{-1} confirmed the presence of meta and para di-substituted aromatic ring as shown in the Figure 4 this agrees with the work done by [15, 16]. The characteristic absorption band at 3437.00 cm^{-1} for stretching vibration confirmed OH group presence in diazo dye. This also corresponds with work done by [15]. The sharp characteristics absorption band shown at 1387.51 cm^{-1} possibly indicate the presence of sulfonic group in the Figure 4. The ^{1}H NMR spectrum shown in Figure 5 contained eleven peaks, of which peaks at 6.09-8.5 ppm confirmed the presence of an aromatic ring in the structure. Peaks at 3.7 ppm and 9.5 ppm confirmed the presence of hydroxyl proton. Peaks at 2.40 ppm was due to the solvent (DMSO) used. The chemical structure of diazo dye as shown in 2 revealed 18 aromatic carbon atoms, but four groups of the carbon atoms were in the same chemical environment. Thus, fourteen (14) aromatic carbon atoms were in different chemical environments. The peaks in the range of 100 – 150 ppm were characteristics of aromatic carbon atoms in the structure of diazo dye.

Figure 5. FTIR bands for diazo dye.



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PULPROG              zg30
TD                  32768
SOLVENT              DMSO
NS                     32
DS                      0
SWH           5095.109 Hz
FIDRES        0.155490 Hz
AQ           3.2156332 sec
RG                    228
DW             98.133 usec
DE               9.50 usec
TE              296.4 K
D1          1.79999995 sec
TD0                     1

======== CHANNEL f1 ========
SFO1       299.8717992 MHz
NUC1                   1H
P1              14.53 usec
PLW1         8.30029964 W

F2 - Processing parameters
SI                  32768
SF         299.8700000 MHz
WDW                    EM
SSB      0
LB                0.25 Hz
GB       0
PC                   1.00
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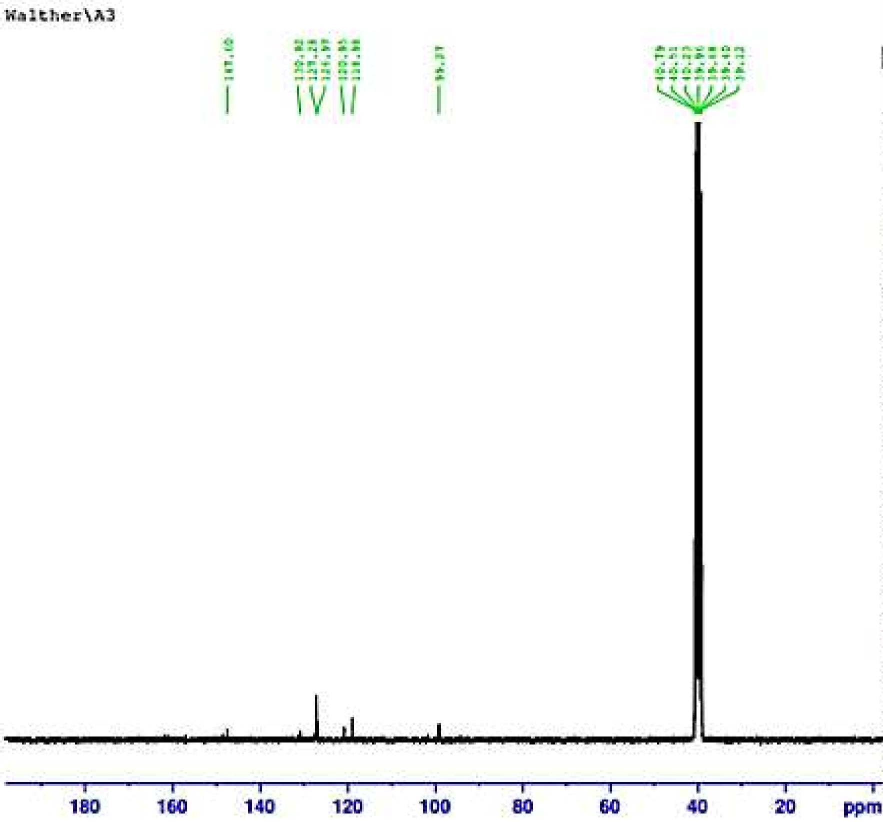
Figure 6. Proton NMR peaks for diazo dye.



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PROCNO                  1

F2 - Acquisition Parameters
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PULPROG           zgpg30
TD                  32768
SOLVENT              DMSO
NS                   4000
DS                      0
SWH          15120.968 Hz
FIDRES        0.461455 Hz
AQ           1.0835285 sec
RG                   2050
DW             33.067 usec
DE              10.00 usec
TE              296.8 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        75.4097604 MHz
NUC1                  13C
P1              11.80 usec
PLW1        41.11000061 W

======== CHANNEL f2 ========
SFO2       299.8711995 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2           90.00 usec
PLW2         8.30029964 W
PLW12        0.21634001 W
PLW13        0.17524000 W

F2 - Processing parameters
SI                  32768
SF          75.4023710 MHz
WDW                    EM
SSB      0
LB                1.50 Hz
GB       0
PC                   1.40
```

Figure 7. ^{13}C NMR peaks for diazo dye.

Table 2. Fastness property of Linen Fibre.

TEST SAMPLE	Light Fastness			Wash Fastness			Rub Fastness		
U_F	3	3+	3	3+	4	3	2+	3	3+
M_A	3	5	4	5	4	3	3+	4	4
M_B	3+	4	5	4+	5	4	4	5	4
M_M	5	4	5	5	5	4+	5	4+	5
D_A	5	4+	4	4	5	3	4	3	5
D_B	4+	4	5	3+	5	4	5	4+	3
D_M	5	5	4	5	5	5	5	4	5

Keys: U_F = Untreated fibre, M_A = Monoazo Acetylation, M_B = Monoazo Benzoylated, M_M = Monoazo Methylated, D_A = Diazo Acetylated, D_B = Diazo Benzoylated, D_M = Diazo Methylated. Grey Scale Rating: 1- Poor; 2- Below Average; 3- Average; 4- Good; 5 Excellent; + - ½.

4. Conclusion

The monoazo and diazo dye were synthesized and characterised by conventional method and their colour properties examined by application on modified linen fibre. The yield of the monoazo and diazo dye were 75.03 and 80.02% respectively showing the dyes have good yield value and it may be economical. The dye-ability study on chemically modified linen showed excellent result with methylated linen fibre. These dyes gave Burgundy and Burnt brown colour for monoazo and diazo dye respectively. On application to fibre, monoazo dye gave a brilliant orange colour while diazo dye shows a deepened colouration on application on fibre showing a brown to deep brown colouration. The remarkable degree of levelness after exposure to xenon arc light, washing and rubbing indicate good penetration and affinity of these dyes to the fibre.

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