

Synthesis, Characterization and Application of Monoazo Disperse Dyes Derived From 4-Aminobenzaldehyde and 4-Amino-3-Nitro-Benzaldehyde as Diazo Components on Polyester

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Abstract: Monoazo disperse dyes were synthesized from 4-aminobenzaldehyde and 4-amino-3-nitrobenzaldehyde as diazo components. The Diazonium solutions from both components were coupled to various coupling components such as 1-naphthol, 2-naphthol, resorcinol, phloroglucinol and phenol to produce series of dyes with hydroxyl group(s). The physical characteristics of the dyes such as melting point, molecular weight, yield and colour were studied. The dyes were characterized using Ultraviolet, Infrared and Gas chromatography - mass spectrometry. The Infrared Spectroscopy confirmed the presence of the functional groups in the intermediates and dyes. The observed functional groups are O-H, N-H, N=N, C=C of aromatic, C=O and C-H. The functional groups absorbed at frequencies consistent with literatures. The mass spectroscopy revealed that the molecular ion peaks were consistent with the molecular mass of the proposed structures while some daughter ions and base peaks were observed based on some fragmentation patterns. The mass spectral data of intermediate 4-amino-3-nitrobenzaldehyde, for instance, showed molecular ion peak at m/z 166 (21% M^+) which was in concordance with the molecular mass (166g/mol) of the compound, while the base peak was observed at m/z 65(100%). Other prominent peaks that appeared at m/z with relative abundance are: 166(21% M^+); 65(100%); 39(43%); 52(40%); 91(25%); 119(20%); 150(1%) and 136(1%) respectively. It was observed that variation of coupling components resulted in different dyes with different colours. The synthesis of series of naphtholic and phenolic azo dyes was successfully achieved using various substituted phenol and naphthol derivatives as the coupling components. Intensity of colours are tinctorially strong black, orange red and golden yellow monoazo disperse dyes. The azo disperse dyes herein synthesized were applied to polyester fabrics and their fastness properties determined and found to be excellent on the substrate.

Key words: 4-amino-3-nitrobenzaldehyde, exhaustion, washfastness, phloroglucinol and disperse dyes.

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I. Introduction

Disperse dyes have low solubility in water, but they can interact with the polyester chains by forming dispersed particles. Their main use is in the dyeing of polyesters, and they find minor use in dyeing cellulose acetates and polyamides. Generally, the structure of disperse dyes is small, planar and non-ionic, with attached polar functional groups like -OH, -NO₂ and -CN. The shape makes it easier for the dye to slide between the tightly-packed polymer chains, and the polar groups improve the water solubility, improve the dipolar bonding between dye and polymer and also affect the colour of the dye (Broadbent, 2011). Disperse dyes have also been defined as sparingly water soluble, nonionic dyes applied to hydrophobic fibres from aqueous dispersions (Philip, 2005). Disperse dyes are classified as either nitroarylamine, azo, or anthraquinone. Almost all contain amino (NH₂) or substituted amino groups but do not contain solubilizing groups such as sulphonic acid (SO₃H) groups. The most dominant group of disperse dyes is the azo disperse dyes which account for over 70% of all disperse dyes manufactured. Disperse dyes, though originally developed to dye cellulose acetate, are now usefully applied to other hydrophobic fibres such as polyester (Meena *et al.*, 2013). Although Lams *et al.* (2014) reported the synthesis of 4-amino-3-nitrobenzaldehyde, there seems to be no report in literature on the effect of nitration in the synthesis of disperse dyes. The remarkable synthetic importance of nitro compounds has ensured long standing studies of their utilization in organic synthesis. Nitro compounds especially aromatic nitro compounds are important for precursors of azo dyes and explosives. In addition, they have proven to be valuable reagents for synthesis of complex target molecules (El-Molla *et al.*, 2013). The newly synthesized azo dyes incorporated nitro moiety seems to be interesting for application to polyester fabrics. Furthermore, optical

measurements and fastness properties of the dyes will be investigated for their dyeing characteristic on polyester. The results in general will reveal the efficiency of the prepared compounds as new azo dyes for commercial usage.

II. Materials and methods

All the chemicals used in the synthesis of the dyes and intermediates were of analytical grade and were used without purification. Melting points were determined by the open capillary method using the Gallenkamp melting apparatus. The visible absorption spectra were measured using Jenway 405 UV/Vis spectrophotometer, IR was measured and recorded in KBr pellets using FTIR-Buck Scientific Model M530, while GC-MS was carried out using the GCMS-system Model 7890BMSD (5977A) Agilent Technology. The rubbing fastness test was carried out with a Crockmeter.

