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Synthesis and Application of Direct Dyes Derived From Terephthalic and Isophthalic Acids on Cotton Fabrics

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Abstract: *The synthesis of direct dyes derived from terephthalic and isophthalic acid using J and H- acids was undertaken with the view of replacing benzidine moiety in the production of direct dyes. The amide derivatives of isophthalic and terephthalic acids were used as the coupling components while aniline and its derivatives were used as the source of diazo components. The amide derivatives were characterized by Gas Chromatography/Mass Spectrometry and Infra-red analysis. The spectroscopic properties of the dyes in various solvents were also examined and most of the dyes showed bathochromic shifts when the solvent was changed to more polar solvents. The dyes also showed positive and negative halochromism with the addition of few drops of hydrochloric acid (HCl). The synthesized dyes were applied to cotton fabrics and their performance properties evaluated. They have good exhaustion in the presence of electrolyte and have good wash fastness properties upon application of after-treating agents of values of 3-4, 4 and 4-5. They also had good fastness properties to light of values between 4-7. Their resistance to rubbing and perspiration had values between 3 and 4-5. The toxicity of the synthesized coupling components was studied using the Dietrich Lorke (LD₅₀) method on Albino mice and they were found to be non-toxic.*

Key words: *Benzidine, direct dyes, exhaustion, electrolyte, cotton, fastness.*

I. Introduction

Benzidine is an organic chemical belonging to the class of amines and used in making numerous dyestuffs. The azo dyes derived from benzidine are important because, unlike simpler classes of azo dyes, they become strongly fixed to cotton without a mordant [1].

It is well known that benzidine is both a mutagenic amine and a human carcinogen [2]. However, because benzidine is carcinogenic, its use for the production of dyes was forbidden. The problems associated with the synthesis of direct dyes from benzidine and urea dyes has resulted in the search for new dyes whose production and use would meet high environmental and safety requirements.

This work is focused on the possibilities of using terephthalic acid and isophthalic acid as “bridging groups” for the synthesis of symmetrical direct dyes. The spectral characteristics of the dyes and also a colorimetric evaluation of the dyes on woven cotton fabric were investigated.

II. Materials and methods

General information

All the chemicals used in the synthesis of the dyes and intermediates were of analytical grade and were used without further purification. Melting points were determined by the open capillary method. The Visible absorption spectra were measured using Jenway UV-visible spectrophotometer; model: 6405. IR spectra were recorded using the FTIR infra- red spectrophotometer and the mass spectra were determined on a GC- MASS spectrometer.

Synthesis of coupling component using terephthalic acid and J-acid as intermediate -N,N'-bis-(8 – hydroxyl -6-sulphony-naphthalene-2-(3)-yl)-phthalamides of terephthalic acid (TJA).

Terephthalic acid (8.3g, 0.05mol) was heated with thionyl chloride (11ml) in chlorobenzene (250ml) in the presence of DMF (1ml) as catalyst [2]. The process was carried out at a temperature of 60-70⁰C for 6 – 9hours. The obtained acidic chloride, without separation was used for the acylation of J-acid.

Acid chloride dissolved in chlorobenzene (250 ml) was added to an aqueous solution of J-acid (0.01mol, 2.4g) at a temperature of 10⁰C and at such a rate as to obtain a pH of 6.8-7.2 [2]. The mixture was heated to 50⁰C and stirred at this temperature for 30 minutes. The solution was then cooled, its pH was adjusted to 7.5-7.75 with 10% aqueous NaOH and the product was salted out, filtered, wash with brine (pH= 7.7) and dried.

Synthesis of coupling component using terephthalic acid and H-acid as intermediate - N,N'- bis-(8-hydroxy-3, 6–disulphony-naphthalene-2-(3)-yl)-phthalamides of terephthalic acid (THA)

This was prepared in a similar manner as described above for TJA, except that H-acid was used instead of J-acid.

Synthesis of coupling component using isophthalic acid and H-acid as intermediate - N,N' – bis-(8 – hydroxyl -3,6 – disulphony – naphthalene – 2-(3)-yl)-phthalamides of isophthalic acid (ISH)

This was prepared in a similar manner as described above for THA, except that isophthalic acid was used instead of terephthalic acid.

Synthesis of coupling component using isophthalic acid and J-acid as intermediate - N, N' – bis-(8 – hydroxyl -6-sulphony-naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (IJA).

