



Synthesis, Spectra Studies and Colour Assessment of Acid Dyes Derived From Benzimidazoles on Nylon 6, 6 Fabric

¹Issa O. Ibrahim, ²A. Giwa, ²U. S. Ameuru

¹Department of Textile Technology, College of Science & Technology, Kaduna Polytechnic, Kaduna

²Department of Polymer & Textile Engineering, Ahmadu Bello University, Zaria, Kaduna

ABSTRACT

Novel azo acid dyes were synthesized from benzimidazole derivative using Gamma acid and J-acid as coupling components in good yield. The dyes were characterised using UV-Visible, NMR and FT-IR spectroscopic techniques. The synthesised dyes were applied on nylon 6, 6 fabrics and gave firebrick and dark red respectively. The percentage dye exhaustion (64-67%) was very good. The dyed fabrics showed moderate to very good fastness to light, wash and perspiration.

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INTRODUCTION

Colourants (dyes, lakes or pigments) are of great industrial and technical applications, ranging from clothes, plastics, paints, prints, ceramics and photographs and so on [1]. All dyes were obtained from natural sources (plant, animal or mineral) until the middle of nineteenth century and as a result, textile materials were only coloured with natural dyes [2]. However, dyeings produced using these dyes generally exhibited poor fastness properties. Synthetic dyes come to light due to the development of synthetic organic chemistry and some early synthetic dyes include picric acid, maurexide, aurine (rosolic acid), Aniline Purple (Mauve or Mauveine), etc. The latter was the first commercial synthetic dye and was introduced by William Henry Perkin in 1856 [3, 4].

Azo dyes (colourants) as described by [2] contain as their common structural feature, the azo ($-N=N-$) chromophore that is attached at either side to two sp^2 carbon atoms. The unique characteristic of azo dyes is the presence in their molecule of one or more azo groups (chromophores) which forms bridges between organic residues, of which at least one is usually an aromatic nucleus.

Benzimidazole is one of the oldest known nitrogen heterocycles [5] and its ring system can be derived by fusion of an imidazole ring to a benzene ring, through the 4-5 bond of

imidazole ring [6]. Although many studies conducted on the extensive use of compounds with azo moiety as dyes have been reported [7, 8, 9], but the use of benzimidazole moiety as dyes is less reported. The goal of this research therefore was to prepare azo dyes from benzimidazole derivatives that incorporated different heterocycles of activity on nylon 6, 6 fabrics.

MATERIALS AND METHOD

Materials

All the chemicals used were of commercial and analytical grade and were used without further purification. Nylon 6, 6 fabrics was obtained commercially and further confirmed using 80% formic acid and melting point determination. Melting points were determined by the open capillary method using the Gallenkamp melting point apparatus (CO10127), expressed in $^{\circ}C$ and are uncorrected. The visible absorption spectra were measured using Cary 300 UV-Visible spectrophotometer (Multi-User Science Research Laboratory, ABU Zaria). The infra-red spectra were measured and recorded on Agilent Technologies Cary 630 FTIR spectrophotometer (Multi-User Science Research Laboratory, ABU Zaria). Proton nuclear magnetic resonance (1H NMR) spectra were recorded with Varian -400 (400 MHz) (Multi-User Science Research Laboratory, ABU Zaria) instrument in dimethyl



sulfoxide (DMSO-d₆) as solvent using tetramethylsilane (TMS) as internal standard and chemical shifts are expressed as δ ppm. The light fastness was carried out using microscopical light fastness Tester (225) (Kaduna Polytechnic).

Methods

Synthesis of 1-(1H-benzimidazol-2-yl)-propan-2-one (Intermediate 1)

Equimolar amounts of ethyl acetoacetate 1 (1.30 g, 0.01 mol) and o-phenylenediamine 2 (1.08 g, 0.01 mol) was fused in an oil bath at 120 °C for about 30 minutes and then poured onto ice/water mixture. The solid product (3) formed was collected by filtration, washed with water and crystallized from ethanol [10].

