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Synthesis of Heterocyclic Monoazo Disperse Dyes Derived from 4-Amino-2-chloro-6,7-dimethoxyquinazoline

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Abstract: The quinazoline skeleton is an important part of many alkaloids and has been isolated from some plants such as those obtained from the Rutacea family. The quinazoline moieties have been found to exhibit many pharmacological properties and such when used to prepare dyes could show some friendly influence on humans. In view of these, this study described the synthesis of monoazo dyes from 4-amino-2-chloro-6,7-dimethoxyquinazoline. The 4-amino-2-chloro-6,7-dimethoxyquinazoline was diazotized and coupled with arylamine and phenolic coupling compounds to afford six monoazo disperse dyes. The results of the absorption maxima of the dyes were found to depend on the substituents in the diazo and coupling components and varied from 370 nm to 517 nm and 704 nm in dimethylformamide (DMF). The dyes on polyester fabrics and acrylics fabrics showed good fastness to light and washing but excellent fastness to sublimation. Thus, the results of the investigation revealed that the dyes have affinity for the two substrates (polyester fibre and acrylic fibre). The dyes were characterized, using IR, ¹H NMR, ¹³C NMR and UV-Visible analysis.

Key words: 4-amino-2-chloro-6,7-dimethoxyquinazoline, azo dyes, synthesis, polyester fibre, acrylic fibre, fastness

INTRODUCTION

The quest for environmentally friendly azo dyes of high wet fastness on polyester is increasing in recent times (Burkinshaw, 1994). In addition there are rising global legislative pressures to stop the use of azo dyes that contain carcinogenic components. The heterocycles, both natural and synthetic are known to have good biological and pharmaceutical activities. It has even been claimed to be the first field to foster the industrial exploitation of heteroaromatic amines (Karci, 2005).

The 4-amino-2-chloro-6,7-dimethoxyquinazolines are important synthons for the synthesis of several biologically active molecules. For instance, a large number of compounds possessing fused nitrogen-containing heterocyclic skeletons including 4-amino-quinazolines have been found to exhibit excellent anticancer activity (Samieh *et al.*, 2008; Campbell *et al.*, 1987; Joseph *et al.*, 2010). Thus, from available literatures, there is no report of the use of 4-amino-2-chloro-6,7-dimethoxyquinazoline in the synthesis of azo disperse dye compounds.

Herein, we report the synthesis of some new 3-chloro-6,7-dimethoxyquinazoline azo disperse dye

derivatives from 4-amino-2-chloro-6,7-dimethoxyquinazoline. Also, the application of the azo disperses dyes on polyester fabrics and acrylic fabrics have been evaluated.

MATERIALS AND METHODS

Materials and apparatus: This study was conducted between 2011 and 2012 at organic chemistry research laboratory, Delta State University, Abraka, Delta State, Nigeria.

All the reagents and solvents used were of reagent-grade quality and purchased from commercial suppliers. Melting points were determined on a Buchi SMP-20 melting point apparatus. Infrared spectra (in KBr pellets) were recorded on Shimadzu (8400), FT-IR spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Mercury 200BB series spectrometer. DMSO-d₆ was used as NMR solvent. Chemical shifts were reported in δ units in parts per million (ppm) downfield from the internal standard, tetramethylsilane (TMS). The purity of the azo compounds was monitored by Thin Layer Chromatography (TLC), using silica gel to coated plates,

F₂₃₄ (Merck, aluminium sheets). UV-Visible spectra were determined on a Genesys 10S V1.200 series spectrophotometer.

Methods

Diazotization: Compound 1, 4-amino-2-chloro-6,7-dimethoxyquinazoline (1.0 g, 2 mmol) was pasted with NaNO₂ (0.45 g, 21 mmol) and water (10 mL) to a smooth slurry and this mixture was added to a well-stirred mixture of HCl (d = 1.18, 4 mL) and ice (4.0 g) at 0-5°C. The reaction mixture was stirred for 30 min to produce diazonium salt 2.