This was prepared in a similar manner as described above for TJA, except that isophthalic acid was used instead of terephthalic acid.

III. General Method Of Diazotisation

Aniline, p-chloro aniline, p-nitroaniline and p-anisidine were diazotized in a conventional manner using direct and suspension methods [3].

Diazotisation of aniline and p- anisidine; The amines (0.00365mol, 0.4g aniline) and (0.00365mol, 0.5g p-anisidine) were respectively dissolved in 1ml of HCl and cooled to 0-5°C in an ice bath equipped with a magnetic stirrer. Sodium nitrite (0.7g, 0.00673 moles) dissolve in 10ml of distilled water was added drop wisely over a period of 30 minutes while stirring for another 45 minutes. Urea (0.5g) was then added to the mixture and stirring was continued for another 10 minutes to achieve complete diazotization.

Diazotization of p-chloro aniline and p- nitro aniline

The amine (0.00365mol, 0.5g) was dissolve in 1ml of hot concentrated HCl and cooled very rapidly to 0-5°C in an ice bath equipped with a magnetic stirrer by addition of ice to obtain a fine suspension of the amine-hydrochloride. Sodium nitrite (0.7g) dissolve in 10ml of distilled water was added drop wisely over a period of 30 minutes while stirring for another 45 minutes. Urea (0.5g) was then added to the mixture and stirring was continued for another 10 minutes to achieve complete diazotization.

Preparation of dyes A₁, A₂, A₃ and A₄

Disazo dyes were prepared by coupling the diazotized amines (aniline, p-anisidine, p-chloroaniline and p-nitroaniline (0.013mol) from above procedures with (0.005mol, 3.12g) of the coupling component(N,N' – bis-(8 – hydroxyl – 6 – sulphony – naphthalene-2-(3)-yl)-phthalamides of terephthalic acid)dissolved in 50ml of water at pH=12-12.5 and 10-15°C. The dye was salted out using NaCl (20%) filtered off and dried in air.

Preparation of dyes A₅, A₆, A₇ and A₈

The dyes were obtained by coupling the diazonium ions obtained from aniline, p-anisidine, p-chloroaniline and p-nitroaniline respectively, with(0.005mol, 3.63g) of the coupling component obtained using terephthalic acid and H-acid (N, N'-bis-(8-hydroxy-3,6-disulphony-naphthalene-2-(3)-yl)-phthalamides of terephthalic acid.

Preparation of dyes B₁, B₂, B₃, and B₄; The procedure is same as above, except that the coupling component used was obtained using J-acid and isophthalic acid- N,N'-bis-(8-hydroxy – 6-sulphony-naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (IJA)

Preparation of dyes B₅, B₆,B₇ and B₈; The procedure is same as above, except that the coupling component used was obtained using isophthalic acid and H-acid (N,N'-bis-(8-hydroxy-3,6-disulphony-naphthalene-2-(3)-yl)-phthalamides of isophthalic acid) .

Dyeing and fastness properties measurement

The dye bath was prepared using a liquor ratio of 50:1; the volume of dye required was 2ml to give 2% depth of shade on weight of fabric measured in a beaker. 1g of cotton fabric was wetted in water for 1 minute and excess water squeezed out. The wetted fabric was then introduced into the beaker/dye bath containing electrolyte(0.7g NaCl), on a thermostated steam bath with the dyeing liquor temperature at 40°C and raised to the boil after a period of 30 minutes while constantly agitating the sample. The dyeing was carried out at this temperature for 1 hour. After dyeing was completed, the fabric was removed,thoroughly rinsed in cold running tap water and dried in air at room temperature. The optical density of the dye bath liquor was measured before and after dyeing for the calculation of percentage exhaustion.

Wash fastness using current I.S.O 3 washing tests [4], light fastness, fastness to rubbing and perspiration were determined by the standard procedure [5]. The results are summarized in Table 5 and Table 6 respectively.

Effect of varying the concentration of electrolyte, effect of varying dyeing time on exhaustion, effect of temperature on dyeing and effect of varying percentage shade on dyeing and exhaustion were also studied.

