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Synthesis, Characterization and Solvatochromic studies of 3-{2-(5-Bromothiazol-2-yl) diazeny l}-4-Bromopyridine-2, 6-Diamine

Savanor Prasanna M., Jathi Keshavayya*, Bhat Subramanya K. and Tantry Rajesh N.
Department of Chemistry, Kuvempu University, Shankaraghatta 577 451, Karnataka, INDIA

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Abstract

The 3-{2-(5-bromothiazol-2-yl)diazenyl}-4-bromopyridine-2,6-diamine was synthesized by carrying the diazotization of 5-bromothiazol-2-amine in coupling with 4-bromopyridine-2, 6-diamine as a coupling component to yield a azo dye. The structure of the dye was confirmed by UV-visible spectrophotometry, Fourier Transfer Infrared spectroscopy (FTIR), LC-MS, ^{1}H and ^{13}C NMR spectroscopic methods. The change in the absorption maxima of the synthesized compound in different solvents were determined, the solvatochromic property of the dye showed a medium red shift in different solvents and has shown the moderate solvent dependency over the bathochromic shift.

Keywords: Azo dye,*4-bromopyridine-2, 6-diamine* and thiazole.

Introduction

Azo dyes are the very important class of chemical constituents having enormous applications in diversified fields such as leather, polymer, paper, paint and coating industries as a dyeing agent[1-3]. It is also used in the pharmaceutical and food industries as a coloring agent. Among the different types of dyes, azo dyes have gained lots of importance due to its versatile applications in many functional areas such as, storage components in the DVD-R (Digital versatile Disc-Recordable)[4], electro-photographic toners as charge controlling agents, developers in powder coating materials[5-9], textile industries for dying the cotton fibers, fabrics, poly acetates and poly esters by dispersion dying method[9-11]. Normally, compounds which are having the hetero atoms in the ring system exhibits a more shift in the absorption maxima in different solvents compared to the normal plane ring system and it is well illustrated with the reported literature, especially dyes derived from the heterocyclic compounds like thiazole, quinoline, thiadiazole and benzothiazole[12-17]. Different heterocyclic azo compounds will have different absorption maxima which in-turn depends on the nature of the compound, especially-conjugation, resonance, co-ordination and tautomerism. The nature of the media affects the tautomerice quilibria of the compound which in-turn related to the absorbance of the radiation. Hence the solvatochromic property of the compound in different solvents has the significance and it contemplated us to study the solvent effect in different solvents ranging from less polar to more polar solvents.

Material and Methods

All analytical grade chemicals of were used without further purification. The melting range of the compound was taken in an open capillary tube which was uncorrected. The Thin layer chromatography (TLC) performed in-order to check the preliminary purity of the compound using Merck silica gel 60 F254 coated aluminium plates. The ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrum was taken in DMSO-d_6 solvent using Bruker AMX 400 spectrometer and TMS is used as an internal reference standard. FTIR spectrum was taken on Shimadzu-FTIR Infrared spectrometer in KBr (cm^{-1}). Liquid chromatography with the mass spectrometer (LC-MS) was taken on Agilent 1200 series LC and MicromasszQ spectrometer. Electronic spectra were recorded using Shimadzu UV-1800 UV-Visible spectrophotometer in various solvents at the concentration of ~1µmol. VARIO EL-III (Elementar Analysensysteme GmBH) was used for taking the elemental analysis of the compound.

Hydrochloric acid (18%, 20mL) was taken in 100 mL two neck round bottomed flask, added 5-bromothiazol-2-amine (2.0 g, 11.1 mmol) in one portion and stirred for 60 minutes. The beige turbid mass obtained was cooled to 0-5°C by using the crushed ice bath. In a separate conical flask, solution of $NaNO_2$ (0.69 g, 14.5 mmol in 2.5 mL of water) was cooled and added drop-wise to the above beige turbid mass about 15 minutes. The resulting reaction mixture was stirred for 30 minutes, formed a clear dark brown solution. Under the cooled condition ~0-5°C, a coupling component (pre-cooled solution of 4-bromopyridine-2, 6-diamine {2.1g, 13.37mmol} in 10mL of Acetic acid) was added to the formed diazonium salt solution over a period of 20 minutes ;the color of the reaction mass was changed from dark brown to dark brown red color. The reaction mixture was stirred for another 1 h. The completion of the reaction was confirmed by the TLC. After completion of the reaction, the reaction mixture was added to the ice cold water (150 mL) with stirring and the precipitated product was filtered off to get the crude compound (dark brown solid). The crude compound was made slurry with the DCM (35 mL), stirred about 10-15 minutes; the