2.1 Synthesis of 4-amino-3-nitro benzaldehyde

Acetic anhydride (150 cm³) was added to 4 - acetylaminobenzaldehyde (I) (60 g) and heated to 105 °C with vigorous stirring until it has dissolved. The reaction mixture was rapidly cooled in an ice bath to 30 °C to obtain a fine precipitate (I). Concentrated nitric acid (24 cm³) and acetic anhydride (60 cm³) were carefully mixed and the mixture was added dropwise to the stirred suspension of 4- acetyl aminobenzaldehyde at such a rate that the temperature did not rise above 35 °C. After the addition of about one third of the acid, colourless crystals were deposited which were shown to be 4- acetyl aminobenzylidenediacetate (II) (Lams *et al.*, 2014). The acid was further added dropwise so as to dissolve the diacetate. Towards the end of the addition, the temperature was allowed to rise to 50 °C. The mixture was stirred at this temperature for a further 15 mins and then poured into an ice water (800 cm³). The precipitated 4- acetyl amino -3- nitrobenzylidenediacetate was filtered off, washed thoroughly with ethanol and then with water and dried. Recrystallized from ethanol, the diacetate was obtained as pale yellow needles (III). Concentrated hydrochloric acid (200 cm³) was added to 70 g of the diacetate and heated on a water bath for 15 min and cold water (300 cm³) was added. The precipitated 4-amino-3-nitrobenzaldehyde was filtered off, washed with water and dried. It was then purified by recrystallization from water to obtain orange needle-like crystals (IV) (Lam *et al.*, 2014).

2.2 Synthesis of 4- aminobenzaldehyde

To 600 cm³ of distilled water in a beaker, 30 g (0.125 mol) of crystalline sodium sulfide monohydrate was added. Sulphur (15 g) and sodium hydroxide pellets (27 g) were added to the reaction mixture. The mixture was heated in a steam bath for 15-20 minutes with occasional stirring and then poured into a round bottomed flask containing a hot solution of 50 g of p- nitro toluene in 300 cm³ of 95 % ethanol. The mixture was refluxed for 3 hours. The resulting clear but deep red solution was rapidly steam distilled until 1.5 - 2.0 cm³ of condensate was collected. The distillate was clear when the distillation was stopped. The residue in the flask had a volume of 500 - 600 cm³. The solution was rapidly chilled in an ice bath with occasional vigorous shaking and stirring to induce crystallization. After 2 hours in the icebath the golden yellow crystals of 4-aminobenzaldehyde were collected on a Buchner funnel and washed with 500 cm³ of ice water to remove sodium hydroxide. The product was immediately placed in a vacuum dessicator over solid potassium hydroxide pellets for 24 hours. (Budde, 2001). It was purified by recrystallization from ethanol.

2.3 Preparation of the Diazonium salt.

4-Amino-3-nitrobenzaldehyde (3.2 g, 0.02 mol) was added to a mixture of acetic acid (24 cm³) and water (6 cm³), and cooled with stirring to 12 °C in an ice-bath. Sodium nitrite (1.5 g, 0.02 mol) dissolved in water (10 cm³) was added in one portion and concentrated hydrochloric acid 10 cm³ was added immediately. The mixture was maintained at 15 °C for 15 min. Excess nitrous acid was destroyed by adding 0.1 g of urea. The solution was diluted with ice water (200 cm³) to give a clear solution of the diazonium salt (Lams *et al.*, 2014). The same procedure was used for the diazotization of 4-aminobenzaldehyde (See scheme 3)

2.4 Preparation of the coupling component.

The phenol (0.02 mol) was dissolved in 15 cm³ of 15 % sodium hydroxide (NaOH) solution and 200 cm³ ice water. The prepared diazonium solution was added dropwise with stirring at 0-5 °C continuously for 2 hours (Bello *et al.*, 1994). The same procedure was used for other coupling components.

2.5 Preparation of the dyes

The solution of the various coupling components was cooled to 0–5 °C and was treated with a cold solution (0–5 °C) of the diazonium salt (Scheme 3).. The resulting dye was filtered off, washed thoroughly with water until the washing was neutral and dried. The same procedure was followed to prepare coupling solutions with the substituted coupling components (Lams *et al.*, 2014).

2.7 Application of the synthesized dyes onto polyester Fabrics.

The dyeing was carried out on polyester material using the synthesized dyes in the laboratory of Abubakar Tafawa Balewa University, Bauchi. The dyeing process was carried out in a dye bath (beaker) with a liquor ratio of 50:1. A 1% stock solution of each of the dye was prepared and 2 cm³ was taken for each dye solution and put in the dye bath (beaker) and made up to 50 cm³ using distilled water. A 2 % shade dyeing was carried out in a 250 cm³ beaker. Water bath was used in raising the temperature of the bath. 1g of the fabric (Polyester) was wetted for some seconds and excess water squeezed out and then introduced in the dye bath at the temperature of 40 – 50 °C in the electro thermal and allowed to boil in the presence of 2 cm³ toluene as a carrier. The carrier volume was maintained for each dye bath. The time for each dyeing and the temperature was varied accordingly. After this, the fabric was removed and rinsed thoroughly in cold water and allowed to dry at room temperature. Before dyeing commenced, the polyester fibre was scoured in a solution containing 2 g/L sodium carbonate, and 1 g/L detergent for 30 minutes at 70 °C, neutralized in 1 ml/L acetic acid. Percentage exhaustion was calculated to determine the absorption unto the fabric by stripping with DMF and measured the concentration of the dyes on the fabric from the calibration curves.