Aftreatment of the dyed samples and wash fastness test

An aftertreatment was carried out on the dyed samples using 8% formaldehyde, liquor ratio of 50:1, at 60°C for 60 minutes for each sample. The samples were removed, rinsed in water and dried. The wash fastness test as stated above was carried out on the after treated samples and the results are shown in Table 5

Acute toxicity test

The acute toxicity test was carried out in two steps;

1. In the initial investigation, the range of doses producing the toxic effects was established.

2. Based on these results, further specific doses were administered to calculate an LD₅₀ [12].

This is achieved by giving widely differing doses to the animals. e.g. 10, 100, 1000 mg/kg body weight. The result shows whether the substance is very toxic, toxic, less toxic, or only slightly toxic.

Albino mice were used for this test. The mice were weighed and the doses were given based on the mice's weight.

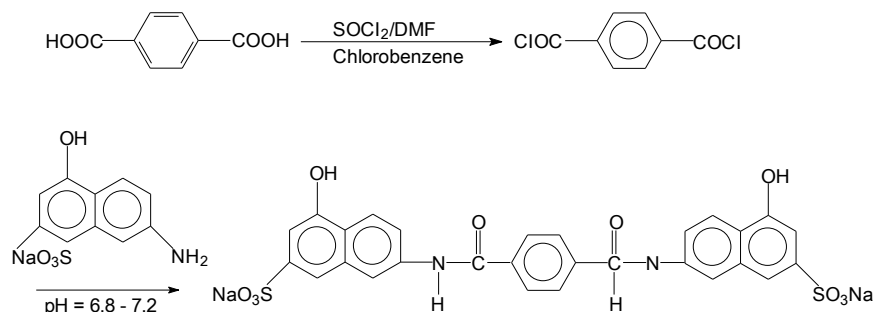
Three (3) animals each was injected for each dose (10, 100, 1000 mg/kg body weight) making a total of nine (9) mice for the initial investigation. Their body reactions were observed immediately and at intervals for 72 hours [13].

Further higher doses of 600, 1000, 1600, 2900 mg/kg body weight were prepared and injected into another set of four new animals and its effects was examined and observed at interval for another 72 hours. The number of death that occurred was recorded and the LD₅₀ was calculated from the minimum toxic dose and maximum tolerated dose [12]. The results are shown in Table 3.

IV. Results and Discussion.

Synthesis of the dyes and intermediates.

Four coupling components were synthesized in the present study. The first two were obtained by heating terephthalic acid in chlorobenzene for 6–9 hours at a pH of 6.8–7.2 in the presence of dimethylformamide as a catalyst. Further reactions were made by reacting the acidic chlorides of terephthalic acids obtained with J-acid and H-acid respectively. The molar mass of N,N'-bis-(8-hydroxy-6-sulphony-naphthalene-2-(3)-yl)-phthalamides of terephthalic acid (TJA) was 624 and has a melting point of 265°C and the colour obtained was brownish with a yield of 81%, while N,N'-bis-(8-hydroxy-3,6-disulphony-naphthalene-2-(3)-yl)-phthalamides of terephthalic acid (THA) has a molar mass of 726 and a melting point of 270°C. The colour obtained was black and has a yield of 79%.



Scheme 1: Synthesis of coupling component using terephthalic acid and J-acid as intermediate - N, N' - bis - (8 - hydroxyl - 6 - sulphony - naphthalene - 2 - (3) -yl) - phthalamides of terephthalic acid (TJA)

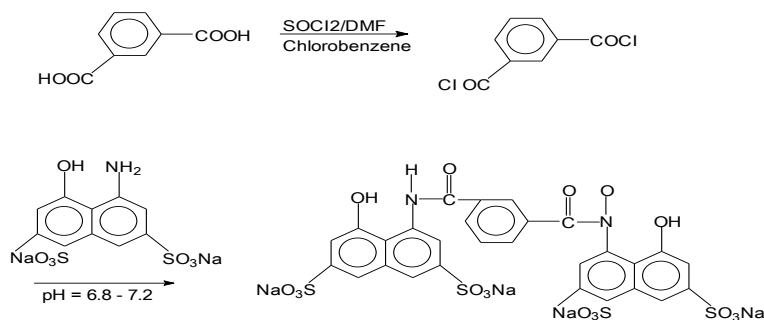
The other two coupling components were obtained by heating isophthalic acid in chlorobenzene as above and the acidic chlorides of isophthalic acids were reacted further with J-acid and H-acid respectively.

N,N' - bis-(8 - hydroxyl - 6 - sulphony - naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (IHA) has a molar mass of 624 and a melting point of 266°C. The colour was brownish and it has a yield of 78%. While

N,N' - bis-(8-hydroxy-3,6 - disulphony - naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (ISH) has a molar mass of 726 and a melting point of 260°C. The colour obtained was cream and it has a yield of 80%.

