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Synthesis and Fastness Properties of Disazo Disperse Dyes Derived from 4-Amino-3-Nitrotoluene

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ABSTRACT

The synthesis and properties of a series of disazo disperse dyes are described. The use of different coupling components does not result in significant shift of the absorption maxima of the dyes which are mainly, a wide range of brown colours. All the dyes synthesized and applied by the thermosol process on 100 % polyester fibres, afforded very good light fastness, excellent washing, crocking and perspiration fastness. The dye structures were characterized by elemental analysis and spectral methods.

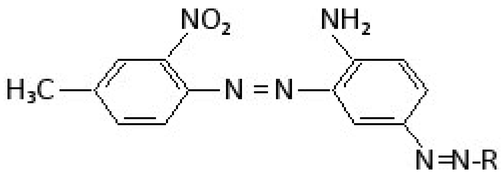
Key words: Synthesis, Fastness, Polyester, Thermofixation.

INTRODUCTION

The somewhat unusual conditions needed to produce an azo dye namely: strong acid plus nitrous acid for diazotization, the low temperature necessary for the unstable diazonum salt to exist, and the presence of electron rich amino or hydroxyl compounds to effect coupling means that azo dyes have no natural counterparts[1]. To this end, azo dyes will continue to attract extensive research activities, more so that disperse azo dyes have found use not only in the textile industry but also in other areas of human endeavour[2]. The use of disazo disperse dyes for colouring synthetic polymers is prevalent due to their increased washing fastness and substantivity.

Several mono-azo pigments synthesized from 4-amino-3- nitrotoluene, C.I. Azoic component 8, which are widely used commercially as paints, printing inks, emulsion paints, mass colouration of viscose and textile printing have been reported[3-6]. However, very few commercial disperse dyes derived from 4-amno-3-nitrotoluene have been reported in literature[7]. One example of such dye is C.I. Disperse Yellow 8, where the coupling component is 3-methyl-5-pyrazolone.'

Hence the goal of the present study was to prepare some disazo disperse dyes of the general structure 1 that possessed the features needed for affinity for the most widely used synthetic fibre such as polyester. Furthermore, the dyeing properties such as washing, light perspiration and crocking fastness were investigated.



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EXPERIMENTAL

Materials

All the chemicals and reagents used were purchased from Aldrich Chemical Company and BDH Chemical Company and are used without further purification.

Melting points of pure dyes were determined by using Gallenkamp heated block apparatus. The purity of the dyes were confirmed by Thin Layer chromatography (TLC) using Whatman 250 mm silica Gel 60 AMK 6F plates (ether/acetone 5:1).

Infra-red spectra were obtained using an ATI Mattson Genesis series FT-IR spectrophotometer. Uv-visible spectra were recorded on a unicam spectrophotometer equipped with Helios scan software in dimethylformamide (DMF) at concentration of $3.4x1\ 0^{-4}$ M. Elemental analyses were carried out on a Perkin Elmer 240C for C, N and H.

The polyester (Terylene) fabric (100 %) was obtained from multichem (Nigeria) Ltd, and pretreated. Dyeings were carried out on polyester (terylene) fabric pieces (1.0 gm) at 1% depth in a bath containing 0.1 g (o.w.f) dispersing agent (Macheasl, Alfprint textile Co. Nigeria) using the thermofixation (thermosol) process. This was followed by reduction clear treatment in a bath containing sodium hydrosulphite (2 g/L), caustic soda (2 g/L) and dispering agent (2 g/L) for 15 mins at 80 °C[8].

The wash fastness of the dyed fabrics was evaluated using ISO washing test No 3[9]. Light fastness assessment was carried out on a Xenotest Model 450 instrument (Quartz-Lapen Gm bH, Hanau) using standard procedure[10].

