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Preparation and Evaluation of Fastness Properties of Carboxylic Acid Group of Heterocyclic Azo Dyes

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Abstract: 4-aminobenzoic acid and 4-amino-2-hydroxybenzoic acid were diazotized and coupled correspondingly with 8-hydroxyquinoline, 5-nitroso-8-hydroxyquinoline, 5-nitro-8-hydroxyquinoline and 5-chloro-8-hydroxyquinoline. The excellent coloured azo dyes were applied on some textile fabrics and their fastness properties evaluated based on the **International Geometric Gray Standard**. The dyes were characterized by FT-IR, NMR and elemental analysis.

Keywords : 4-aminobenzoic acid; 4-amino-2-hydroxybenzoic acid; 8-hydroxyquinoline, 5-nitroso-8-hydroxyquinoline; 5-nitro-8-hydroxyquinoline; 5-chloro-8-hydroxyquinoline; diazotization; coupling reaction; dyeing.

Introduction

Azo dyes represent the largest chemical class of industrial colorants and also the most versatile group of synthetic dyes, which cover the full range of shades of colours [1]. Their ease of preparation by diazotization and azo coupling reactions has made it possible for azo dyes to have been studied more than any other class of dyes [2]. Azo disperse dyes containing aromatic heterocyclic moiety have been investigated due to their superior properties in general [3]. The use of heterocyclic diazo or coupling components in particular has made possible the production of colorants with brilliant colour and chromophoric strength, high level-dying property and excellent fastness properties [4]. Azo dyes based on heterocyclic compounds have been reviewed comprehensively [5]. Heterocyclic azo disperse dyes are used to dye hydrophobic fibers especially polyester and polyamide fabrics due to their excellent properties; they have also been utilized in non-textile applications such as lasers and non-linear optical systems, photodynamic therapy, reprography [6], dye sensitized solar cells [7], and metallochromic indicators.

Experimental

All the reagents were of analytical grade purchased from Sigma-Aldrich and were used without further purification. Melting points were recorded on electrothermal apparatus in open capillaries. The reactions were monitored with TLC and also the purity was ascertained with TLC. Infrared spectra analysis was obtained on SHIMADZU FT-IR 8400S spectrophotometer using KBr discs. The ^{1}H-NMR was recorded on Brucker instrument 400 MHz; chemical shifts were reported on (δ) ppm scale. Microanalysis was obtained on CHN rapid analyzer.

General procedure for diazotization

4-Aminobenzoic acid (5.0 g, 36 mmol) was dissolved in a solution of sodium bicarbonate (1.0 g in 15 mL of H_2O) in 250 mL beaker. Solution of sodium nitrite (3.0 g, 43 mmol in 15 mL of H_2O) was added and the reaction mixture immersed in ice-salt bath and cooled to 0 ^oC. Cold concentrated HCl (18 mL) was then added in drops with vigorous stirring for over 30 min and ensuring that the temperature never exceeded 5 ^oC. Excess drops of the acid were added and the solution test with starch iodide paper until immediate blue colour was observed on the iodide paper.

General procedure for coupling reaction

8-Hydroxyquinoline (5.29 g, 36 mmol) was dissolved in 10% KOH (40 mL). The solution was cooled to 0 ^oC in an ice-salt bath and then the prepared cold diazonium salt from above was stirred and added very slowly by the wall of the beaker with vigorous stirring for over 45 min. Little quantity of ice blocks was added to help maintain the temperature below 10 ^oC. After the addition of the whole diazonium salt, the reaction mixture was left in the ice-bath for further 2 h with occasional stirring. It was later neutralized with dilute H_2SO_4 to a pH of 4.5 and then filtered, washed with cold water and allowed air dried. The residual crop was crystallized twice in hot carbon tetrachloride after treatment with charcoal to give shinning red micro-crystalline product. The purity of the new dyes was further ascertained by sporting on the coated TLC plate obtained from Aldrich chemicals and inserted in the saturated developed chamber of solvent mixture of ethyl acetate and benzene.