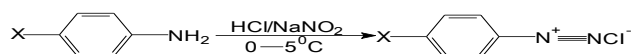
These were synthesized based on the literature methods [2]. The physical characteristics are shown in Table 1.

The coupling components were studied and analysed using GC-Mass spectrometry.

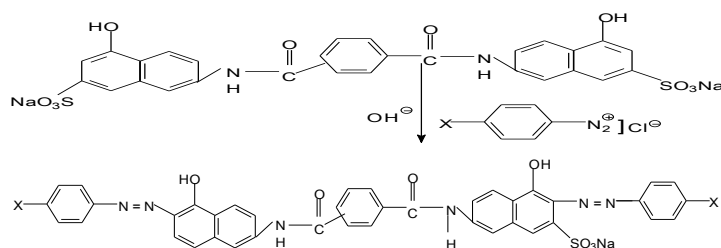


Scheme2: Synthesis of coupling component using isophthalic acid and H-acid as intermediate N, N' – bis - (8 – hydroxyl – 3, 6 – disulphony – naphthalene – 2 - (3)-yl) -phthalamides of isophthalic acid (ISH).

The dyes synthesized were obtained by diazotising four primary aromatic amines namely; aniline, p-anisidine, p-chloroaniline and p-nitroaniline using direct and suspension methods of diazotisation. The diazo component was each coupled to the four coupling components obtained to get sixteen different dyes. The yields of the dyes were relatively high and the dyes had sharp melting point which may be due to absence of impurity. The colours of crystals obtained were bright ranging from different shades of orange, purple, brown, green, navy blue and red. The colours of the dyed materials were of bright and brilliant shades as well.



(a) Diazotization of primary amine.



X = H, CH₃, Cl, NO₂

Scheme 3: Reaction of the diazotized amine with the coupling component

Table 1; Physical Characteristics Of The Dyes.

Dye No. Molar Mass(Gmol⁻¹)Melting Point(^oC) %Yield Colour Of Crystal Colour Of Dyed Sample

Dye No.	Molar Mass(Gmol ⁻¹)	Melting Point(^o C)	%Yield	Colour Of Crystal	Colour Of Dyed Sample
A ₁	834	116-117	81	Orange	Yellow
A ₂	847	199	72	Purple	Brown
A ₃	903	226	64	Deep Orange	Brown
A ₄	878	242-245	68	Brown	Dark brown
A ₅	834	208	70	Deep orange	Orange
A ₆	847	205	69	Purple	Brown
A ₇	903	206	80	Orange	Brown
A ₈	878	209	74	Brown	Dark brown
B ₁	1040	238	72	Brown	Yellow
B ₂	1053	241-246	83	Light purple	Pink
B ₃	1109	262	78	Dark green	Light green
B ₄	1084	245	81	Dark purple	Army green
B ₅	1040	183	75	Orange	Yellow
B ₆	1053	190-191	68	Dark green	Light green
B ₇	1109	200	72	Purple	Light purple
B ₈	1084	155	73	Navy blue	Army green
ISH	726	260	80	Cream	-
THA	726	270	79	Black	-
TJA	624	265	81	Brownish	-
IJA	624	266	78	brownish	-

ISH = N, N' – bis - (8 – hydroxyl - 3, 6 – disulphony – naphthalene – 2 - (3) -yl) - phthalamides of isophthalic acid

THA = N, N'-bis-(8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid

TJA = N, N'-bis-(8-hydroxy - 6 – sulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid

IJA = N, N' – bis - (8 – hydroxyl – 6 – sulphony - naphthalene-2 - (3) -yl) - phthalamides of isophthalic acid.

The infra-red spectra of some of the dyes.

The infra-red spectra of the dyes showed similar or closely related absorption band due to presence of similar groupings or bonds present in the dye structures. Dye A₁, A₂, and A₃ obtained from, N, N'-bis-(8-hydroxy - 6 - sulphony - naphthalene - 2 - (3) - yl) - phthalamides of terephthalic acid show absorption peaks due to double bonds -C=C- in aromatic rings between the range 1631-1642cm⁻¹. The presence of a carbonyl group C=O gave rise to a stretching vibrations in these dyes between 1642 - 1840cm⁻¹. They also gave N-H bending vibrations at region of 1631-1642cm⁻¹. The peak due to hydrogen bond stretching shows a peak due to vibrations of hydrogen and other atoms [6].