Off-white crystals, m.p. 97-101 °C, yield: 1.33g (75%); IR (u, cm⁻¹): 3750(O-H str.), 2950-2950(NH str.), 2350(O=C=O str.), 1690(C=O str.), 1550-1500(N-O str.), 1450, 1200-1150(C-O str.); ¹H NMR (δ , ppm): 2.50 (s, 3H, CH₃), 3.73(s, 2H, CH₂), 7.02-7.42 (m, 4H, C₆H₄), 10.90 (s, 1H, NH).

Synthesis of 2-[2-(1H-Benzimidazol-2-yl)-1-methyl ethylidene]-malononitrile (Intermediate 2)

Malononitrile (0.66 g, 0.01 mol) was added to a solution of compound 3 (1.74 g, 0.01 mol) in ammonium acetate (0.8 g, 0.01 mol). The reaction mixture was fused under reflux at 120 °C for 15 minutes. The reaction mixture was then boiled in ethanol (20 ml) for few minutes, and then cooled by pouring onto ice/water mixture. The solid product formed (4) was collected by filtration and crystallized from ethanol [10].

Faint off-white crystals, m.p. above 300 °C, yield: 1.41 g (63%); IR (u, cm⁻¹): 3225-3125 (NH str.), 3021 (CH aromatic str.), 2905-2807 (CH₂, CH₃ str.), 2200, 2192 (2CN str.), 1629, 1480 (C=C str.); ¹H NMR (δ , ppm): 2.53 (s, 3H, CH₃), 3.47 (s, 2H, CH₂), 6.93-6.99 (m, 4H, C₆H₄), 10.60 (s, 1H, NH).

Synthesis of 8-(2-(1-(1H-benzo[d]imidazol-2-yl)-3,3-dicyano-2-methylallylidene)hydrazinyl)-6-amino-4-hydroxynaphthalene-2-sulfonic acid (Dye 1)

6-amino-4-hydroxynaphthalene-2-sulfonic acid (Gamma acid [0.24 g, 0.001 mol]) was dissolved in 1ml of 30% sodium hydroxide (NaOH) solution. Sodium nitrite (NaNO₂ [0.07 g, 0.001 mol]) dissolved in 25 ml of distilled water was gradually added for 15 minutes while stirring in an ice-bath. Concentrated hydrochloric acid (HCl [0.76 ml, 0.025 mol]) was then gradually added to the mixture for 30 minutes while stirring in an ice-bath and the reaction was allowed to proceed for 30 minutes.

To a cold solution (0-5°C) of 2-[2-(1H-Benzimidazol-2-yl)-1-methyl ethylidene]-malononitrile (0.17 g, 0.001 mol) in ethanol (5-10 ml) containing sodium acetate (1.00 g), an equimolar amount (0.001 mol) of diazotized Gamma acid was gradually added while stirring for 30 minutes. The reaction was allowed to proceed for 1 hour and the solid product formed upon cooling in an ice-bath was collected by filtration, washed with water and crystallized from ethanol.

8-(2-(1-(1H-benzo[d]imidazol-2-yl)-3,3-dicyano-2-methylallylidene)hydrazinyl)-6-amino-4-hydroxynaphthalene-2-sulfonic acid (Dye 1): firebrick crystals, m.p. above 300°C; yield: 0.55 g (70%); IR (u, cm⁻¹): 3787, 3712.4(O-H str.), 3369.5(N-H str.), 2079.9(N=C=S str.), 1912(C=C=C str.), 1617.7(C=C str.), 1423.8(S=O str.), 1341.8, 1036.2 (C-N str.), 1099.6(C-O str.); ¹H NMR (δ , ppm): 1.202 (s, 2H, CH₂), 1.875 (s, 3H, CH₃), 1.983-2.366 (t, 6H, 3NH₂), 2.472-2.641 (s, 2H, 2CH), 3.198-3.320 (s, 6H, 2CH₃), 3.741 (s, 3H, 3CH), 5.673 (s, 1H, CH), 7.158-8.453 (m, 14H, C₆H₄, 2C₆H₅), 8.557-8.629 (s, 2H, NH₂), 12.685-12.778 (t, 3H, Aromatic).