2.8 Fastness properties of synthesized dyes

The washing fastness, light fastness, perspiration fastness were carried out on each fabric using the Standard procedures (Giles, 1974).

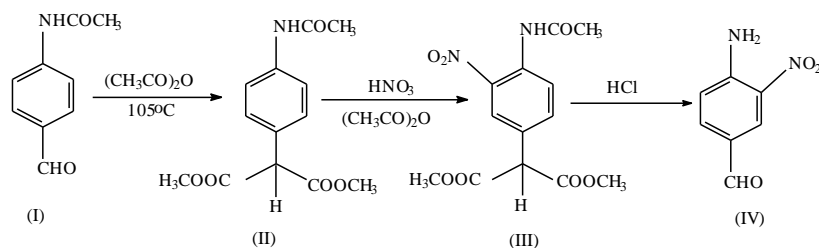
III. Results and Discussion.

3.1 Synthesis of intermediates and dyes.

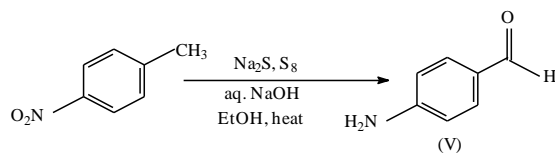
4-Amino-3-nitro-benzaldehyde was synthesized by nitrating 4-acetamido benzaldehyde with fuming nitric acid (d 1.5) in acetic anhydride, as shown in Scheme 1. In this reaction, the formyl group is converted in situ to the diacetate, which helps protect the group from oxidation. The protecting acetyl group were removed by acid hydrolysis to give (IV) as a yellow solid.

p-Aminobenzaldehyde was synthesized by following the reaction steps in Scheme 2. In this Scheme, mixture of crystalline sodium sulphide monohydrate, flowers of sulfur and sodium hydroxide pellets in water was heated on a steam bath with occasional stirring and then poured into hot solution of p-nitrotoluene in 95 % ethanol under reflux. The resulting solution was rapidly steam-distilled. The residue in the flask is diluted with hot water and chilled in an ice bath with vigorous shaking to induce crystallization. Golden yellow crystals of p-aminobenzaldehyde are collected by filtration.

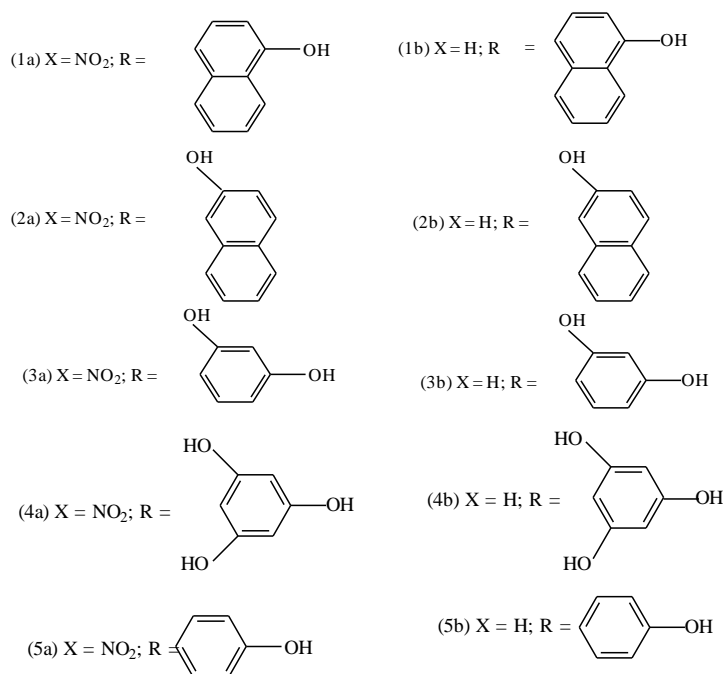
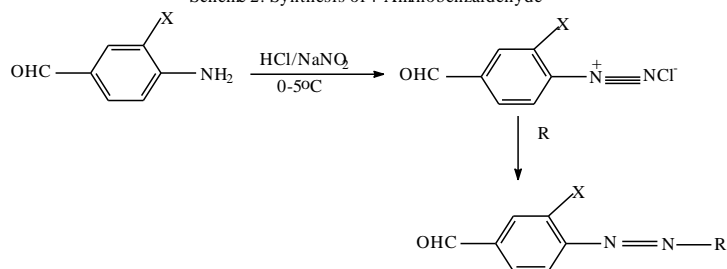
The aminobenzaldehydes produced were thus diazotized in hydrochloric acid and coupling was carried out by addition of the clear diazo solution to the buffered solution of the substituted phenols and naphthols, giving dyes in (1-5) in good yield and in a reasonably pure form as summarized in Scheme 3.