At a region of between 3392-3425cm⁻¹ hydrogen bonding broadens the peak and shifts them to lower wavelength. They also show absorption peaks due to C=N stretching at a region of 1631-1642cm⁻¹ and peaks due to C-SO₃H at 1250-1300cm⁻¹.

Dyes A₅ and A₇ obtained from, N, N'-bis-(8-hydroxy - 3, 6 - disulphony - naphthalene - 2 - (3) - yl) - phthalamides of terephthalic acid shows absorption peaks due to double bonds -C=C- in aromatic rings between the range 1640cm⁻¹. The presence of a carbonyl group C=O gave rise to a stretching vibrations at 1646cm⁻¹. They also gave N-H bending vibrations at region of 1641-1642cm⁻¹. The peak due to hydrogen bond stretching shows a peak due to vibrations of hydrogen at a region of between 3442cm⁻¹. Hydrogen bonding broadens the peak and shifts them to lower wavelength. They also show absorption peaks due to C=N stretching at a region of 1641-1642cm⁻¹ and peaks due to C-SO₃H at 1300-1310cm⁻¹.

Dyes B₃ and B₇ shows absorption peaks due to double bonds -C=C- in aromatic rings between the range 1575-1630cm⁻¹. The presence of a carbonyl group C=O gave rise to a stretching vibrations at 1651cm⁻¹. They also gave N-H bending vibrations at region of 1646-1651cm⁻¹. The peak due to hydrogen bond stretching shows a peak due to vibrations of hydrogen at a region of between 3394- 3422cm⁻¹. They also showed absorption peaks due to C=N stretching at a region of 1646-1651cm⁻¹ and peaks due to C-SO₃H at 1275-1350cm⁻¹.

Generally all the dyes have absorption peaks due to -N=N- stretching at between 1575-1631cm⁻¹ which is prominent in all dyes spectra. These regions are in conformity with the characteristics of IR absorption peaks [7].

Table 2; THE INFRA-RED SPECTRA OF THE DYES

Functional group	-N=N-	-C=C	C=O	N-H	C=N	C-H	O-H	CSO ₃ H
Type of vibration	stretching	bending	stretching	bending	stretching	stretching	stretching	
A ₃	1575	1642	1642	1642	1642	3000	3425	1260
B ₃	1630	1646	1651	1646	1646	2850	3422	1350
A ₇	1580	1642	1646	1642	1642	2940	3442	1300
A ₁	1550	1642	1558	1642	1642	3192	3392	1300
A ₂	1631	1631	1634	1631	1631	2085	3420	1250
B ₇	1575	1651	1651	1651	1651	2087	3394	1275
A ₅	1630	1641		1641	1641			131

THA-stage 1									
STOCK 10mg/ml			100mg/ml				1000mg/ml		
no on mouse	wt of mouse(g)	Vol. of injection(ml)	no on mouse	wt of mouse(g)	Vol. of injection	no on mouse	wt of mouse	Vol. of injection	
1	21	0.21	4	20	0.2	7	27	0.27	
2	21	0.21	5	21	0.21	8*	20	0.2	
3	30	0.3	6	24	0.24	9	20	0.2	

Stage 2					
STOCK	600mg/ml	1000mg/ml	1600mg/ml	2900mg/ml	
No on mouse	1	2	3	4*	
Weight of mouse(g)	31	36	29	31	
Volume of injection(ml)	0.31	0.36	0.29	0.31	

IJA -stage 1									
Stock 10mg/ml			100mg/ml				1000mg/ml		
No on mouse	Wt on mouse	Vol. of injection	No on mouse	Wt of mouse	Vol. of injection	No on mice	Wt of mouse(g)	Vol. of injection(ml)	
1	23	0.23	4	27	0.27	7	22	0.22	
2	21	0.21	5	21	0.21	8	18	0.18	
3	27	0.27	6	25	0.25	9	26	0.26	

Stage 2					
Stock	1200mg/ml	1600mg/ml	2900mg/ml	5000mg/ml	
No on mice	1	2	3*	4*	
Weight of mice	23	25	26	28	
Volume of injection	0.23	0.25	0.26	0.28	

$$LD_{50} = [\text{Maximum tolerated dose} \times \text{minimum toxic dose}]^{1/2}$$

$$= [1600 \times 2900]^{1/2} = 2154$$

The synthesized coupling components were used for the acute toxicity test. The test was carried out in two stages. In the initial investigation, different doses of 10mg/ml, 100mg/ml and 1000mg/ml were prepared and given to the animals (albino mice) based on their respective body weight (which was obtained using a weighing balance) as shown in Table 3. After injecting the substance into the 9 albino micethey were observed for 72 hours for change in body reaction based on the effect of the injected substance. At the end of 48hours,only mice number 8 of 20g which was injected with 0.2ml of 1000mg/ml in stage 1 died.