Synthesis of 8-(2-(1-(1H-benzo[d]imidazol-2-yl)-3,3-dicyano-2-methylallylidene)hydrazinyl)-7-amino-4-hydroxynaphthalene-2-sulfonic acid (Dye 2)

7-amino-4-hydroxynaphthalene-2-sulfonic acid (J-acid [0.24g, 0.001 mol]) was dissolved in 1ml of 30% sodium hydroxide (NaOH) solution and the synthesis was carried out as in Dye 1 above. 8-(2-(1-(1H-benzo[d]imidazol-2-yl)-3,3-dicyano-2-methylallylidene)hydrazinyl)-7-amino-4-hydroxynaphthalene-2-sulfonic acid: dark red crystals, m.p. above 300°C; yield: 0.66 g (84%);



IR (ν , cm^{-1}): 3362.4(N-H str. Aliph.), 2081.3 (N=C=S str.), 1487.2(C=C str.), 1386.6, 1177.8 (S=O str.), 1267.3(C-N str. Ar.), 1103.3, 1043.7 (2C-N str.).

Dyeing Procedure

Dyeing was carried out using a material to liquor ratio of 1:50. Shade (3%) was used for dyeing On Weight of the Fabric (OWF). The dye was dissolved in distilled water (5 ml) with constant stirring; the pH was adjusted to 5 using glacial acetic acid (1ml). The dye solution (50 ml) was transferred into a beaker and placed on the mantle. The temperature was allowed to rise to 60°C after which the semi-dried nylon fabric was immersed in the beaker while the temperature was allowed to rise to about 100°C. This was constantly monitored with a thermometer. The dyeing was carried out for one hour and this procedure was repeated for the second dye. The dyed fabrics were then removed, thoroughly washed with water and dried at ambient conditions. The colour of the dyes on nylon 6, 6 fabrics is indicated (Table 1).

Fastness properties

The colour fastness to light, washing, and perspiration was determined according to the standard methods [11, 12]. Data are indicated in Table 2.

Colour Fastness to Light

The colour fastness to light was carried out using microscal light fastness tester. A swatch of each dyed fabric was attached to the specimen holder of a microscal light fastness tester and the holder set in the tester. The samples were exposed to light (mercury lamp type MB/U, 500W) for 48 hours. The samples were then assessed on 'IWS' viewing cabinet and compared with the Blue wool light fastness reference standards, which consists of eight blue wool of different colour strength.

Colour fastness to washing

The colour fastness to washing was determined using ISO wash fastness test number 3. Each dyed fabric (10 cm x 4 cm) was taken and sandwiched between two pieces of bleached adjacent cotton fabrics and stitched. The sample and the adjacent fabrics were immersed and washed together in 100ml beaker containing

soap solution (15ml) and sodium carbonate (10ml) at 60 °C for 30 minutes, using liquor ratio of 50:1. The changes in colour of the dyed specimens were assessed after drying using the Grey scale.

Colour Fastness to Perspiration

Two artificial perspiration solutions were prepared according to the following:

Acidic solution: L-Histidine monohydrochloride monohydrate (0.5g), sodium chloride (5 g) and sodium dihydrogen phosphate-1-hydrate (2.2g) were dissolved in distilled water (1 L). The pH was adjusted to 5.5 by 0.1N sodium hydroxide solution.

Alkaline solution: L-Histidine monohydrochloride monohydrate (0.5 g), sodium chloride (5 g) and di-sodium hydrogen phosphate-2-hydrate (2.5 g) were dissolved in distilled water (1 L). The pH was adjusted to 8 by 0.1N sodium hydroxide solution.