Preparation of 2-amino-5-ethylcarbazole-azo-2-chloro-6,7-dimethoxy quinazoline, 3a: Compound 3a was obtained by adding the diazonium salt solution 2 portionwise to the coupling component, 3-amino-9-ethylcarbazole (0.9 g, 4 mmol) dissolved in 5 mL of acetic acid with stirring for 5 min. The reaction mixture was further stirred for 3 h and the precipitated azo compound was isolated by filtration and washed with water and recrystallized from ethanol to give a dark green solid (0.76 g, 40%), M.P = 200-202°C; ¹H NMR; (199.96 MHz) DMSO-d₆: 8.62 (2H, s, quinazoline-H), 7.61 (2H, s, Carbazole-H), 7.25 (1H, s, Carbazole-H), 5.45 (6H, s, OCH₃), 3.92 (2H, s, CH₂), 2.43 (3H, s, CH₃); ¹³C NMR; (199.96 MHz): 162.81, 156.22, 152.89, 149.61, 143.89, 106.29, 104.10, 104.02, 56.91, 56.82, 40.90, 40.58, 40.16, 39.75, 39.33. FT-IR (KBr): 3694 cm⁻¹ (ν NH), 3049 cm⁻¹ (ν C-H_{str}), 1647 cm⁻¹ (ν C=C_{str}), 1073 cm⁻¹ (ν C-O-C_{str}), 791 cm⁻¹ (ν C-Cl_{str}); UV (DMF), λ_{max} (nm); 522.

Preparation of 2-amino-5-methylpyrazoleazo-3-chloro-6,7-dimethoxy quinazoline, 3b: Compound 3b was obtained following a procedure similar to that used for the formation of compound 3a, to give a yellow solid (0.95 g, 66%), M.P = 199-201°C; ¹H NMR (DMSO-d₆, 199.96 MHz) 8.65 (1H, s, NH), 7.00-7.60 (2H, s, quinoxaline-H), 5.20 (3H, s, CH₃), 3.92 (6H, s, OCH₃), 2.45 (2H, s, NH₂); ¹³C NMR; (DMSO-d₆; 199.96 MHz): 162.49, 151.01, 152.22, 149.97, 142.96, 105.86, 103.33, 56.65, 56.59, 41.09, 40.08, 40.25, 39.84, 39.42, 39.01, 38.60; FT-IR (KBr): 3652 cm⁻¹ (ν NH_{str}), 2883 cm⁻¹ (ν C-H_{str}), 1589 cm⁻¹ (ν C=C_{str}), 1070 cm⁻¹ (ν C-O-C_{str}), 860 cm⁻¹ (ν C-Cl_{str}); UV (DMF), λ_{max} (nm); 387.

Preparation of 2-aminopyrazoleazo-3-chloro-6,7-dimethoxy quinazoline, 3c: Compound 3c was obtained following the procedure described for the formation of compound 3a, thus producing a yellow solid (1.10 g, 79%), M.P = 190-192°C; ¹H NMR (DMSO-d₆, 199.96 MHz) 11.79 (1H, s, NH), 8.91-9.92 (1H, s, quinoxaline-H), 6.90-7.63 (2H, s, quinazoline-H), 3.91 (6H, s, OCH₃), 2.45 (2H, s, NH₂); ¹³C NMR; (DMSO-d₆; 199.96 MHz): 162.72, 156.51,

151.71, 149.800, 142.03, 105.96, 104.30, 102.88, 56.99, 56.93, 40.96, 40.54, 40.11, 39.70, 39.28; FT-IR (KBr): 3344 cm⁻¹ (ν NH_{str}), 3049 cm⁻¹ (ν C-H_{str}), 1589 cm⁻¹ (ν C=C_{str}), 1064 cm⁻¹ (ν C-O-C_{str}), 748 cm⁻¹ (ν C-Cl_{str}); UV-VIS (DMF), λ_{max} (nm): 370.

Preparation of 2,4-dihydroxybenzene 3-chloro-6,7-dimethoxy quinazoline, 3d: The diazonium salt solution previously prepared was added portionwise to the solution of 1,3-dihydroxybenzene (0.5 g, 45 mmol) dissolved in sodium hydroxide solution (1.0 g, 25 mmol) in 20 mL of water with stirring for 5 min. The reaction mixture was further stirred for 2 h and the coloured precipitate was filtered off and recrystallized from CCl₄ to give a yellow solid (1.48 g, 98%), M.P = 198-200°C; ¹H NMR (DMSO-d₆, 199.96 MHz): 8.25 (1H, s, OH), 7.60-7.80 (2H, s, quinoxaline-H), 6.51-7.20 (3H, s, ArH) 3.65-4.25 (6H, s, OCH₃); ¹³C NMR; (DMSO-d₆; 199.96 MHz): 162.62, 155.84, 153.17, 149.28, 144.45, 106.19, 104.27, 103.76, 56.70, 56.53, 41.12, 40.69, 40.28, 39.56, 39.45, 39.02, 38.61; FT-IR (KBr): 3473 cm⁻¹ (ν OH_{str}), 3025 cm⁻¹ (ν C-H_{str}), 1582 cm⁻¹ (ν C=C_{str}), 1070 cm⁻¹ (ν C-O-C_{str}), 769 cm⁻¹ (ν C-Cl_{str}); UV-VIS (DMF), λ_{max} (nm): 422.