In stage 2, Further higher doses (600mg/ml, 1000mg/ml, 1600mg/ml and 2900mg/ml) were given to 4 mice to establish a toxic effect. At the end of 72 hours, mice number 4 having 31g body weight which was injected with 0.31ml of 2900mg/ml concentration died. The maximum tolerated dose is1600mg/ml and the minimum toxic dose is 2900mg/ml.

Similarly, using IJA coupling component,the same procedure was followed in stage 1as above and none of the 9 mice died after 24 and 48 hours.

In stage 2, further higher doses (1200mg/ml, 1600mg/ml, 2900mg/ml and 5000mg/ml) were given to the 4 mice. At the end of 72 hours,mice number 3 which was injected with 2900mg/ml and mice number 4 which was injected with 5000mg/ml died. Therefore,the maximum tolerated dose is also 1600mg/ml and the minimum toxic dose is 2900mg/ml. Therefore,an LD₅₀ was calculated and obtained as 2154 to establish a range of toxicity using the above formula.Therefore the coupling components (THA and IJA) used was non-toxic based on the LD₅₀ obtained from the test. This may be due to the low LD₅₀ value of 2154, as values above 5000 have toxic effect [13].

Spectroscopic properties of the dyes:

The maximum absorption wavelengths in distilled water, dimethylformamide, ethanol, ethanol + hydrochloric acid are shown in Table 4.

TABLE 4:Spectroscopic properties of the dyes

Dye No	$\epsilon_{max} \times 10^3$ in water	λ_{max} in water (nm)	λ_{max} in DMF (nm)	λ_{max} in ethanol (a)	λ_{max} in ethanol + a drop of HCl (b)	Change in λ_{max} (b-a)
A ₁	9.30	510	505	510	515	+5
A ₂	4.93	505	510	505	510	+5
A ₃	6.16	480	505	505	510	+5
A ₄	4.41	490	505	505	505	0
A ₅	8.33	485	505	510	505	-5
A ₆	7.89	495	535	505	510	+5
A ₇	8.09	505	510	510	505	-5
A ₈	5.79	500	505	505	505	0
B ₁	9.79	510	505	510	510	0
B ₂	5.25	480	510	510	510	0
B ₃	7.69	480	505	510	515	+5
B ₄	5.34	505	520	505	505	0
B ₅	8.79	505	525	505	510	+5
B ₆	7.23	520	510	510	515	+5
B ₇	8.58	505	505	505	508	+3
B ₈	7.05	510	505	505	505	0

From the results in Table 4, dye A₁ which was obtained from aniline using N, N'-bis-(8-hydroxy - 6 – sulphony – naphthalene – 2 - (3) - yl) - of terephthalic acid (TJA) absorbed at 510nm in distilled water. Dye A₂obtained using p- anisidine and TJA as coupling component absorbed at 505nm. Similarly, dye A₃ and A₄ obtained from p- chloroaniline and p- nitroaniline using TJA as coupling component absorbed at480nm and 490nm respectively. Thus dye A₁ is more bathochromic than dyes A₂, A₃and A₄ as it absorbed at a longer wavelength.

Dyes A₅, A₆, A₇ and A₈ were obtained using N, N' –bis-(8-hydroxy - 6 – sulphony – naphthalene – 2 - (3) - yl) - phthalamides of isophthalic acid (IJA). A₅ absorbed at 485nm in distilled water while dyes A₆,A₇ and A₈ absorbed at 495nm, 505nm and 500 nm respectively in distilled water. Thus, dyes that absorbed at a lower wavelength indicate that they require higher energy for excitation.