Scheme 1: Synthesis of 4-Amino-3-Nitrobenzaldehyde (IV)



Scheme 2: Synthesis of 4-Aminobenzaldehyde



Scheme 3: Synthesis of the Dyes

3.2 Physical characteristics of the intermediates and dyes

The physical characteristics of the intermediates and dyes are reported in Tables 1 and 2 respectively. The molecular weights of the synthesized dyes ranged from the highest 321 which was obtained for dyes 1a & 2a to the lowest 226 which is found in dye 5b. The entire dyes were synthesized in good to excellent yields. The melting points of the intermediates and dyes ranged from 72-311 °C which is as a result of variation of the substituents attached. There are two factors that affect the melting point of organic compounds. The size of the molecule and the force of attraction between the molecules. If the melting point of two pure samples shows a clear difference in their melting points, it indicates that the two compounds must have different structural arrangements or they must have different arrangements of atoms or configurations (Amrita, 2013).

Table1: Physical characteristics of the synthesized intermediates

Intermediates	Meltingpoint (°C)	Molecularweight (g/mol)	Yield (%)	Colour
Diacetate	109 – 11	310	82	Pale yellow
Intermediate A	206 – 208	166	74	Orange
Intermediate B	72 – 75	121	67	Orange

Table 2: Physical characteristics of the synthesized dyes

Dyes	Melting point (° C)	Molecular weight (g/mol)	Yield (%)	Colour
Dye 1a	140 – 141	321	83	Light orange
Dye 1b	129 – 131	276	80	Brick red
Dye 2a	113 – 115	321	77	Dark red
Dye 2b	167 – 169	276	87	Brick red
Dye 3a	284 – 285	287	59	Deep brown
Dye 3b	251 – 252	242	66	Brown
Dye 4a	310 – 311	303	69	Coffee brown
Dye 4b	245 – 246	258	76	Dirty brown
Dye 5a	204 – 205	271	81	Dark yellow
Dye 5b	233 – 234	226	77	Orange

In organic compounds, the presence of polarity or especially hydrogen bonding, generally leads to higher melting point (Amrita, 2013). Consider dyes 3a, 3b, 4a and 4b these, dyes have higher melting points compared to their counterparts this is because of the presence of multiple polar groups on the dye molecule. Dye 4a has the highest melting point which can also be attributed to the high molecular size. Dyes 1a and 2a were obtained by coupling 1-naphthol and 2-naphthol to the same diazonium salt 4- amino -3 nitro benzaldehyde. Dye 1a gave a light orange colour while dye 2a gave a dark red colour. This is however not surprising because changing the hydroxy group from the para position to the ortho position will have an effect on the colour i.e bathochromic effect. With the hydroxyl group, ortho to the azo chromophoric group, it is expected to be hydrogen bonded and therefore more bathochromic shift than when it is para to the azo chromophoric group (i.e deepening of shade). For Dyes 1b and 2b, despite the change in the position of the hydroxyl group the colour of the dyes did not change this may be attributed to the absence of the nitro group on the diazonium salt.

The -OH group has both positive inductive and mesomeric effects on the ring system. It activates the ring towards electrophilic aromatic substitution. The presence of multiple OH on the dye increases the colour intensity due to the fact that the hydroxyl group is an auxochrome thereby intensifying the dye colour Morrison and Boyd (2002).

3.2 Infra-red spectra of the synthesized intermediates and dyes

The IR spectra of all the compounds were run in nujol using FTIR Buck Scientific M530. The infrared spectra of the synthesized dyes (1a, 3a, 4a and 5a) showed absorption bands due to the stretching vibration of O-H of phenol and naphthol, C=C of aromatic and Ar-H stretching vibration at 3160 - 3448 cm^{-1} , 1589 - 1637 cm^{-1} and 3030 - 3100 cm^{-1} respectively. The presence of one or more aromatic rings in a structure is readily determined from the C-H and C=C-C ring-related vibrations. The C-H stretching which occurs above 3000 cm^{-1} but less than 3150 cm^{-1} is typically exhibited as a multiplicity of weak-to-moderate bands, compared with the aliphatic C-H stretch. The structure of the bands is defined by the number and positions of the C-H bonds around the ring, which in turn are related to the nature and number of other substituents on the ring. The appearance and ratio of these band structures is strongly dependent on the position and nature of substituents on the ring (Coates, 1996).