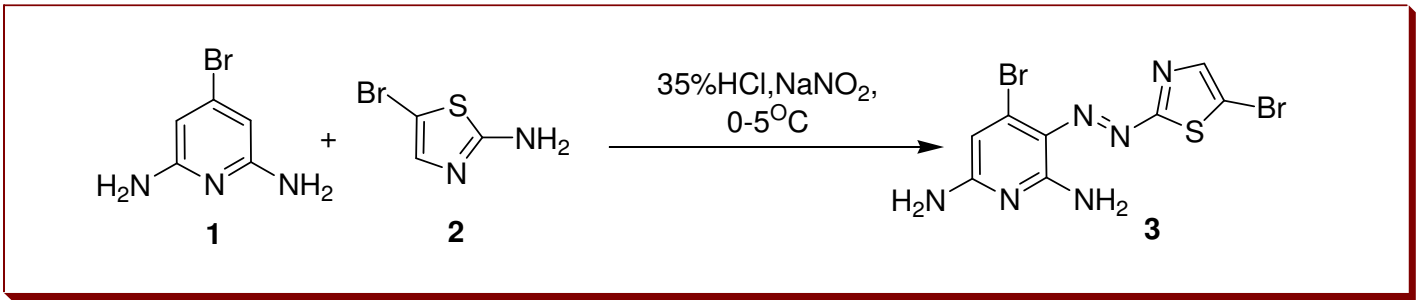
solids obtained were filtered off and recrystallized with the ethanol to get the brown red colored title compound (3) 1.24g (Yield-29.38%).

3-{2-(5-bromothiazol-2-yl) diazenyl} -4-bromopyridine-2, 6-diamine: Elemental analysis: Calculated for $C_8H_6Br_2N_6S$, C, 25.42; H, 1.60; N, 22.23; Found: C, 25.28%; H, 1.59%; N, 22.20%. ^{1}H-NMR (400 MHz, DMSO-d6): δ ppm, 6.06 (s, 1H, CH-Pyridine ring), 7.70 (bs, 2H- NH_2), 7.79 (s, 1H, CH-Thiazole ring), 8.42 (bs, 1H- NH_2) 9.57 (bs, 1H-NH_2). ^{13}C-NMR (100 MHz, DMSO-d6): δ ppm, 107.22 (C-Br, Thiazole), 107.96 (C-Br, Pyridine), 120.49 (C-H-Pyridine ring), 138.96(C-H-Thiazole ring), 143.22 (C-N-azo-Pyridine ring), 152.41(C-NH_2-Pyridine ring), 160.99 (C-NH_2-Pyridine ring), 179.18 (C-N-azo-Thiazole ring). IR (KBr): ν_{max} (cm^{-1}), 3211.81 (NH_2), 3089.89 (NH_2), 1661.83(N=N). LCMS: *m/z* = 379.0, (M + 2). Melting point: 280 ^oC.λ_{max}= 491 cm^{-1} (DMSO Solvent), Molar extinction coefficient (ε) = 2.25x10^6

Results and Discussion

The title compound, 3-(2-(5-bromothiazol-2-yl) diazenyl)-4-bromopyridine-2, 6-diamine was synthesized according to the scheme-1, by the diazotization of 5-bromothiazol-2-amine under chilled condition maintaining the temperature 3 to 5^{O}C. The diazonium salt formed during the course of reaction was stirred at -2 to 0^{O}C for 25 min in acetic acid after the addition of coupling component which was synthesized according to the reported literature[18]. TLC was run for the confirmation of the reaction, showed the starting material absence and a new non-polar spot compared with the starting material-thiazole amine. The crude compound after the work-up gave the dark brown solid which was purified by making slurry with the dichloromethane (DCM) followed bysuccessive filtration under suction and dried under vacuum at room temperature to yield a desired solid compound-3. Pure compound was obtained byrepetitive recrystallization by using ethanol. The synthesized compound 3-(2-(5-bromothiazol-2-yl) diazenyl)-4-bromo pyridine-2,6-diamine was confirmed by ^{1}H-NMR, ^{13}C-NMR, FTIR, elemental analysis and mass spectraldata figure 2-5.