Perspiration fastness was determined according to ISO, E04 test method[11]. Perspiration fastness test was determined according to ISO, 105-E04 1994 standard method. Both alkaline and acid perspiration tests were evaluated. Crocking fastness was tested according to AATCC Test method[10].

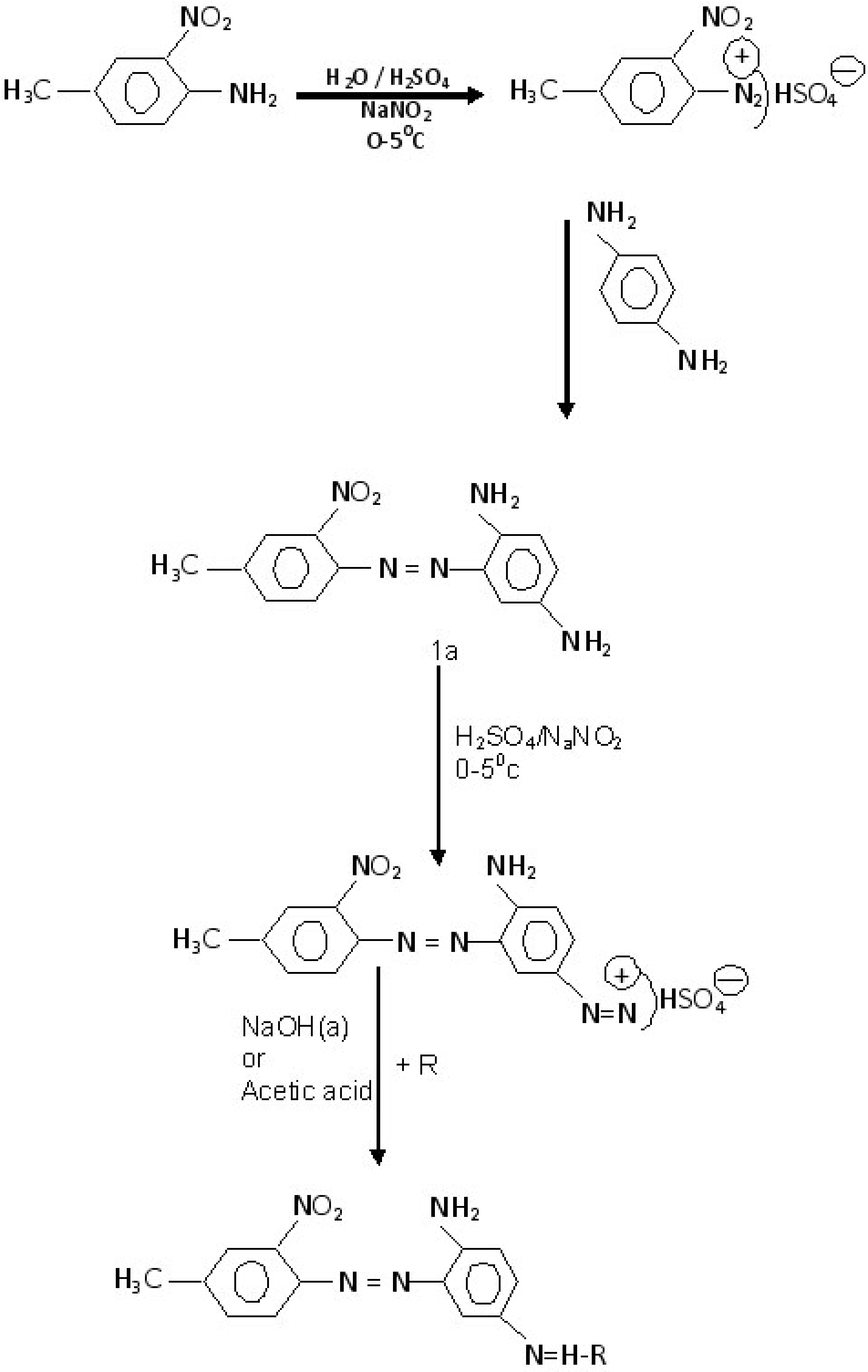
Synthesis

Dye synthesis of disperse dyes (scheme 1) was carried out by utilizing the following standard preparation[12-13]. 2-nitro-4-methylphenyl azo-2,5-diaminobenzene (1a) used in the synthesis was obtained in 53 % yield, by diazotizing 4-amino-3-nitrotoluene (4.0 g, 0.263 mole) dissolved in a mixture of water (50 mmL) and concentrated sulphuric acid (8 mL), boiled and cooled. This was followed by the addition of sodium nitrite solution (3.73 g in 10 mL water) dropwise with stirring for 15 mins to give the diazonium salt solution. 1,4-diaminobenzene (2.84 g, 0.263 mole) was dissolved in glacial acetic acid (20 mL) and slowly added to the diazolised amine and the mixture stirred vigorously for 2 hrs to give a dark brown solid of the monoazo dye (1a) as shown in scheme 1.

Method 1

Synthesis of 2-nitro-4-methylphenylazo-2-aminophenylazo-4-hydroxynaphthalene (dye 1).

The monoazo dye (1a) (2.0 g; 0.0073 mole) was diazotized by dissolving it in a mixture of concentrated sulphuric acid (8 mL) and distilled water (50 mL). The solution was cooled with ice to 0-5°C and a cold solution of sodium nitrite (4.0 g, 0.58 mole in 10 mL of water) was added dropwise with continuous stirring for 15 mm. The excess of nitrous acid was destroyed by the addition of 10 % urea solution. The diazonium salt solution obtained above, was added slowly with vigorous stirring into a solution of 1-naphthol (1.0 g; 0.007 mole) in a 2.0 M sodium hydroxide (60 mL) for 2 hrs. The crude product was filtered, washed and dried. Recrystallization from hot boiling carbon tetrachloride yielded a dark brown solid dye (1.9 g; 60.5 %) mp 270 °C. TLC showed only one component of dye 1, R_f 0.60 (ether/acetone, 5:1). Similar dyes were prepared by using different phenolic compounds as coupling components (see table 1).