Specifically speaking, using IR spectrum of dye 4a as representative example of the azo dyes, the highest but broad band observed at 3402 cm^{-1} was as a result of phenol O-H group. In most chemical environments, the hydroxyl group does not exist in isolation, and a high degree of association is experienced as a result of extensive hydrogen bonding with other hydroxyl groups. The impact of hydrogen bonding is to produce significant band broadening. The absorption bands at 1618 cm^{-1} and 3030-3100 cm^{-1} depicted the presence of C=C and Ar-H respectively. The C=O absorptions of all the dyes were prominent at 1680-1766 cm^{-1} for the intermediates and dyes. Confirming the presence of the aldehyde functionality. The C=O absorption is

almost always one of the most characteristic in the entire spectrum, and it is also the most intense spectral feature. Careful observation of the carbonyl absorptions of the intermediates and dyes in Table 3 reveal that the carbonyl absorption are within the normal frequencies of absorption. Diacetate absorbs at 1766 cm^{-1} , due to the carbonyl absorption of the ester group present. Intermediate (IV) at 1705 cm^{-1} , Intermediate (V) at 1711 cm^{-1} , Dyes 1a, 3a, 4a and 5a absorbs at 1710 cm^{-1} , 1701 cm^{-1} , 1740 cm^{-1} and 1685 cm^{-1} respectively.

With an aldehyde being a special case, where the carbonyl group is terminal, and only has one substituent, the other being a single hydrogen atom. The diagnostic carbonyl absorption frequency is dependent on the electronic characteristics of the substituent group, which in turn defines the chemical characteristics and reactivity of the specific carbonyl compound. Spatial, structural factors and conjugation play an important role in the observed carbonyl frequency and this includes connection to an aromatic ring or conjugation to a C=C or another C=O (Coates, 1996). The C-H stretch of all the compounds absorbed below 2900 cm^{-1} which is in agreement with literatures (Morrison and Boyd, 2002). Associated with the terminal aldehydic C-H stretch at 2740 cm^{-1} for diacetate, 2820 cm^{-1} and 2830 cm^{-1} for intermediates IV and V, 2721 cm^{-1} , 2820 cm^{-1} , 2780 cm^{-1} and 2866 cm^{-1} for dyes 1a, 3a, 4a and 5a. Conjugated with the group and the carbonyl absorption frequency is correspondingly lowered. Often, the frequency ranges for the different classes of carbonyl compound overlap, and the carbonyl frequency alone is not sufficient to characterize the functional group (Imadegbor *et al.*, 2014). Another important absorption frequency is the absorption of the azo group N=N at 1450-1470 cm^{-1} which is characteristic of all the dyes and a confirmation that coupling reaction was successful. Note that only the primary and secondary amines exhibited the most characteristic group frequencies at 3354 cm^{-1} for diacetate, 3433-3310 cm^{-1} for Intermediate IV and 3400-3330 cm^{-1} for intermediate V respectively which are associated with the N-H stretch. The infrared spectrum is very diagnostic, because it helps to readily differentiate the functional groups present.

Table 3: Infrared spectra of the synthesized intermediates and dyes

Dyes/Intermediates	Frequency of absorption(cm^{-1})	Functional Groups Present
Diacetate	1766 (s)	C=O stretching(ester)
	1362 (m)	N=O stretching
	3354 (s)	N-H stretching(2° aromatic amines)
	2940	C-H(CH_3)stretching
	1695 (s)	C=C stretching (aromatic)
	2740	C-H stretching(aldehydes)
	2820	C-H stretching(aldehydes)
Intermediate A	3310,3433	N-H stretching(1° aromatic amines)
	3108	C-H(aromatics)
	1556 (s)	C=C stretching (aromatics)
	1363 (m)	N=O stretching
	1705 (s)	C=O stretching(aldehydes)
Intermediate B	3080	C-H stretching(aromatics)
	3330-3400 (s)	N-H stretching(1° amines)
	2830	C-H stretching(aldehydes)
	1590 (s)	C=C stretching(aromatics)
Dye 1A	1711 (s)	C=O stretching(aldehydes)
	3250-3542 (s)	O-H stretching
	1365 (m)	N=O stretching
	1615 (s)	C=C stretching (aromatics)
	1457 (m)	N=N stretching(azo)
	2721	C-H stretching(aldehydes)
Dye 3A	1701 (s)	C=O stretching(aldehydes)
	3200-3500 (b)	O-H stretching
	1355 (w)	N=O stretching
	1580 (s)	C=C stretching (aromatics)
	1695 (s)	C=O stretching
Dye 4A	1430 (m)	N=N stretching(azo)
	2820	C-H stretching(aldehydes)
	3016 (m)	C-H stretching(aromatics)
	3220-3410 (s)	O-H stretching
	1710 (s)	C=O stretching(aldehydes)
	1345	N=O stretching
	3090 (m)	C-H stretching (aromatics)
Dye 5B	1615 (s)	C=C stretching (aromatics)
	2780	C-H stretching (aldehydes)
	1433	N=N stretching (azo)
	3210-3490 (s)	O-H stretching
	1685 (s)	C=O stretching (aldehydes)
	1366 (m)	N=O stretching
	1591 (s)	C=C stretching (aromatics)
1455 (m)	N=N stretching (azo)	