Solvent effect: Typical absorption spectrums of compound-3 weretaken in different solvents, at varying concentration of 10^{-6}–10^{-8} M (as showed in figure-1) and the summary of the results obtained were given in table-1. The visible absorption spectra of the compound-3 were found to exhibit strong solvent dependency, which didn't showed regular variation with the polarity of the solvents.Increase in thepolarity of the solvent resulted in bathochromic shift.



Scheme-1
Synthesis of 3-{2-(5-bromothiazol-2-yl)diazenyl}-4-bromopyridine-2,6-diamine

Table-1
Absorbance maxima of the compound (3) in different solvents

Sl.No.	Solvents	λ_{max} (nm)
1	Dimethyl sulfoxide (DMSO)	491.01
2	N,N-Dimethyl formamide (DMF)	478.97
3	Methanol	481.23
4	Dioxane	486.18
5	Tetrahydrofuran (THF)	473.10
6	Ethanol	482.15
7	Acetone	479.88
8	Isopropyl alcohol	482.57

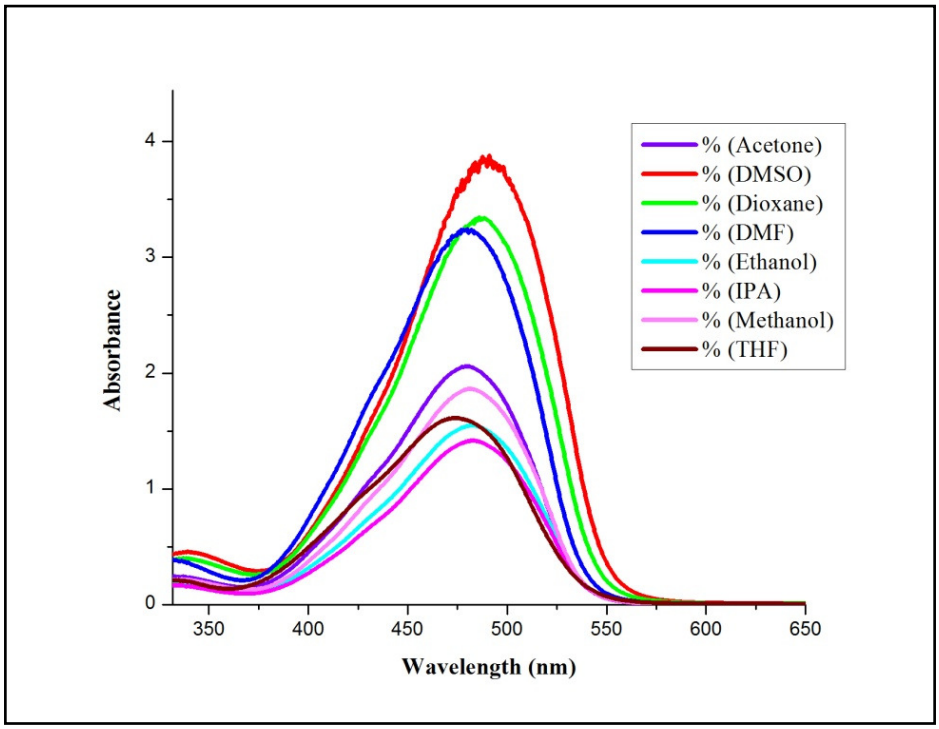


Figure-1
Absorbance spectra of the compound (3) in different solvents

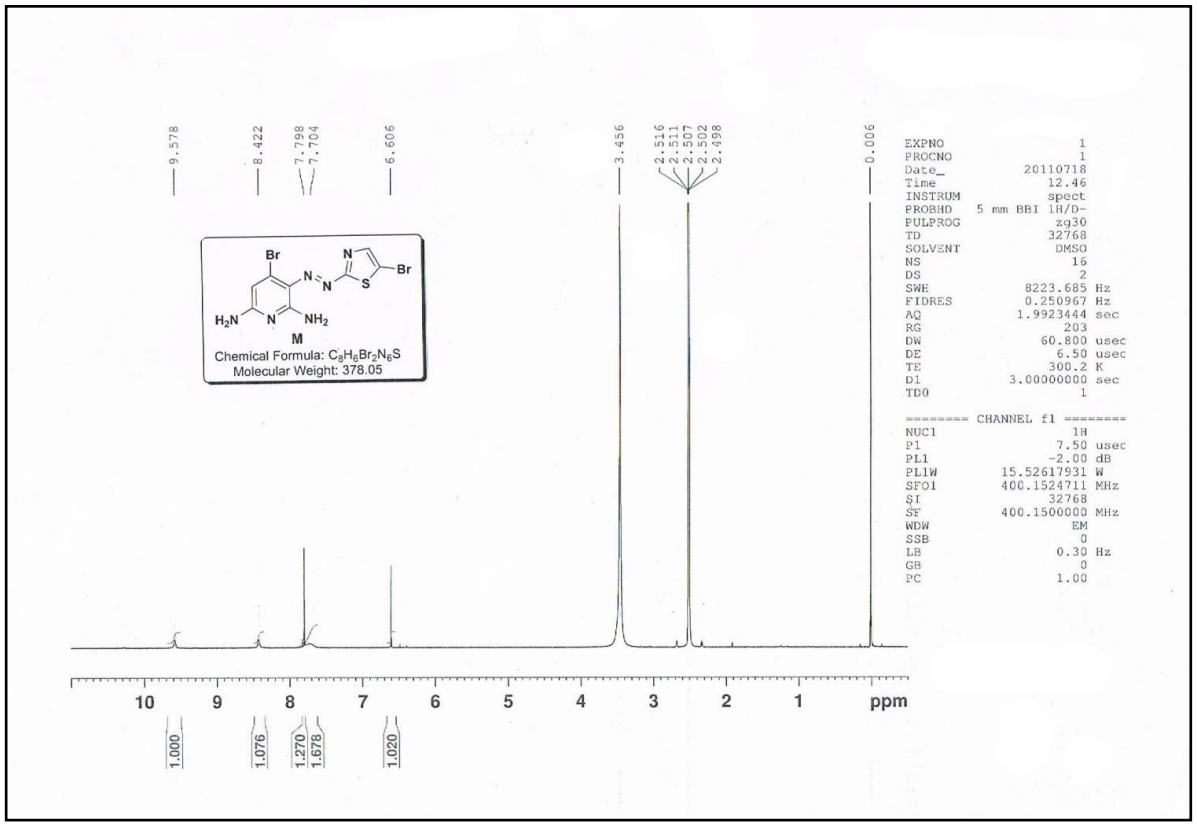


Figure-2