The coloured sample was stitched between two pieces of bleached cotton sample. The composite sample was then immersed for 30 minutes in the acidic perspiration solution at (37 ± 2) °C with occasional agitation and squeezing to ensure complete wetting. The test sample was placed between two glass plates under a force of about 5 Kg. The plates containing the composite samples were left for about 6-8 hours. The same procedure was followed with another composite sample using the alkaline perspiration solution. The effect on the colour of the test samples was assessed using the Grey scale for colour change.

RESULTS AND DISCUSSION

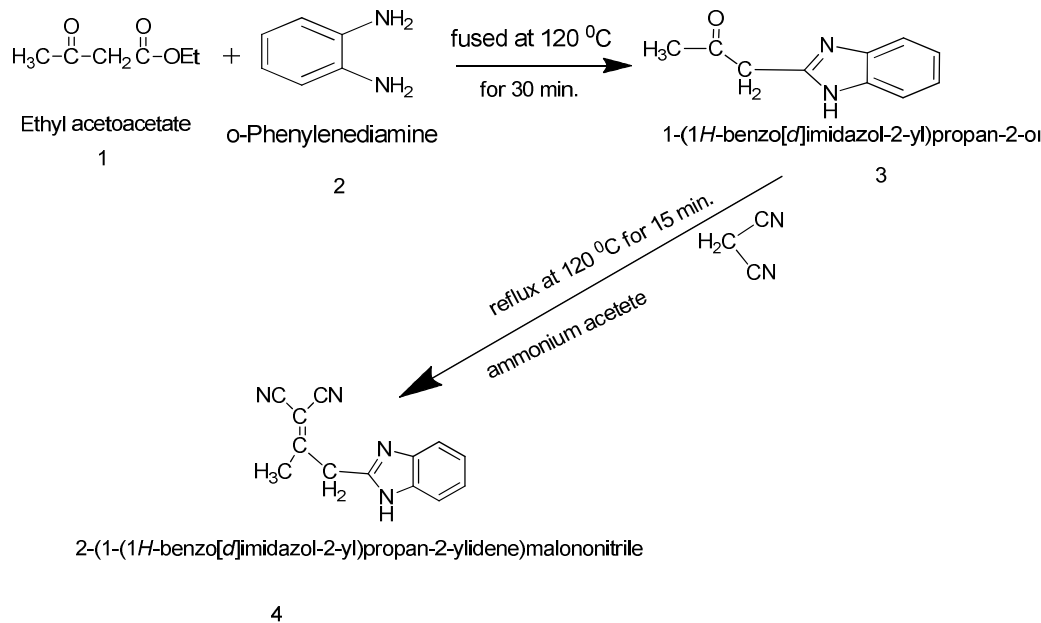
Syntheses of Intermediates and Dyes

The reaction of ethyl acetoacetate (1) with o-phenylenediamine (2) in an oil bath at 120 °C gave the 1-(1H-benzimidazol-2-yl)-propan-2-one (3). The melting point and yield were 97-101 °C and 75% respectively. The structure of intermediate 3 was established on the basis of analytical and spectral data. The reaction of compound 3 with malononitrile in ammonium acetate at 120 °C gave the Knoevenagel condensation product (4). The analytical and

spectral data of intermediate 4 are in agreement with the assigned structures (see scheme 1).