2866 (m)

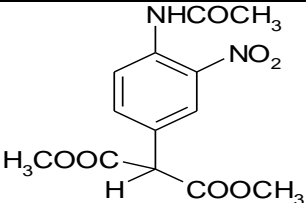
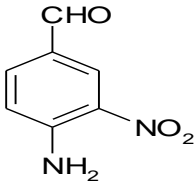
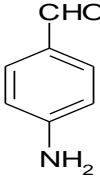
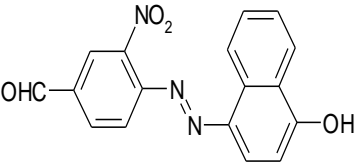
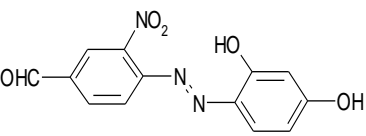
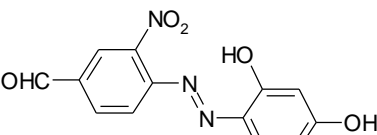
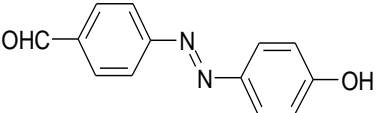
C-H stretching (aldehydes)

s = strong, m = medium, w = weak, b = broad

3.3 GC-MS Fragmentation patterns of the synthesized intermediates and dyes.

The result of the mass spectra data of the intermediates and some selected dyes 1a, 3a, 4a and 5a were reported in Table 4.

Table 4: GC-MS fragmentation patterns of the synthesized intermediates and dyes

Dyes	Mol.Wt	Proposed Identity	R.Time	m/z (% Abundance) of fragments
Diacetate	310		21.8	310(26% M ⁺);43(100%);65(32%);119(30%);191(5%);264(4%);251(4%);103(3%);39(2%);133(2%);149(1%);91(1%).
Int A	166		17.1	166(21% M ⁺);65(100%);39(43%);52(40%);91(25%);119(20%);150(1%);136(1%).
Int B	121		10.1	121(98% M ⁺);120(100%); 65(99%); 91(85%); 39(50%); 52(15%); 27(12%).
Dye 1A	321		10.5	323(12% M ⁺);133(100%);103(15%);77(14%);91(7%);119(5%);51(3%);281(3%);63(2%);145(2%);243(1%);161(1%);
Dye 3A	287		20.8	284(10% M ⁺);43(100%);57(70%);73(60%);28(55%);97(30%);131(12%); 227(1%);185(1%);
Dye 4A	303		24.8	320(10% M ⁺);55(100%);83(40%);111(20%);97(20%);279(10%);149(10%);167(6%);249(5%);41(4%).
Dye 5B	226		23.4	226(11% M ⁺);93(100%);65(78%);121(40%);77(29%);105(17%); 197(1%);

The molecular ion peaks obtained from all the spectra were consistent with the molecular mass of the proposed structures while some other daughter ions and base peaks were observed based on the characteristic patterns. The mass spectral data of intermediate IV, for instance, showed molecular ion peak at m/z 166 (21 % M⁺) which was in concordance with the molecular mass (166 g/mol) of the compound 4-amino-3-nitro benzaldehyde while the base peak was observed at m/z 65(100 %) see Table 4. Other prominent peaks that

appeared at m/z with relative abundance are as follows: 166(21 %M⁺); 65(100 %); 39(43 %); 52(40 %); 91(25 %); 119(20 %); 150(1 %); 136(1%); respectively as reported in Table 4 were due to some fragmentation processes. Similarly, dye 5b showed molecular ion peak at m/z 226 which is consistent with the molecular mass (226 g/mol) with base peak at m/z 93. Other prominent peaks appeared at m/z with relative abundance at 226(11 %), 197(1 %); 121(40 %);105(17 %); 93(100 %); 77(29 %); 65(78 %) respectively. Dye 3a has a molecular ion peak of M-3 with the following fragments: 284(10 %); 43(100 %); 57(70 %); 73(60 %); 28(55 %) 97(30 %);131(12 %); 227(1 %); 185(1 %).

3.4 UV-visible absorption spectra of the dyes

The UV/Visible spectral characteristics of the dyes indicate that they absorbed at very high wavelengths up to 650 nm. This is as a result of extended conjugation contributed by the C=C and the conjugative linkage performed by the N=N group. This is in agreement with earlier report by Bello and Griffiths (1989) as per benzenoid uv-visible absorption. The results showed that the dyes absorbed at much longer wavelengths. The uv- visible absorption spectrum of dye 5b as a representative of the synthesized dyed showed an absorbance λ_{max} at 650nm in DMF when compared with dye 5a with 600nm. It is however surprising since the presence of the nitro group on dye 5a is supposed to shift the absorbance to a longer wavelength. Again, dye 1a did not show any shift on protonation while dye 1b showed a red shift of 150nm on protonation. Molar extinction coefficient was calculated using the beer lamberts law. The results are presented in the Table 5. The dyes all have good extinction coefficient an indication that the tinctorial strength of the dyes are good.