Preparation of 4-aminobenzonitrile azo 3-chloro-6,7-dimethoxy quinazoline, 3e: The titled Compound, 3e, was obtained following a procedure similar to that used for obtaining compound 3a, to give a cream coloured solid (0.75 g, 49%), M.P = 218-220°C; ¹H NMR (DMSO-d₆, 199.96 MHz), 8.45 (1H, s, ArH), 7.61 (2H, m, ArH), 7.01 (2H, s, OCH₃), 2.45-3.81 (2H, s, NH₂); ¹³C NMR; (DMSO-d₆; 199.96 MHz): 162.59, 155.85, 153.01, 149.28, 144.20, 106.13, 104.09, 103.74, 56.64, 56.59, 41.13, 40.71, 40.30, 39.89, 39.46, 39.05, 38.63; FT-IR (KBr): 3239 cm⁻¹ (ν NH_{str}), 3092 cm⁻¹ (ν C-H_{str}), 1592 cm⁻¹ (ν C=C_{str}), 1064 cm⁻¹ (ν C-O-C_{str}), 794 cm⁻¹ (ν C-Cl_{str}); UV-VIS (DMF), λ_{max} (nm); 459, 517.

Preparation of 2-hydroxynaphthaleneazo-3-chloro-6,7-dimethoxy quinazoline, 3f: The titled compound, 3f was obtained following a procedure similar to that used for compound 3d, producing a brown solid (0.91 g, 55%) M.P = 210-212°C; ¹H NMR; (DMSO-d₆; 199.96 MHz): 7.60-8.45 (6H, m, naphthalene-H), 6.40-7.10 (2H, s, quinoxaline-H), 5.95 (1H, s, bonded OH) 3.95 (6H, s, OCH₃); ¹³C NMR; (DMSO-d₆; 199.96 MHz): 162.81, 156.13, 153.03, 149.54, 144.13, 131.09, 130.74, 127.85, 106.32, 104.16, 104.08, 56.89, 56.78, 40.98, 40.56, 40.15, 39.73, 39.31; FT-IR (KBr): 3681 cm⁻¹ (ν OH_{str}), 3018 cm⁻¹ (ν C-H_{str}), 1592 cm⁻¹ (ν C=C_{str}), 1067 cm⁻¹ (ν C-O-C_{str}), 739 cm⁻¹ (ν C-Cl_{str}); UV-VIS (DMF), λ_{max} (nm): 516, 704.

Dye application

Polyester fabric: Polyester fabric was dyed in a pressure dyeing machine at a liquor ratio of 20:1. The dyebaths

were prepared with the synthesized azo dyes 3a-f, using Lignosulphonate as the dispersing agent. The pH of the dye liquor was adjusted to 5 with acetic acid. Dyeing was performed and continued for 60 min at 130°C to 135°C. The dyed polyester fabric was subjected to reduction-cleared treatment at 85°C for 10 min in a solution of sodium hydroxide, 2 g L⁻¹ hydrosulphite, 2 g L⁻¹ and then treated in a betaine amphoteric surfactant in water, washed with water and then dried (Giles, 1974; Burkinshaw, 1994).

Acrylic fabric: The dyeing of acrylic fabrics was carried out in an Ahiba Texomat dyeing machine at 90°C for one hour, using a 3°C min⁻¹ temperature gradient of weight of fibre and two percent dispersing agent and one molar equivalent of N, N-dimethylethylene diamine. The pH of dye bath was 5, adjusted using formic acid and liquor ratio of 60:1. The dyed fabrics were removed after dyeing from the hot dyebath, soaped off, rinsed with water and air-dried (Giles, 1974).

Fastness tests

Wash fastness: The wash fastness of the 1% of dyeings were determined according to ISO standard method (ISO, 1994). The composite samples measuring (10×5 cm) were washed with soap solution (2 g L⁻¹ Na₂CO₃, 5 g L⁻¹ soap solution, liquor ratio 50:1) for 30 min at 60°C in an Atlas Launder-O meter. The change in colour of the treated test

specimens and the degree of staining of the two adjacent undyed fabrics were evaluated using the Grey scales.