Scheme 1: Synthesis of Disazo dyes derived from 4-amino-3-nitrotoluene

Method II

Synthesis of 2-nitro-4-methyl phenylazo-2-aminophenylazo- 3-chloro-4-aminobenzene (dye 10)

Concentrated sulphuric acid (8 mL) was added to a dispersion of dye (1a) (2.0 g; 0.007 mole) in water (50 mL). The mixture was cooled to 0-5 °C and cold sodium nitrite (3.7 g; 0.053 mole in 10 mL water) was added dropwise with vigorous stirring for 15 mins urea solution was added to remove excess of nitrous acid. The resultant diazonum salt solution was then added to a solution of 2-chloroaniline (3 mL) in glacial acetic acid (20 mL) with vigorous stirring for 2 hrs and the product was filtered, washed with water and dried. The crude product was recrystallized from hot boiling carbontetrachioride to yield a brown powdered dye (10) (1.87 g, 62 %), mp = 280 °C, TLC analysis using ether/acetone (5:1) gave R_f 0.52. Similar compounds were prepared by using different substituted arylamino compounds as coupling components (see table 1).

RESULTS AND DISCUSSION

Synthesis

4-Amino-3-nitrotoluene (1) (an aromatic pigment) was the starting material for the studies. Scheme 1 shows that the first step of the synthesis is the diazotization of the starting material and subsequent coupling with 1,4-diaminobenzene to give the monoazo dye (1a). In this regard, (1) was treated with nitrous acid according to a published method[12]. The yield of (1a) was relatively moderate (53.0 %). In the second step of the reaction sequence, (1a) was diazotized and the diazonium salt obtained was coupled with various phenolic and amino compounds (R) (see table 1) to give the corresponding disazo disperse dyes.