Table 5: Maximum Absorption Wavelength (λ_{max}) of the Dyes in Different Solvents

Dye No	Maximum Absorption Wavelength λ_{max} (nm)				Mol. Ext coefficient ($Lmol^{-1}cm^{-1}) \times 10^4$	
	Acetone	Ethanol	Toluene	Ethanol/HCl	DMF	
1a	450	650	650	650	650	4.9
1b	500	500	650	650	600	5.7
2a	650	650	500	650	650	4.9
2b	650	550	650	550	650	5.7
3a	550	650	650	650	600	5.5
3b	650	400	650	650	600	6.6
4a	650	650	650	650	650	5.2
4b	650	650	600	650	650	6.2
5a	650	650	500	650	600	5.9
5b	650	650	650	600	650	7.0

3.5 Effect of time on dye exhaustion

Figures 1-3 shows the effect of time on the dye exhaustion of dyes. From the Figs, there is a progression in the percentage exhaustion with increase in dyeing time. This indicates that the longer the dyeing time, the greater the amount of dye molecules absorbed by the fibre. More dyes penetrate into the polymer at longer dyeing time resulting in high percentage exhaustion and deeper shade. It was observed that all the dyes showed higher exhaustion at longer dyeing time.

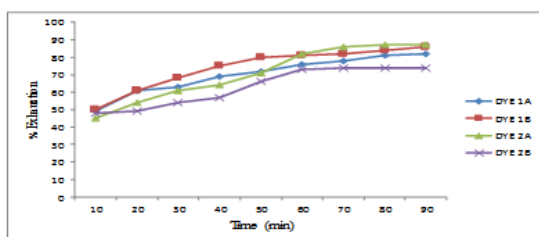


Figure 1: Effect of Time on Dye Exhaustion of Polyester Fabric (Dyes1a-2b).

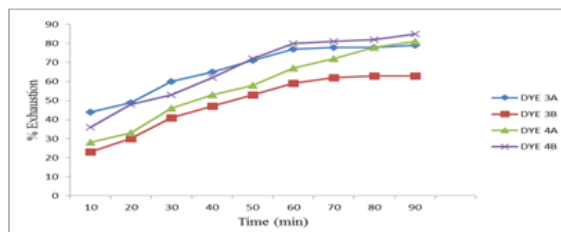


Figure 2: Effect of Time on Dye Exhaustion of Polyester Fabric (Dyes3a-4b).

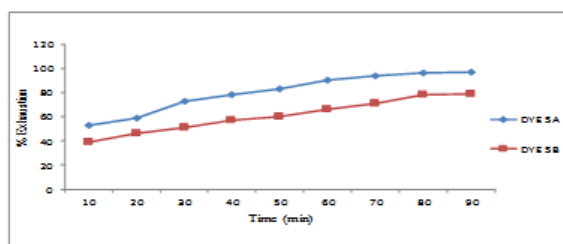


Figure 3: Effect of Time on Dye Exhaustion on Polyester Fabric (5a-5b).

3.6 Effect of temperature on dye exhaustion

Figures 4-6 shows the results of the effect of temperature on the dye exhaustion of dyes. From the Figs, representation, it is very clear that temperature change affects dyeing. All the dyes applied to the polyester fabric show a high exhaustion at temperature near the boil. This is because there is greater segmental mobility of the fibre polymer chains at higher temperature and this eases penetration of dye molecules into the fibre. High temperature also made the pores of the fibre to open and thus enhance the penetration of the dye molecules. In dyeing of polyester with disperse dyes, temperature control is very essential.

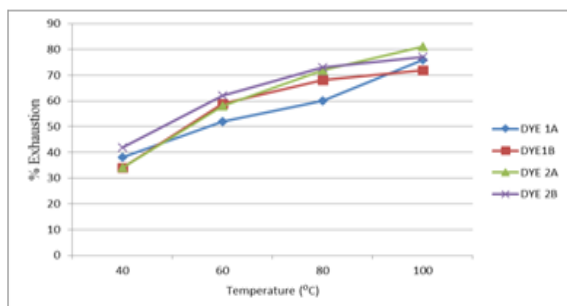


Figure 4: Effect of Temperature on Dye Exhaustion on Polyester Fabric (Dyes 1a-2b).

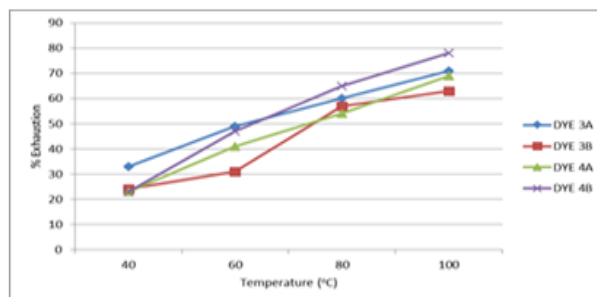


Figure 5: Effect of Temperature on Dye Exhaustion on Polyester Fabric (3a-4b).