4-(8-hydroxyquinolin-5-azo)benzoic acid (9): brick red colour, mp 246-247 ^oC, FT-IR spectrum (KBr) cm^{-1}: 3570-2900 (br O-H strch), 1670 (C=O), 1605 (N=N), 1560, 1548 (C=N, C=C Aromatics). ^1H-NMR (DMSO-d_6), δ: 11.10 (br, COO**H**), 8.78 (d, H2 of quinoline), 8.25 (2H, d, H2 of benzoic ring), 8.10 (2H, d, H3 of benzoic), 7.95 (d, H4 of quinoline), 7.75 (1H, d, H6 of quinoline), 7.15 (t, H3 of quinoline), 7.05 (d, H7 of quinoline) and 5.50 (s, OH). Elemental analysis calculated for $C_{16}H_{11}N_3O_3$ %: C 65.53; H 3.78; N 14.38, found: %: C 65.58; H 3.74; N 14.45

4-(8-hydroxy-5-nitrosoquinolin-7-azo)benzoic acid (10), golden red colour, mp 264-265 ^oC, FT-IR spectrum (KBr) cm^{-1}: 3570-2900 (br O-H strch), 1670 (C=O), 1620 (N=N), 1580, 1505 (C=N, C=C Aromatics). ^1H-NMR (DMSO-d_6), δ: 9.30 (br, COO**H**), 8.78 (d, H2 of quinoline), 8.40 (s, H6 of quinoline), 8.25 (2H, d, H2 of benzoic), 8.10 (2H, d, H3 of benzoic acid), 7.85 (d, H4 of quinoline), 7.15 (t, H3 of quinoline), and 5.53 (s, OH). Elemental analysis calculated for $C_{16}H_{10}N_4O_4$ %: C 59.63; H 3.13; N 17.38, found: %: C 59.69; H 3.08; N 17.46

4-(8-hydroxy-5-nitroquinolin-7-azo)benzoic acid (11) reddish colour, mp 272-273 ^oC, FT-IR spectrum (KBr) cm^{-1}: 3570-2900 (br O-H strch), 1670 (C=O), 1620 (N=N), 1580, 1555 (C=N, C=C Aromatics). ^1H-NMR (DMSO-d_6), δ: 9.30 (br, COO**H**), 8.95 (s, H2 of quinoline), 8.70 (s, H6 of quinoline), 8.65 (d, H4 of quinoline), 8.25 (2H, d, H2 of benzoic acid), 8.10 (2H, s, H3 of benzoic acid), 7.7.53 (t, H3 of quinoline) and 5.50 (s, OH).. Elemental analysis calculated for $C_{16}H_{10}N_4O_5$ %: C 56.81; H 2.98; N 16.56, found: %: C 56.90; H 3.04; N 16.51

4-(5-chloro-8-hydroxyquinolin-7-azo)benzoic acid (12) as reddish brown colour, mp 278-279 ^oC, FT-IR spectrum (KBr) cm^{-1}: 3570-2900 (br O-H strch), 1680 (C=O), 1610 (N=N), 1590, 1540 (C=N, C=C Aromatics). ^1H-NMR (DMSO-d_6), δ: 9.30 (br, COO**H**), 8.90 (s, H2 of quinoline), 8.40 (d, H4 of quinoline), 8.25 (2H, d, H2 of benzoic), 8.05 (2H, d, H3 of benzoic acid), 7.95 (s, H6 of quinoline), 7.35 (d, H3 of quinoline) and 5.50 (s, 2OH). Elemental analysis calculated for $C_{16}H_{10}ClN_3O_3$ %: C 58.64; H 3.08; Cl 10.82; N 12.82, found: %: C 58.71; H 3.08; Cl 10.76; N 12.88

4-(8-hydroxyquinolin-5-azo)-2-hydroxybenzoic acid (**13**) dark red colour, mp 266-267 ^oC, FT-IR spectrum (KBr) vmax, cm^{-1}: 3570-2900 (br O-H strch), 1670 (C=O), 1620 (N=N), 1580, 1555 (C=N, C=C Aromatics). ^1H-NMR (DMSO-d_6), δ: 9.30 (br, COO**H**), 8.78 (d, H2 of quinoline), 8.10 (d, H6 of benzoic acid), 7.86 (d, H4 of quinoline), 7.75 (d, H6 of quinoline), 7.60 (d, H5 of benzoic acid), 7.52 (s, H3 of benzoic acid), 7.15 (t, H3 of quinoline), 7.05 (d, H7 of quinoline) and 5.50 (2H, s, 2OH). Elemental analysis calculated for $C_{16}H_{11}N_3O_4$ %: C 62.14; H 3.58; N 13.59, found: %: C 62.21; H 3.53; N 1.65