Light fastness: The light fastness of all the dyed samples were tested using an Atlas ES 25 Weather-O meter (Xenon arc) according to AATCC Test Method (AATCC, 1993). The test conditions were: Black panel temperature: 60°C, Relative humidity: 30±5%, Chamber Temperature: 50°C, Irradiance: 0.75 W/m², counter setting: 54 KJ/m². The dyed samples were exposed to these conditions and the change in colour of the fabrics (2×6 cm) were rated against standard blue wool samples (grade 1-8): 1 (poor), 8 (excellent) (Giles, 1974; Suwanruji *et al.*, 2004).

Sublimation: The sublimation test was carried out according to ISO, 105-PO1 1993 test method (ISO, 1993). The dyed fabric samples were treated in a sublimation testing machine at 177°C for 30 sec after heat setting at 180°C for 60 sec. The tested fabrics were rated against the Standard Grey scales (grade 1-5); 1 (poor), 5(excellent).

RESULTS AND DISCUSSION

The six azo disperse dyes were prepared by coupling of the diazotized compound 1 with heterocyclic and carbocyclic coupling components (Paula, 1995; Zollinger, 2003) (Fig. 1). The synthesized azo compounds 3a-f are relatively high melting point colored substances.

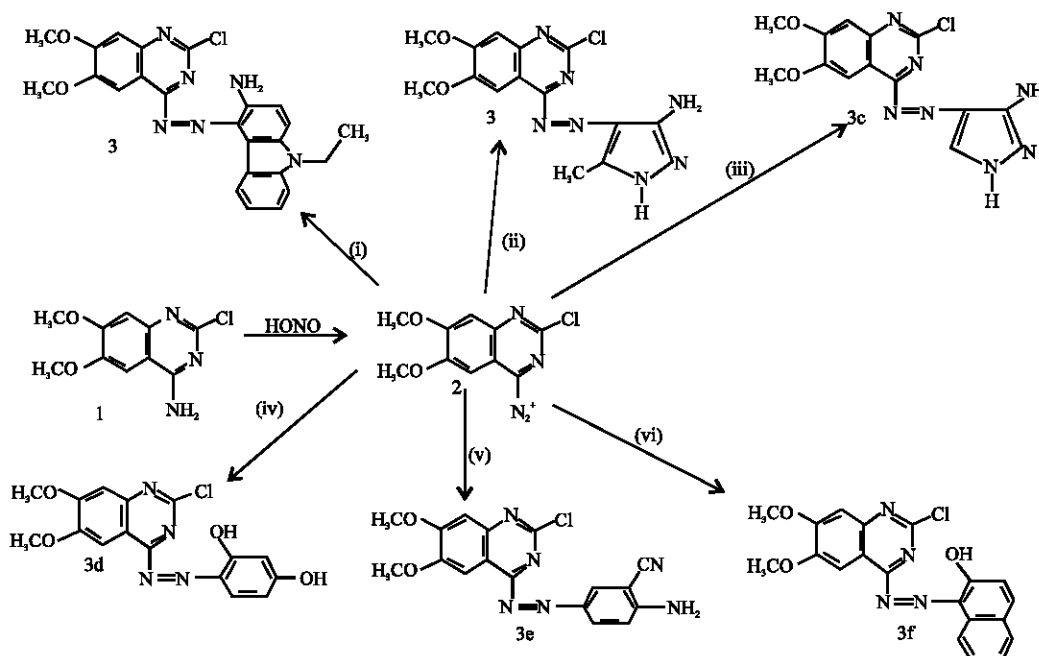


Fig. 1: Synthesis scheme for the preparation of dyes 3a-f by diazotization of 4-amino-2-chloro-6,7-dimethoxyquinazoline and coupling with the following amines and phenols: (i) C₁₅H₁₄N₂, (ii) C₄H₇N₂, (iii) C₃H₅N₃, (iv) C₁₀H₈O, (v) C₇H₆N₂, (vi) and C₆H₆O₂

The 3-chloro-6,7-dimethoxyquinazoline azo disperse dye derivatives were characterized using ¹H NMR, ¹³C NMR, IR and UV-Visible spectroscopy. The infrared spectra of the azo compounds (in KBr) showed NH bands at 3239-3694 cm⁻¹ region for compounds 3a, b, c and e. The FT-IR also showed broad bands at 3473-3681 cm⁻¹ which was assigned to OH groups for compounds 3d and f. The spectra also showed medium bands at 2883-3092 cm⁻¹ which was assigned to aromatic C-H stretching vibrations. The bands at 1064-1070 cm⁻¹ are indicative of the presence of C-O-C groups in the dye structure. Also observed in the region 1582-1529 cm⁻¹ in the IR spectra are the presence of C = C groups in the aromatic rings. The presence of C-Cl groups were also observed at 748-791 cm⁻¹ region in all the compounds.