^{1}H NMR of compound in DMSO-d_6

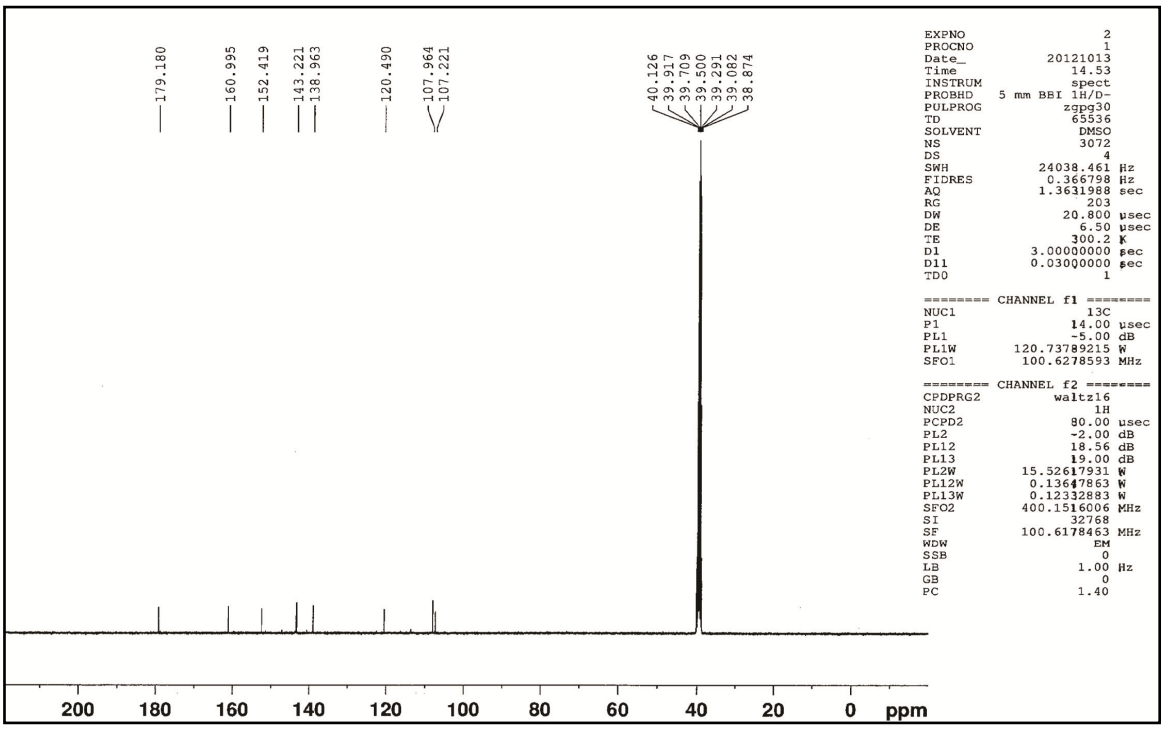


Figure-3
^{13}C NMR of compound-3 in DMSO-d_6

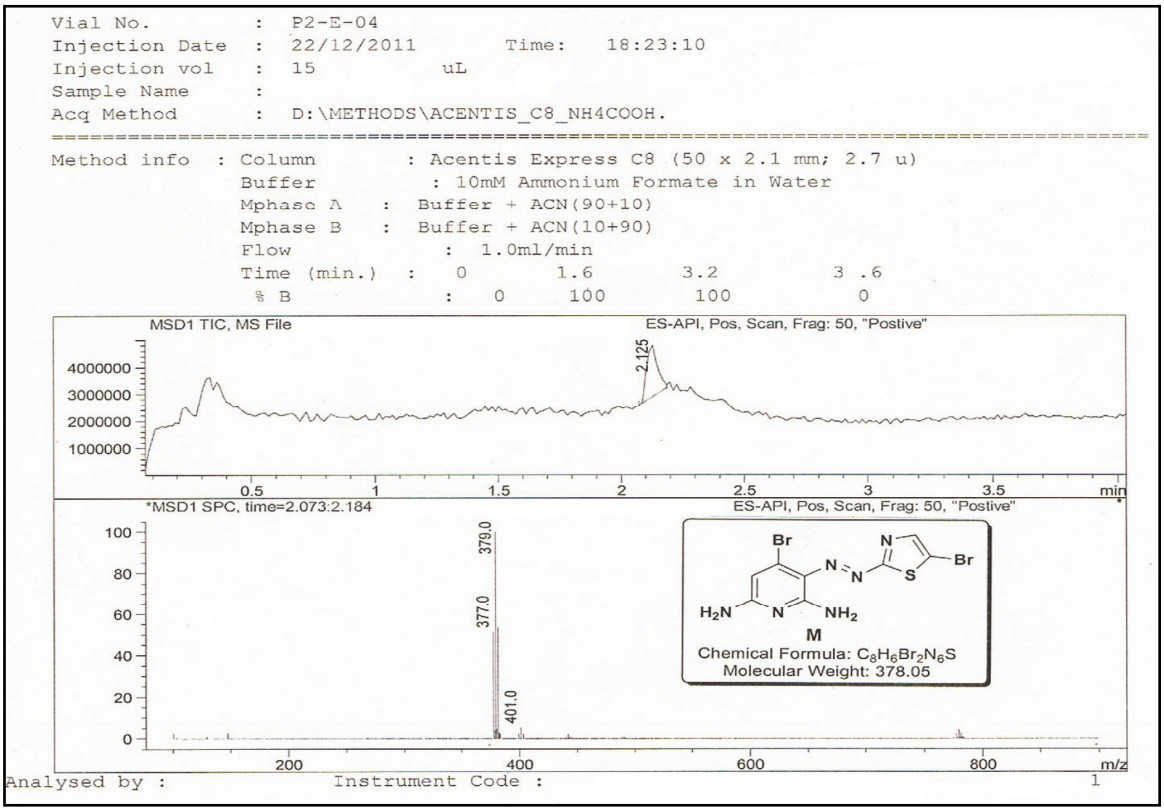


Figure-4
MS Spectrum of compound 3

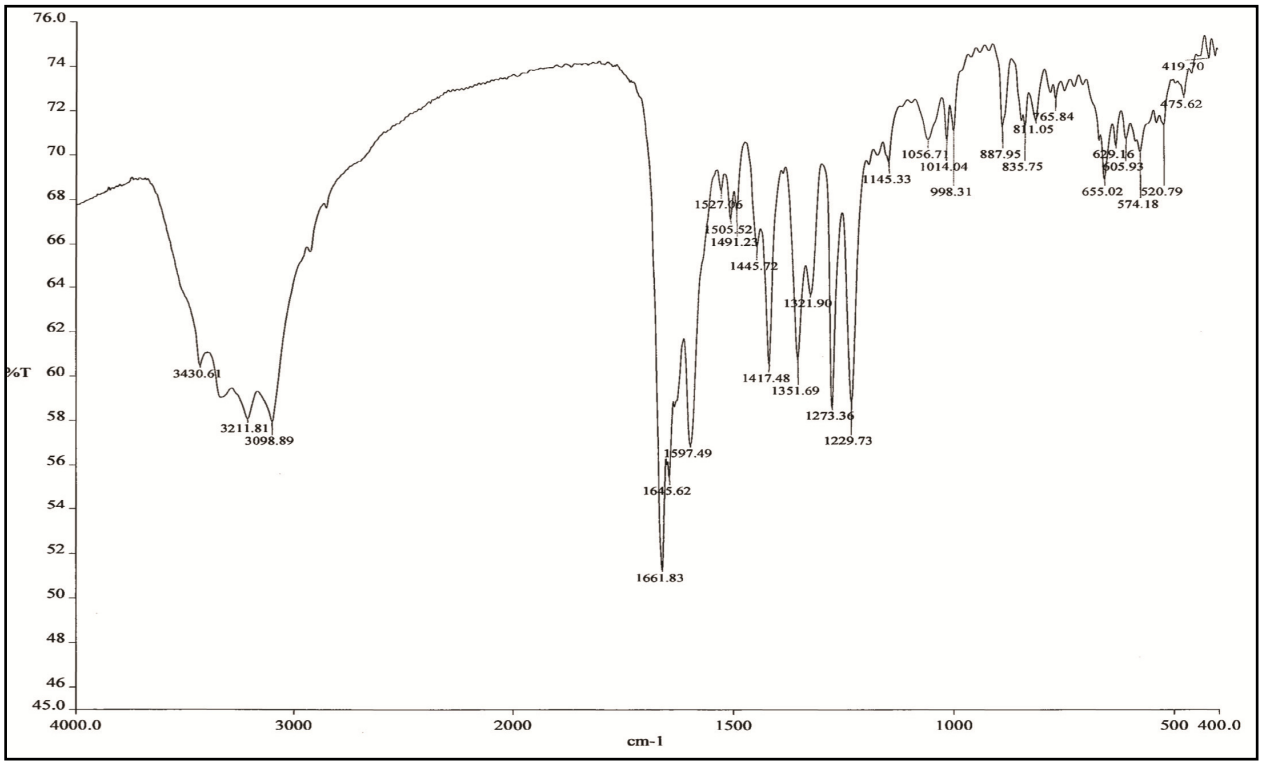


Figure-5
FTIR Spectrum of compound-3

Conclusion

In present study, novel thiazolyl based azo dye was prepared by classical method of azo coupling reaction. Azo dye obtained in high yield and purity via simple purification procedures. Synthesized compound characterized by ^{1}H and ^{13}C NMR, UV–Vis spectroscopy, elemental analysis, mass spectrometry and FTIR which confirms the proposed structure. The electronic absorption spectrum of azo dye was recorded in solvents with different physicochemical properties. As the dielectric constant of solvent increased, the band originated by π–π^* electronic transitions shifted to higher wavelength. Positive solvatochromism observed upon increasing the solvent polarity. Reported azo dye can be used as solvent polarity indicator.