4-(8-hydroxy-5-nitrosoquinolin-7-azo)-2-hydroxybenzoic acid (**14**) brownish-orange colour, mp 256-258 ^oC, FT-IR spectrum (KBr) vmax cm^{-1}: 3570-2900 (br O-H strch), 1690 (C=O), 1600 (N=N), 1570, 1557 (C=N, C=C Aromatics). ^{1}H-NMR (DMSO-d_6), δ: 9.32 (br, COO**H**), 8.78 (s, H2 of quinoline), 8.40 (s, H6 of quinoline), 8.10 (d, H6 of benzoic), 7.85 (d, H4 of quinoline), 7.60 (d, H5 of benzoic acid), 7.50 (d, H3 of benzoic acid), 7.15 (t, H3 of quinoline) and 5.50 (s, 2OH). Elemental analysis calculated for $C_{16}H_{10}N_4O_5$ %: C 56.81; H 2.98; N 16.56, found: %: C 56.89; H 3.06; N 16.48

4-(8-hydroxy-5-nitroquinolin-7-azo)-2-hydroxybenzoic acid (15) deep red colour, mp 286-288 °C, FT-IR spectrum (KBr) vmax cm^{-1}: 3570-2900 (br O-H strch), 1680 (C=O), 1610 (N=N), 1560, 1545 (C=N, C=C Aromatics). ^{1}H-NMR (DMSO-d_6), δ: 9.32 (br, COO**H**), 8.95 (d, H2 of quinoline), 8.70 (s, H6 of quinoline), 8.65 (d, H4 of quinoline), 8.05 (d, H6 of benzoic acid), 7.60 (d, H-5 of benzoic acid), 7.53 (d, H3 of quinoline) and 5.53 (s, 2OH). Elemental analysis calculated for $C_{16}H_{10}N_4O_6$ %: C 54.24; H 2.85; N 15.81, found: %: C 54.29; H 2.88; N 15.78

4-(5-Chloro-8-hydroxyquinolin-7-azo)-2-hydroxybenzoic acid (16) dark red colour, mp 289-290 °C, FT-IR spectrum (KBr) vmax cm^{-1}: 3570-2900 (br O-H strch), 1670 (C=O), 1610 (N=N), 1580, 1545 (C=N, C=C Aromatics). ^{1}H-NMR (DMSO-d_6), δ: 9.30 (br, COO**H**), 8.90 (d, H2 of quinoline), 8.40 (d, H4 of quinoline), 8.05 (d, H6 of benzoic), 7.85 (1H, s, H6 of quinoline), 7.60 (d, H5 of benzoic acid), 7.50 (s, H3 of benzoic acid), 7.35 (d, H3 of quinoline) and 5.51 (s, 2OH). Elemental analysis calculated for $C_{16}H_{10}ClN_3O_4$ %: C 55.91; H 2.93; Cl 10.31; N 12.23, found: %: C 55.98; H 2.93; Cl 10. 26; N 12.27.

Dyeing method (general procedure)

All the prepared azo dyes have very poor solubility in water. The synthesized dye **9** (0.30 g) was dissolved in dimethylformamide (10 cm^3) in 250 mL 2-necked flask attached to a reflux condenser and a thermometer. Acetone 50 cm^3 and was added and solution was agitated and the silk and wool fabrics were inserted. The dye bath was warmed gently by raising the temperature every 5 min till boiling commenced. It was refluxed at the boiling with occasional agitation for 50 min and quickly cooled to room temperature. The dyed fabric was rinsed with water and dried in air. The same procedure was carried out with other dyes.