Dye B₁ obtained from aniline using N, N'-bis-(8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid(THA) absorbed at 510nm in distilled water. Dyes B₂ and B₃ obtained from THA both absorbed at a wavelength of 480nm in distilled water while dye B₄ absorbed at 505nm. Thus dye B₁ is more bathochromic than B₂, B₃ and B₄ by a wavelength of 30nm and 5nm respectively. Similarly, dyes B₅ obtained from aniline using isophthalic acid and H-acid to obtain N, N'-bis - (8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of isophthalic acid(IHA) absorbed at 505nm in distilled water. B₆, B₇ and B₈ obtained using same coupling component IHA absorbed at 520nm, 505nm and 510nm respectively. Thus dye B₆ is more bathochromic than B₅, B₇ and B₈, while dyes B₅ and B₇ are more hypsochromic than dyes B₆ and B₈.

Spectrophotometric measurements therefore showed that the spectra of the disazo dyes possesses visible absorption peaks whose intensity changes with the polarity of the solvent. This is probably due to the aggregation of the dyes [15]. A strongly polar solvent such as water considerably affected the spectra/absorption maxima of the dyes. The dyes derived from J-acid, derivatives of terephthalic acid (A₁-A₄), exhibited bathochromic shift in relation to bands of dyes derived from isophthalic acid (A₅-A₈).While in the case of dyes

derived from H-acid, an opposite effect was observed, i.e. the absorption bands of dyes derived from terephthalic acid (B₁- B₄) shifted hypsochromically in relation to dyes derived from isophthalic acid (B₅- B₈). This confirms the existence of conjugation between two parts of dye.

Solvatochromic effects

With increasing polarity of the solvent, the absorption maximum is shifted to longer wavelengths [13]. The interaction of the solvent with the dye molecule is greater in polar solvent [8]. Most of the shifts in maximum absorption wavelength observed were bathochromic for majority of the dyes where measurements were done in solvent of higher polarity. For most of the dyes, the maximum absorption wavelengths values shifted to longer wavelengths when the solvent is changed from ethanol to dimethylformamide (DMF). Although some of the dyes had negative solvatochromism, i.e. a hypsochromic shift to lower wavelength in the visible absorption spectrum when the solvent was changed from ethanol to dimethylformamide. Some of the dyes showed no change in wavelengths from ethanol to DMF, for example, dye A₃, A₄, A₇, A₈, B₁, B₆, B₇ and B₈. This is a clear indication that, the visible band is due to $\pi \rightarrow \pi^*$ transition since a positive solvatochromism occurred in some of the dyes and $n \rightarrow \pi^*$ transition since a negative solvatochromism also occurred in some of the dyes [10].

Halochromism (Effect of acid on visible absorption band)

Eight of the synthesized dyes exhibit positive halochromism (for examples dyes A₁, A₂, A₃, A₆, B₃, B₅, B₆), in acidic ethanol solution, indicating a bathochromic shift of +5nm in the dyes above. Also dye B₇ in a neutral solution of ethanol absorbed at 505nm but maximally absorbed at 508nm in acidic ethanol solution, indicating a bathochromic shift of +3nm.

However, some of the dyes showed a negative halochromism. For example, dyes A₅ and A₇ absorbed in neutral ethanolic solution both at 510nm but absorbed maximally both at 505nm in acidic solution of ethanol, indicating a hypsochromic shift of -5nm. The dyes that exhibited positive and negative halochromism can be used as indicators in acid-base titration.

Fastness properties of the dyes.

The wash fastness results before after- treatment of the dyed fabric as shown in Table 5 were in the range of very poor to poor, rating of between 1-3 on the grey scale, except for dye B₁ which had moderate fastness of 3 -4. This poor wash fastness is as a result of the presence of two or more sulphonic acid groups present in high molecular weight direct dyes which makes them water-soluble in the dye bath and on the fibre. This accounts for the relative ease with which the dye is removed from the fibre on washing in water [12]. The poor wash fastness is also attributed to the characteristics of direct dyes on cellulose when not aftertreated.

Fastness to washing upon the after-treatment process: As a result of the poor wash fastness properties obtained, the original samples were subjected to an after treatment process using 8% formaldehyde. The results obtained are shown in Table 5.