The ^1H NMR spectra of the intermediates displayed signals at 2.50 and 2.53 ppm respectively, which correspond to the terminal methyl ($-\text{CH}_3$) groups. The peaks at

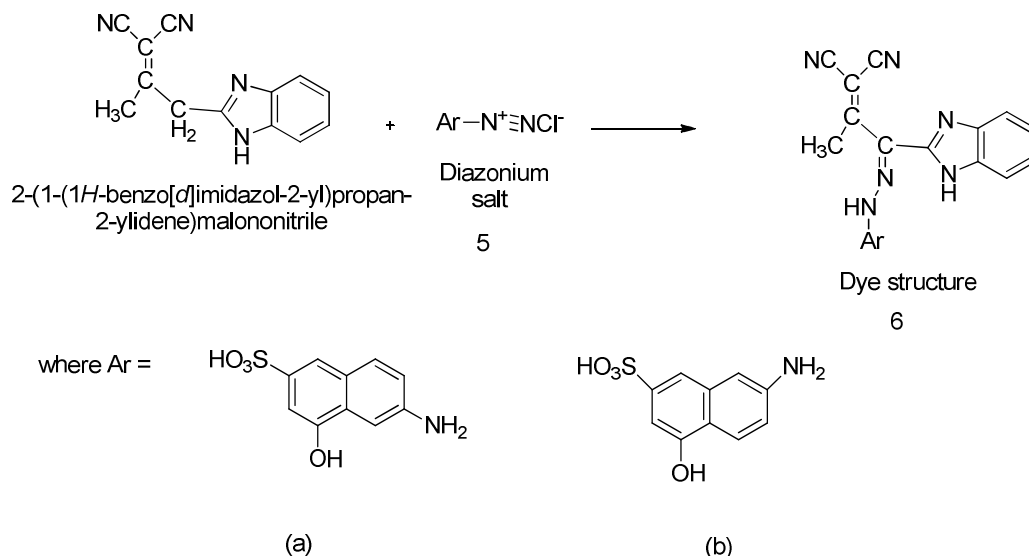
3.47-3.73 ppm showed the methylene ($-\text{CH}_2-$) groups of the propan-2-ylidene. The aromatic protons showed signals at 6.93- 7.42 ppm as multiplets for all the intermediates. Protons associated with NH_2 substituent were observed at 10.60-10.90 ppm.



Scheme 1: Synthesis of the Intermediate

The reactivity of compound 4 with diazonium salts namely 6-amino-4-hydroxynaphthalene-2-sulfonic acid (Gamma acid) (5a) and 7-amino-4-hydroxynaphthalene-2-sulfonic acid (J-acid) (5b) was studied. The reaction occurred in ethanolic/sodium acetate solution at 0-5 °C to give the arylhydrazone derivatives (6a) and (6b) respectively (see scheme 2). The analytical and spectral data of the dyes were in consistent with their respective structures (see experimental section). Thus, the ^1H NMR spectrum of the dye 'dye 1' displayed

signals at 1.202 and 1.875 ppm due to methylene ($-\text{CH}_2-$) and methyl ($-\text{CH}_3$) protons respectively. The peaks at 1.983-2.366 ppm and at 8.557-8.629 ppm revealed NH_2 group. Methyne groups ($-\text{CH}-$) are indicated by the signals at 2.472-2.641 ppm and 3.198-3.320 ppm. The aromatic protons showed signals at 7.158-8.453 ppm as multiplets, which correspond to C_6H_4 and C_6H_5 moieties. This dye also showed signals at 12.685-12.778 ppm, which is attributed to OH group linked to aromatic compound.



Scheme 2: Syntheses of the Dyes

Solvatochromism

Table 1: Wavelength of Absorption maxima and Molar Absorptivity of the Synthesized Dyes

Dye Number	ϵ_{\max} in DMF $\times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$	DMF $\lambda_{\max}(\text{nm})$	Distilled Water $\lambda_{\max}(\text{nm})$	Ethanol $\lambda_{\max}(\text{nm})$ a	Ethanol +HCl $\lambda_{\max}(\text{nm})$ b	Change in $\lambda_{\max}(\text{nm})$ (b-a)
D1	0.71	555	518	539	538	-1
D2	0.71	516	516	502	512	+10

The absorption spectra of the synthesized dyes were measured in various solvents and the molar absorptivity for each dye was calculated as listed in Table 1 above. Wavelength of absorption maxima (λ_{\max}) and molar absorptivity (ϵ_{\max}) of the synthesized dyes were 555nm and 516 nm and $7.1 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $7.14 \text{ l mol}^{-1} \text{ cm}^{-1}$ in DMF respectively. The λ_{\max} shifts in different solvents are brought about by the solvatochromic effect resulting from changes in the dielectric constant of the solvents [13].