Wash fastness test

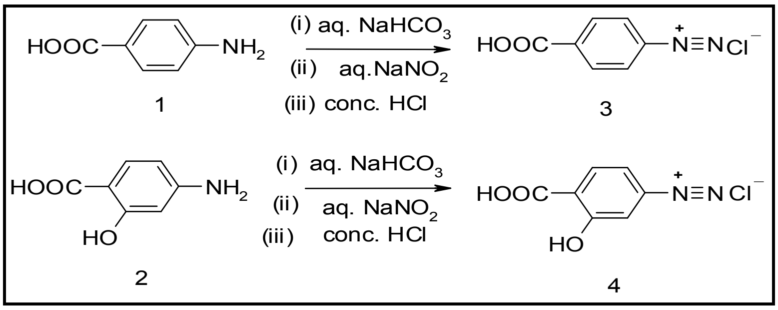
A specimen of the air dried dyed fabric was sewed between pieces of undyed silk and cotton and also wool and cotton fabrics of equal size and were mechanically agitated in wash wheel in soap solution at 60 °C for 30 min The change in colour of the dyed materials and the staining on the undyed materials was ascertained according to the international geometric gray scale (1 for poor and 5 for excellent fastness) and recorded as presented in the table.

Fastness to sublimation

Small pieces of the dried dyed fabrics were sewed between a piece of undyed silk fabric and cotton fabric and also wool and cotton fabrics of equal size. It was treated with sublimation fastness tester at 160 °C for 40 s and later at 180 °C for another 40 s and any colour change and stains on two undyed fabrics sewed together was examined base on the international geometric gray standard (1 and 5 for poor and excellent respectively) as presented in the table.

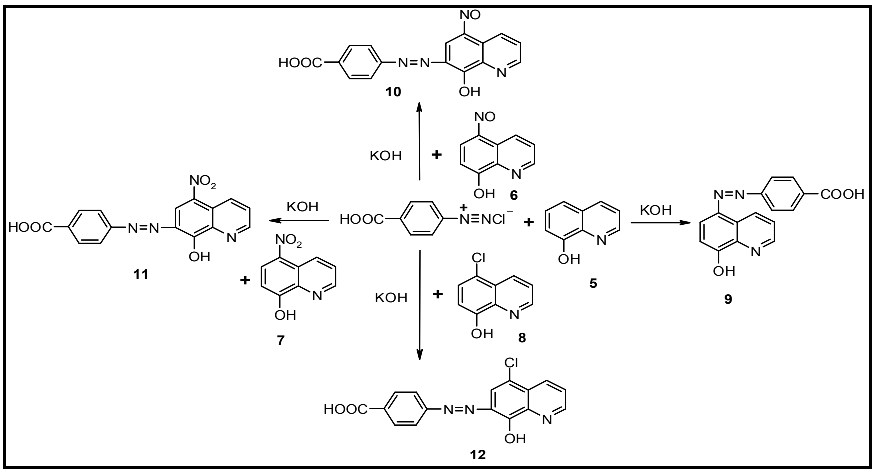
Results and Discussion

Aqueous solutions of 4-aminobenzoic acid **1** and 4-amino-2-hydroxybenzoic acid **2** in sodium bicarbonate and sodium nitrite were diazotized with concentrated hydrochloric acid in separate beakers in ice-salt baths at 0-10 °C to form the diazonium salts **3** and **4 (scheme 1);**