The ¹H NMR spectra measured in DMSO-d₆ showed an N-H proton at δ 11.79. The various protons and their environments are also shown. The chemical shifts of ¹³C NMR spectra are in accordance with the desired synthesized products.

The electronic spectral data, showed that the azo dye compounds prepared using carbocyclic coupling components, interestingly recorded relatively higher λ_{max} values than those obtained from heterocyclic coupling components; except compound 3a with a λ_{max} of 522 nm. Thus, the other azo dye compounds such as 3b and c showed a hypsochromic shift. This is contrary to earlier findings that heterocyclic azo compounds show bathochromic shift than their benzenoid analogues (Shuttleworth and Weaver, 1990; Zollinger, 2003). The azo dye compounds 3e and f showed multiplet of absorption bands corresponding to bands at 459 to 517 nm and 516 to 704 nm, respectively. These data are in agreement with those previously reported for similar compounds (Otutu *et al.*, 2011; Paula, 1995).

Fastness properties: The dyed fabrics for the fastness testings were determined at pH 5 and were then assessed with the grey scales.

Light fastness: Table 1 shows the results of the light fastness tests on polyester and acrylic fabrics. The results showed that the light fastness of the dyes gave a better performance on polyester fabric (grade 5 to 5/6) than that of acrylic fabric except dyes 3a and b which gave ratings of 4/5 on polyester fabric. The substituents on the diazo and coupler components such as-NH₂ and-OH groups ortho to the azo groups appeared to have lowered the light fastness ratings of dyes 3a and b. These results correlated with previous findings that electron donating

Table 1: The light and sublimation fastness of azo dyes 3a-f (1% owf) on polyester and acrylic fabrics

Dye	Fabric	Light	Sublimation
3a	Polyester	4/5	5
	Acrylic	5	5
3b	Polyester	4/5	5
	Acrylic	5	5
3c	Polyester	5/6	5
	Acrylic	4/5	5
3d	Polyester	5/6	5
	Acrylic	5	5
3e	Polyester	5/6	5
	Acrylic	4/5	5
3f	Polyester	5	5
	Acrylic	4/5	5

Table 2: The Wash fastness of azo dyes 3a-f (1% owf) on polyester and acrylic fabrics

Dye	Fabric	Change	Staining			
			Cotton	Nylon	Acetate	Acrylic
3a	Polyester	5	5	4	5	5
	Acrylic	4/5	5	4	5	5
3b	Polyester	5	5	4	5	5
	Acrylic	5	5	4	5	5
3c	Polyester	5	5	4/5	5	5
	Acrylic	4/5	5	4/5	5	5
3d	Polyester	4/5	5	4	5	5
	Acrylic	4/5	5	4/5	5	5
3e	Polyester	4/5	5	4/5	5	5
	Acrylic	4/5	5	4/5	5	5
3f	Polyester	5	5	4	5	5
	Acrylic	4/5	5	4/5	5	5

Grey scale grading ranges from 1 (poor) to 5 (excellent) for light fastness, grey scale grading ranges from 1 (poor) to 8 (excellent)

groups such as-OH and-NH₂ ortho to the azo group lowers light fastness (Otutu *et al.*, 2011; Evans and Stapleton, 1978).

Sublimation fastness: The results of the sublimation fastness of the dyes on polyester fabrics and acrylic fabrics is summarised in Table 1. The sublimation fastness performance of the synthesised dyes on polyester fabrics and acrylic fabrics showed excellent ratings of 5. This is attributed to the polar groups (Such as-OH, NH₂) present in both the diazo and coupler groups of the dye molecule (structure) (Shuttleworth and Weaver, 1990).

Wash fastness: Table 2 shows the colour fastness of polyester fabrics and acrylic fabrics dyed with the dyes. The results showed good to excellent wash fastness of grade 4/5 which indicates that the dyes have affinity for polyester fabrics and acrylic fabrics. However, the dyes have more affinity to polyester fabrics than acrylic fabrics except dyes 3d and e where their wash fastness ratings were the same. The higher ratings showed by the dyes on polyester fabrics must be due to the higher crystalline structure compared to acrylic fabrics (Karci, 2005).