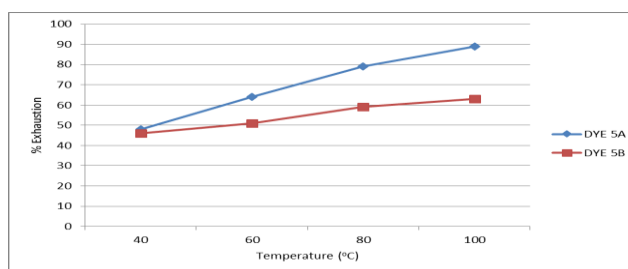


Figure 6: Effect of Temperature on Dye Exhaustion on Polyester Fabric (Dye 5a-5b).

3.7 Wash fastness

The results of the fastness properties of the dyes are shown in Table 6. The dyes showed good to excellent fastness to washing on polyester fabric. The overall result however, shows that the wash fastness of the dyes is good to excellent. The excellent wash fastness of the dyes is due to their hydrophobic character and the planarity conferred on them by the polar substituent groups. The polar substituent groups on the dye molecules contribute greatly to the strength of the dye – fibre bond. The degree of staining of the undyed fabric was good as well. The process of attachment of the dye molecules to fibre molecules can be made by mechanical entrapment or by chemical linkage. Fastness characteristic of individual dye depends on the relative orientation of the dye molecule with the fibre molecule and various forces involved in the dye-fibre interaction i.e whether ionic, covalent, van der-Waals and dipole interactions. The fastness characteristics of the dyes also depend on their structure and the chemical and physical structure of the fibre molecule on which the dye is being applied (Iyun, 2013). Therefore once the dye molecules find their way into the fibre and they are attached to it, they become difficult to remove, more so that it is only sparingly soluble in water. Infact a remarkable degree of brightness and levelness was observed after washing which shows a clear indication of good penetration and excellent affinity of these dyes to the fibre.

3.8 Fastness to light

The result from Table 6 shows that the light fastness of these dyes are generally good on the polyester fibres. In an attempt to trace the relationship between chemical structure and light fastness, it was observed by Maradiya (2010), that there is no absolute value for the light fastness of a dye. The rating obtained for a given dye in any fading test depends on many factors, the most important are, concentration and/or degree of aggregation of dye within the fabric, nature of the fabric in which dye is dispersed; the characteristic incident radiation, molecular structure and substantivity. The light fastness rating of dyes ranged from 4-7 which is moderate to outstanding. From the results obtained, it was observed that the ratings for the dyes with the nitro substituent (Dyes 1a, 2a, 3a, 4a & 5a) were better than their counterparts. This may be attributed to the extended conjugation present in the dyes implying that the intrinsic photo-stabilities of dyes on the fabric are similar.

3.9 Fastness to perspiration

The dyes showed very good to excellent fastness to perspiration properties on polyester fabric. The overall results however show that the perspiration fastness values of the dyes are good and also perspiration properties to acid and alkali are similar.

Table 6: Dyeing Properties of Dyes (1a-5b) on polyester fabric

Dye No	Wash Fastness		Light Fastness	Rubbing Fastness	Perspiration	
	Colour change	Staining			Acid	Alkali
1a	5	5	7	5	5	5
1b	4	4	5	5	5	5
2a	5	5	7	5	4	5
2b	5	4	4	5	4-5	4
3a	4-5	5	5	5	5	5
3b	4	4	4	5	2-3	5
4a	4-5	5	5	5	2-3	5
4b	4-5	4	4	5	5	5
5a	4	5	5	5	5	5
5b	5	5	5	5	5	5

IV. Conclusion

In conclusion, it was discovered that variation of coupling components resulted in different dyes with different colours. The spectroscopic analysis of all the synthesized dyes and their intermediates revealed the functional groups present and confirmed the identity of the synthesized dyes. The synthesis of series of naphtholic and phenolic azo dyes was successfully achieved using various substituted phenol and naphthol derivatives as the coupling components. Intensity of colours are tinctorially strong black, orange red and golden yellow monoazo disperse dyes. Their synthesis is generally convenient and economical. The nature of the substituent in the coupling components also has a great influence on the visible absorption and shade of dyeings. Thus, the azo disperse dyes herein synthesized and applied to polyester fabrics showed very good to excellent fastness properties to washing, light and perspiration and of good commercial values..

Conflict of Interests The authors declare that there is no conflict of interests regarding the publication of this paper.

Data availability statement:

The research data used to support the findings of this study are included within the research article. Other supplementary files such as the spectra generated during the research are available from the corresponding author on reasonable request.

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