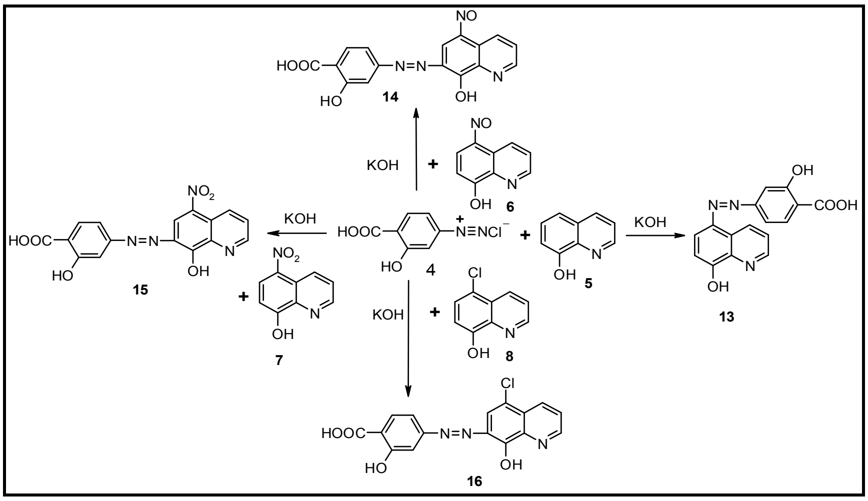
Scheme 1

The diazonium salt **3** was then coupled respectively with 8-hydroxyquinoline **5**, 5-nitroso-8-hydroxyquinoline **6**, 5-nitro-8-hydroxyquinoline **7** and 5-chloro-8-hydroxyquinoline **8** in alkaline medium of 10% KOH to produce excellent micro crystalline azo dyes: 4-(8-hydroxyquinolin-5-ylazo)benzoic acid **9**, 4-(8-hydroxy-5-nitrosoquinolin-7-azo)benzoic acid **10**, 4-(8-hydroxy-5-nitroquinolin-7-azo)benzoic acid **11** and 4-(5-chloro-8-hydroxyquinolin-7-azo)benzoic acid **12 (scheme 2);**



Scheme 2

Again the diazonium salt **4** was also coupled with 8-hydroxyquinoline **5**, 5-nitroso-8-hydroxyquinoline **6**, 5-nitro-8-hydroxyquinoline **7** and 5-chloro-8-hydroxyquinoline **8** in alkaline medium of 10% KOH to produce another four derivatives of excellent micro crystalline azo dyes: 4-(8-hydroxyquinolin-5-azo)-2-hydroxybenzoic acid **13,** 4-(8-hydroxy-5-nitrosoquinolin-7-azo)-2-hydroxybenzoic acid **14,** 4-(8-hydroxy-5-nitroquinolin-7-azo)-2-hydroxybenzoic acid **15** and 4-(5-chloro-8-hydroxyquinolin-7-azo)-2-hydroxybenzoic acid **16** respectively **(scheme 3);**



Scheme 3

The structures of the dyes were ascertained based on their spectral data: in the FT-IR spectrum, all the dyes showed very broad band between 3590-2700 cm^{-1} assigned to the O-H groups, 1700-1670 for the C=O groups, 1610-1550 assigned for the –N=N- of the azo groups. The elemental analysis of the compounds was in agreement with the molecular formulas: (**9,** $C_{16}H_{11}N_3O_3$), (**10**, $C_{16}H_{10}N_4O_4$), (**11**, $C_{16}H_{10}N_4O_5$), (**12**, $C_{16}H_{10}ClN_3O_3$), (**13**, $C_{16}H_{11}N_3O_4$), (**14**, $C_{16}H_{10}N_4O_5$), (**15,** $C_{16}H_{10}N_4O_6$) and (**16,** $C_{16}H_{10}ClN_3O_4$). The ^{1}H-NMR also gave further support of the structures.

Dyeing of silk and wool fabrics with the synthesized azo dyes:

Dyeing was carried out in aqueous solution of DMF/Acetone/acetic acid. They gave very good to excellent shades on the silk and wool fabrics and showed excellent wash fastness and good sublimation fastness base on the international geometric gray standard (1 and 5 for poor and excellent respectively) as presented in the table.

Table : fastness properties of synthesized heterocyclic azo dyes

Dye no	**Wash fastness (1-5)**		**Stain on undyed fabric after washing (1-5)**		**Sublimation fastness (1-5)**		**Stain on undyed fabric after sublimation (1-5)**	
	Silk,	**wool**	**Silk/cotton**	**wool/cotton**	**Silk,**	**wool**	**Polyester,**	**cotton**
9	4-5,	**4.0**	4.0	**4-5**	4-5,	**4.5**	4-5	5
10	4-5,	**4.5**	5.0	**4-5**	5.0,	**4,5**	5	4-5
11	4-5,	**4.5**	4-5	**5.0**	4-5,	**4.0**	4	4
12	4-5,	**4.0**	4-5	**4.0**	4-5,	**4.5**	4-5	4
13	5.0	**4.5**	4-5	**4.0**	4.0,	**4.5**	4-5	5
14	5.0,	**4.0**	4-5	**5.0**	4-5,	**4.0**	4-5	5
15	5.0,	**4,5**	4-5	**5.0**	4-5.	**4.5**	4-5	5
16	5.0,	**5.0**	4-5	**5.0**	4-5,	**4.0**	4-5	5

Conclusion

The prepared dyes showed good to excellent fastness properties and therefore can be used as industrial colourants both in the textile and plastic industries.

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