Table 2 also showed that there is no staining of adjacent cotton, acetate and acrylic fabrics, whereas staining was observed on the adjacent nylon fabrics.

CONCLUSION

Azo disperse dye derivatives of 3-chloro-6,7-dimethoxyquinazoline were synthesized and their application on polyester and acrylic fabrics was evaluated. The azo disperse dyes were isolated and characterized by a number of spectroscopic methods. The results of the spectral studies of each dye were consistent and hence confirm the predicted structures. The azo disperse dye compounds prepared from carbocyclic coupling components showed relatively higher λ_{max} values than their heterocyclic coupling components which is contrary to earlier findings. The wash fastness test results suggest that all the dyes have affinity for polyester fibre and acrylic fibre since they gave good to excellent wet fastness grades (ratings). At the same pH, the colour yield on acrylic fabrics was more than that of polyester fabrics which showed higher exhaustion on acrylic fabrics than on polyester fabrics.

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REFERENCES

AATCC, 1993. American association of textile chemists and colourists. Technical Manual, Research Triangle Park, North Carolina.

Burkinshaw, S.M., 1994. Application of Dyes. In: The Chemistry and Application of Dyes, David, R.W. and H. Geoffery (Eds.). Plenum Press, New York, London, pp: 326-331.

Campbell, S.F., M.J. Davey, J.D. Hardstone, B.N. Lewis and M.J. Palmer, 1987. 2,4-diamino-6,7-dimethoxyquinazolines. 1. 2-[4-(1,4-benzodioxan-2-ylcarbonyl)piperazin-1-yl] derivatives as α 1-adrenoceptor antagonists and antihypertensive agents. *Am. J. Med. Chem.*, 30: 49-57.

Evans, N.A. and I.W. Stapleton, 1978. Structural Factors Affecting the Lightfastness of Dyed Fibers. In: The Chemistry of Synthetic Dyes, Venkataraman, K. (Ed.). Academic Press, New York, pp: 221-227.

Giles, C.H., 1974. A Laboratory Course in Dyeing. Soc. Dyers and Colourists (SDC), Bradford, UK., pp: 93-101.

ISO, 1993. Textile-Test for colour fastness part PO1: Colour fastness to sublimation. Part E02: Colour Fastness to Sea Water, ISO/FDIS 105-E02, http://www.iso.org/iso/home/store/catalogue_tc/catalogue_detail.htm?csnumber=52231

ISO, 1994. Textile-test for colour fastness part CO6 colour fastness to washing. Part C06. Colour Fastness To Domestic And Commercial Laundering (ISO 105-CO6: 1994), http://www.zjff.net:81/files/20110513/1305249979640_23.pdf

Joseph, A., P. Aravinda, K.K. Srinivasan, K. Tukaram, T.T. Angel, E.M. Jessy and K.S. Rajeev, 2010. Synthesis and anticancer activity of some novel 3-(1,3,4-thiadiazol-2-yl)-quinazolin-4-(3H)-ones. *Orbital-Electron. J. Chem.*, 2: 158-167.

Karci, F., 2005. Synthesis of disazo dyes derived from heterocyclic components. *Coloration Technol.*, 121: 275-280.

Otutu, J.O., E. Osabohien and E.M. Efurhievwe, 2011. Synthesis and spectral properties of Hetaryl Monoazo dyes derived from 2-amino-5-nitrothiazole. *Orient. J. Chem.*, 27: 1369-1396.

Paula, Y.B., 1995. Organic Chemistry. 1st Edn., Prentice Haul Inc., New York, pp: 658-659.

Samieh, F., M.T. Ahmad, H. Hoosbang and K. Hojatollah, 2008. A synthesis of some new 4-arylidene-5(4H)-oxalone azo dyes and an evaluation of their solvatochromic behaviour. *Arkivoc*, 15: 115-123.

Shuttleworth, L. and M.A. Weaver, 1990. Dyes for Polyester Fibres. In: The Chemistry and Application of Dyes, David, R.W. and H. Geoffery (Eds.). Plenum Press, New York, USA.

Suwanruji, P., H.S. Freeman and D. Zhao, 2004. Studies toward a universal dye for textile fibres. *Color. Technol.*, 120: 220-225.

Zollinger, H., 2003. Colour Chemistry Synthesis, Properties and Application of Organic Dyes and Pigments. 3rd Edn., John Wiley and Sons, New York, USA., ISBN 3906390233, pp: 68-69.