The yields of the dyes prepared are shown in Table 1. The melting point criterion for purity shows that the dyes generally melt over a narrow temperature range difference of 1-2, hence the dyes were sufficiently pure.

The visible absorption spectra of the dyes were recorded in DMF, the results of which are summarized in Table 1. All the dyes showed a multiple of absorption bands except dye 1 corresponding to bands in the region of 326-420 nm and 420-580 nm.

From Table 1, the infra-red spectral data of the dyes showed absorption frequencies of -OH and -NH, stretching vibrations, asymmetric and symmetric -NO_2 vibrations, C=O stretching vibration for dye 5 and C-O-C stretching vibrations for dye 8. All these agreed with that reported in the literatures[14-17].

Fastness properties

Light fastness

The light fastness testing results (Table 3) showed that all the dyes have very good light fastness on polyester fibre with a rating of 7. The high photostability of the dyes on polyester fibre could be attributed to the nitro group in the position ortho to the azo group. This tends to corroborate the work done on the effects of substituent groups on the light fastness of azo dyes. Thus, high electron density around the azo group generally lowers light fastness, whereas low electron density brings about an increase[18].

Wash fastness

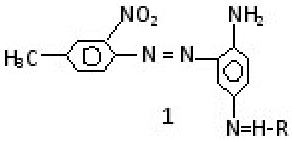
The wash fastness testing data of the dyes (Table 3) showed that all the dyes recorded excellent performance on polyester. The high fastness to washing on PET indicates that the dyes have high affinity for the polyester fibre.

Perspiration fastness

The results of the perspiration fastness test. Show that both alkaline and acidic perspiration fastness on PET is excellent. The high perspiration fastness of the dyes may be due to the state of the dyes in the fabrics, being in form of insoluble particles to the attack of most chemicals in aqueous solution[14].

However, the results obtained from the crocking fastness test gave relatively poor performance on PET except the dry rubbing fastness of dyes 1, 5, 6, 7, 8, 9 and 10 which gave moderate ratings.

Table 1: Characterization data for disazo dyes derived from 4-amino-3-nitrotoluene



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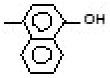
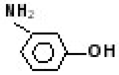
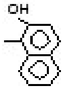
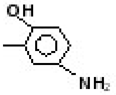
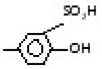
Dye	R	Synthesis method and recrystallization solvent	Pure yield (%)	MP (°C)	λmax (nm)	εmax $Lmol^{-1}$ cm^{-1}	IR (KBr)cm^{-1}
1		1A	61.0	270	446	16,500	3350 (Ar-OH) 3186 (Ar-NH_2) 1528 (Ar-NO_2) 1305 (Ar-NO_2) 721 (Ar-ring)
2		1A	55.0	217-219	328,446	63,900	3437 (Ar-OH) 3190 (Ar-NH_2) 1512 (Ar-NO_2) 1310 (Ar-NO_2) 722 (Ar-ring)
3		1A	62.0	200	328,420	26,700	3340 (Ar-OH) 3185 (Ar-NH_2) 1504 (Ar-NO_2) 1306 (Ar-NO_2) 721 (Ar-ring)
4		1A	52.0	208-210	420,580	39,600	3434 (Ar-OH) 3309(Ar-NH_2) 1527(Ar-NO_2) 1308 (Ar-NO_2) 842 (Ar-ring)
5		1A	58.0	285	420,580	63,600	3448 (Ar-OH) 3182 (Ar-NH2) 1525 (Ar-NO_2) 1309 (Ar-NO_2) 1744 (C=0) 791 (Ar-ring)