Table 5: Fastness rating to washing

DYE NO.	CHANGE IN COLOUR Rating before	STAINING ON COTTON aftertreatment	CHANGE IN COLOUR Rating upon	STAINING ON COTTON aftertreatment
A ₁	3	4-5	4-5	5
A ₂	2	3	3-4	4
A ₃	3	3	4	4
A ₄	3	3-4	4-5	5
A ₅	2	3-4	3-4	4-5
A ₆	2-3	3	4	4-5
A ₇	3	3	4	4-5
A ₈	2	3-4	4-5	5
B ₁	3-4	4-5	4-5	5
B ₂	2	4-5	4-5	5
B ₃	2	4-5	4	5
B ₄	2	4-5	4	4
B ₅	3-4	4-5	4-5	5
B ₆	2	4-5	4	4-5
B ₇	1-2	4-5	4	5
B ₈	3	4-5	4-5	4-5

The results were greatly improved as all the dyes had good to moderate fastness to washing of between 3- 4, 4 and 4-5 as compared on the grey scale while staining on the adjacent fabric are from 4 - 5 indicating that they are rarely stained. This after-treatment worked on the principle of increasing the size of the dye molecule or decreasing the solubility in water by forming a methylene linkage between two of the dye molecule. Either of these effects restricts the ability of the dye to diffuse out of the fibre during washing [3].

Table 6: Fastness to rubbing and light fastness ratings of the dyed samples.

DYE NO	DRY	WET	DRY	WET	LIGHT RATING
	CHANGE IN COLOUR		STAINING ON COTTON		
A ₁	4-5	5	4	5	6
A ₂	5	4-5	5	4	5
A ₃	5	4	5	4	6
A ₄	5	4	5	4	5
A ₅	5	4-5	5	4-5	5
A ₆	4-5	4-5	4-5	4	5
A ₇	5	4-5	5	4-5	4
A ₈	5	4	5	4	6
B ₁	5	4-5	5	4-5	7
B ₂	5	4-5	5	4-5	5
B ₃	4-5	4-5	4-5	4-5	5
B ₄	5	4-5	5	4-5	7
B ₅	4-5	4-5	4-5	4-5	4
B ₆	5	4	5	4-5	4
B ₇	5	4	4-5	4	5
B ₈	4-5	4-5	4-5	4-5	7

Table 7: Fastness to perspiration

DYE NO	ALKALINE		ACID	
	CHANGE IN SHADE	STAINING	CHANGE IN SHADE	STAINING
A ₁	3	4	4	4
A ₂	3	3	3	4
A ₃	4	4	3	3
A ₄	3	3	3	3
A ₅	3	3	3	3
A ₆	3	2	3-4	4
A ₇	4	3	4	4
A ₈	3	3	4	4
B ₁	4	4	4	5
B ₂	4	5	4	5
B ₃	3	4	4	4
B ₄	4	4	4	4
B ₅	4	4	3	4
B ₆	4	4	4	4
B ₇	3	4	3	4
B ₈	4	3	5	5

The fastness to rubbing was done using a crockmeter and the results show that they have very good fastness to rubbing using wet and dry fabric. The results in Table 7 shows that the dyed samples in alkaline solution of histidine had good fastness properties to perspiration based on ratings between 3 and 4, with little and moderate staining on the adjacent fabric while the dyed samples in acidic solution had better resistance to perspiration based on rating of 3, 4 and 5 mostly for all the dyes. They also had good to moderate fastness to light.

V. Conclusion

The synthesis of direct dyes from terephthalic and isophthalic acid using J-acid and H-acid was undertaken. The type of bridging group used affects λ_{max} only to a slight extent, which indicate the transition of conjugation by the diamidesystem. The chosen method of acid chloride synthesis in an organic solvent (chlorobenzene) allows one to prepare products in a simple way, preventing partial decomposition. The selected method for the synthesis of disazo dyes is simple and makes it possible to prepare dyes in high yield.

Generally, the exhaustion of the dyes were very good on cotton fabric with poor wash fastness properties. Though, improvement was made upon after-treating the dyed samples with formaldehyde. They had good to moderate fastness to light, rubbing and perspiration. These dyes had bright and some deep shades on cotton due to high exhaustion and greater planarity of the dyes.

Based on the performance properties obtained, one can state that the obtained dyes can replace urea dyes and dyes derived from benzidine with similar structures.

Their practical properties such as light fastness, etc. especially those of the derivatives of J-acid are higher than those of the H-acid derivatives except for fastness to perspiration where the latter is better. The type of bridging group used in the dye synthesis plays an important part, with the best effect being obtained with the derivatives of isophthalic acid. They are observed to be relatively non-toxic and therefore can be used to dye apparel.

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