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References

1. Ahmed K.A., Elhennawy H.M. and Elkashouti M.A., Microwave Assists the Synthesis of Pyridone azo Dyes and their Application in Polyester Printing, *Research Journal of Chemical Sciences* **2(11)**, 14-19 **(2012)**

2. El- Kashouti M.A., Tawfik S.S., Ahmed K.A., Mohamed Sh. S., Application of the synthesized Arylazopyrazolopyrimidine dyes in Printing Polyester and Polyamide Fabrics, *Research Journal of Chemical Sciences,* **2(9)**, 79-89 **(2012)**

3. Ravi R. Vidule, Shirodkar S.G., Synthesis and Antimicrobial studies of few New Substituted 2-methyl-3-(aryldiazenyl) pyrazolo[5,1-b]quinazolin-9(3H)-ones, *Research Journal of Chemical Sciences,* **3(6)**, 60-68 **(2013)**

4. Hyeyoung P., Eung-Ryul K., Dong J K., and Haiwon L.,Synthesis of Metal-Azo Dyes and Their Optical and Thermal Properties as Recording Materials for DVD-R, *Bulletin of the Chemical Society of Japan*, **(75),** 2067–2070 **(2002)**

5. Hans-Tobias M., Eduard M., Ruediger B., Pflieger D and Bansi L K., Use of Iron azo complex compound a charge controllagents, *US-PATENT*-**2002/0028401** A1 1-10 **(2002)**

6. Kazuhito Watanabe, Numazu., ToshikiNanya, Mishima, Toner for developing electrostatic latent image*US-PATENT*-**5,597,673,** 1-14 **(1997)**

7. Ryuzo Ueno Nishinomiya, Masaya Kitayama Takarazuka, Kenji Minami Sennan, Hiroyuki Wakamori, Hyogo-ken, Azo compounds and process producing the same, *US-PATENT*-**6,409,812 B1**, 1-6 **(2002)**

8. Birkett K.L and Gregory P., Metal Complex Dyes as Charge Control Agents, *Dyes and Pigments,* **(7),** 341-350, (**1986)**

9. Ashkar S.M., El-Apasery M.A., Touma M.M. and Elnagdi M.H., Synthesis of Some Novel Biologically Active Disperse Dyes Derived from 4-Methyl-2,6-dioxo-1-propyl-1,2,5,6-tetrahydropyridine- 3-carbonitrile as Coupling Component and Their Colour Assessment on Polyester Fabrics, *Molecules,* **(17)**, 8822-8831 **(2012)**

10. Khosravi A., Moradian S., Gharanjig K., Afshar T.F., Synthesis and spectroscopic studies of some naphthalimide based disperse azo dyestuffs for the dyeing of polyester fibres, *Dyes and Pigments,* **(69)**, 79-92 **(2006)**

11. Metwally M.A., Abdel-Galil E, Metwally A and Amer F. A., New azodisperse dyes with thiazole, thiophene, pyridone and pyrazolone moiety for dyeing polyester fabrics, *Dyes and Pigments,* **(92)**, 902-908 **(2012)**

12. Arcoria A., Cerniani A., Giorgi R. D., Longo M. L and Toscanoa R. M., Carrier dyeing of polyester fibre with some disperse azo dyes, *Dyes and Pigments*(**11**), 269-276 (**1989)**

13. Ertan N., Synthesis of some hetarylazopyrazolone dyes and solvent effects on their absorption spectra*, Dyes and Pigments*, **44(1)**, 41-48 **(1999)**

14. Ertan N. and Eyduran F., The synthesis of some hetarylazopyridone dyes and solvent effects on their absorption spectra. Dyes and Pigments, **27(4)**, 313-320 **(1995)**

15. Snavely F.A. and Yoder C.H., Study of tautomerism in arylazopyrazolones and related heterocycles with nuclear magnetic resonance spectroscopy, *Journal of Organic Chemistry,* **33(2),** 513-516 **(1968)**

16. Lestina G.J. and Regan T. ., Determination of the azo-hydrazonotautomerism of some 2-pyrazolin-5-one dyes by means of nuclear magnetic resonance spectroscopy and 15N-labeled compounds, *Journal of Organic Chemistry,* **34(6)**, 1685-1686 **(1969)**

17. Saylam A., Seferoglu Z and Ertan N., Synthesis and spectroscopic properties of new hetarylazo 8-hydroxyquinolines from some heterocyclic amines, *Dyes and Pigments*, **76(2)**, 470-476 **(2008)**

18. Gary M., Allan J G., Joseph B C., Kevin B., Michael M., Cooke G., Vincent M R., Model Systems for Flavoenzyme Activity: Interplay of Hydrogen Bonding and Aromatic Stacking in Cofactor Redox Modulation, *Organic letters* **6(3)**, 385-388 **(2004)**