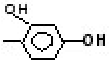
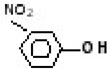
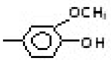
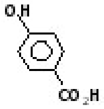
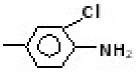
6		1A	67.0	242	420,580	28,200	3520 (Ar-OH) 3170 (Ar-NH$_2$) 1526 (Ar-NO$_2$) 1318 (Ar-NO$_2$) 722 (Ar-ring)
7		1B	51.0	270	466,580	12,800	3723 (Ar-OH) 3407 (Ar-NH$_2$) 1532 (Ar-NO$_2$) 1325 (Ar-NO$_2$) 721 (Ar-ring)
8		1B	35.9	276	420,580	75,800	3570 (Ar-OH) 3409 (Ar-NH$_2$) 1528 (Ar-NO$_2$) 1250 (Ar-NO$_2$) 721 (Ar-ring)
9		1A	68.1	292	448,380	44,700	3432 (Ar-OH) 3167(Ar-NH$_2$) 1525(Ar-NO$_2$) 1310 (Ar-NO$_2$) 721 (Ar-ring)
10		2A	62.0	280	420,580	57,900	3448 (Ar-NH$_2$) 1525 (Ar-NO$_2$) 1333 (Ar-NO$_2$) 791 (Ar-ring)

Table 2: Elemental Analysis of dyes 1 – 20

Dye	Formula	Mol. wt.	C(%)		H(%)		N(%)	
			Found	**Calc.**	**Found**	**Calc.**	**Found**	**Calc.**
1	$C_{23}H_{18}N_6O_3$	426	64.78	64.72	4.25	4.29	19.71	19.70
2	$C_{19}H_{17}N_7O_3$	391	58.33	58.31	4.36	4.38	20.00	25.05
3	$C_{25}H_{18}N_6O_3$	426	6418	64.71	4.25	4.26	19.71	19.70
4	$C_{19}H_{17}N_7O_3$	391	58.31	58.27	4.38	4.35	25.05	25.01
5	$C_{20}H_{16}N_6O_5$	420	57.14	57.09	3.84	3.81	19.99	19.98
6	$C_{19}H_{16}N_6O_4$	392	58.16	58.13	4.11	4.07	21.42	21.45
7	$C_{19}H_{15}N_7O_5$	421	56.16	56.11	3.59	3.53	23.27	23.24
8	$C_{20}H_{18}N_6O_3$	390	61.53	62.54	4.65	3.63	21.53	21.49
9	$C_{19}H_{18}N_6O_3$	420	57.14	57.11	3.84	3.78	19.99	19.95
10	$C_{19}H_{18}N_7O_2Cl$	409.6	55.68	55.63	3.94	3.96	23.92	23.88

Table 3: Fastness Properties of Dyes 1 – 20 on Polyester fabrics

Dye	Wash Fastness	Perspiration		Crocking fastness		Light fastness
		Alkaline	Acid	Dry	Wet	
1	5	5	5	3	2	7
2	5	5	5	2	2	7
3	5	5	5	2	2	7
4	5	5	5	2	2	7
5	5	5	5	3	2	7
6	5	5	5	3	2	7
	5	5	5	3	2	7
8	5	5	5	3	2	7
9	5	5	5	3	2	7
10	5	5	5	3	2	7

Grey scale ratings ranged from 1 (poor) to 5 (excellent)
The Grey scale of light fastness ranged from 1-2 (very poor)
3 (poor) to 8 (excellent)

CONCLUSIONS

A series of disazo disperse dyes were prepared from the coupling reactions between aromatic amino or hydroxyl-compounds (couplers) and diazotized 4-amino-3-nitrotoluene, and their fastness properties were very good.

All the dyes prepared in this study, exhibited different shades of brown on polyester and from the fastness evaluations, the dyes have high affinity for polyester especially when dyed, using the thermofixation process. The high light fastness of the dye may be due to the election-withdrawing (-NO_2) group substituent ortho to the azo group in the dye molecule.

Finally, with the high light fastness performance of the dyes on polyester, they could be very good colours for the dyeing of polyester upholstery trim in the automotive sector and also for textile fibres meant for use as curtains.

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