The absorption maxima of Dye D2 (see table 1) showed bathochromic shifts when a small amount of HCl was added to the dye solution in ethanol. This is in agreement with [14], who attributed this to the increase in dipole moment of the molecule upon excitation, which results in stabilization of the excited state more than the ground state. As a result of this, the

separation between the ground and excited state energies is decreased and the absorption spectrum is red-shifted. Dye D1, however showed hypsochromic shifts (see table 1). This is due to decrease in dipole moment of the dye in the excited state as compared to the ground state, consequently stabilizing the ground state energy in polar solvents.

Solvatochromism, (the change in position and sometimes intensity of a UVvisible absorption band as a result of a change in the polarity of the medium) is therefore caused by differences in solvation of the ground and the first excited state of the light absorbing molecule. Negative solvatochromism (blue shift) will result if the ground state molecule is better stabilized by solvation (with increasing solvent polarity) than the molecule in the excited state. Positive solvatochromism (red shift) will on the other hand



take place if better stabilization of the molecule in the first excited state relative to the ground state (with increasing solvent polarity) occurs [14, 15].

Colour Assessment and Dyeing Properties

The results of fastness as well as the colour shades assessment on tested fabrics (nylon 6, 6) are listed in Table 2.

Table 2: Colour shades and Fastness Properties of the Synthesized Dyes on Nylon 6, 6 fabrics

Dyed Fabric Number	Dye Shade (%)	Colour Shade	Fastness			
			Light	Washing	Perspiration	
					Acidic	Alkaline
D1	3	Fire brick	5	3	3	4
D2	3	Dark red	3	3	4	4

The novel dyes were applied to nylon 6, 6 fabric at 3% depth on heating mantle and the dyeing gave fire brick/ dark red (Table 2). The dyed fabrics were analysed on qualitative tests by estimation of fastness shades with Grey scale. The results were expressed in terms of colour ratings 1-8 for light fastness and 1-5 for washing and perspiration fastness (Table 2). The dyes generally gave good levelness and fibre penetration on nylon. The light fastness for dye 1 is very good with rating 5, while for dye 2, the light fastness is fair with rating 3. The high light fastness rating for dye 2 occurred as a result of the presence of -OH group in the Para position in the dyes. This is in complete agreement with [10] who suggested that, the presence of -OH group in the Para position of the dye will give minimum fading. The washing fastness for dye 1 and dye 2 is good with rating 3. Perspiration fastness in acidic medium for dye 1 is good with rating 3, but in alkaline medium, the fastness is very good with rating 4. Perspiration fastness in acidic and alkaline media for dye 2 is very good with rating 4. The high ratings for change in colour at both acidic and alkaline conditions for dye 2 indicate that the sensitivity of the dyed samples is not related to pH. This may be due to the stability of the dye towards degradation under either acidic or basic conditions [10].

CONCLUSION

A new series of monoazo acid dyestuffs based on 1-(1H-benzimidazol-2-yl)-propan-2-one 3 were synthesized from ethyl acetoacetate and o-phenylenediamine as starting materials. The data obtained by various

analytical techniques confirmed the structures of intermediate and the dyes. The electronic absorption spectra of the synthesized dyes gave a wavelength range of 516-555 nm in DMF at uniformly absorption intensity of $0.71 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$. The dyes were investigated for their dyeing characteristics on nylon 6, 6 fabrics. The dyes gave bright and dark intense hue of red on nylon 6, 6 fabrics. They showed good to very good fastness to light, washing and very perspiration. The novel azo acid dyes gave good fastness results when compared with known commercial acid dyes.

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