



## Synthesis and UV Study of Series of Phenolic Azo Dye

Ritika N. Tiwari<sup>1</sup>, Manisha M. Kodape<sup>1\*</sup>, Nandkishor D. Gawhale<sup>2</sup> and Ashwini A. Wadurkar<sup>1</sup>

<sup>1</sup>Department of Chemistry, Sant Gadge Baba Amravati University, Amravati, 444, 602, Maharashtra, India

<sup>2</sup>Department of Chemistry, G.S. Tompe College, Chandur Bazar, Dist. Amravati, 444 704, Maharashtra, India  
mmkodape@gmail.com

Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

Received 22<sup>nd</sup> March 2016, revised 3<sup>rd</sup> May 2016, accepted 8<sup>th</sup> June 2016

### Abstract

The synthesis and application of azo dyes synthesized from naphthylamine to give diazonium salt solution. This salt is then coupled with various substituted phenols which furnish derivatives of azo dyes. These are the largest group of organic dyes for their applications in many areas of dyestuff industry, pharmacy due to the presence of azo (-N=N-) linkage. The present work is an efficient method for the synthesis of 1-naphthyl-azo-2-naphthanol with the high yielded product, water as a solvent, short time, low temperature, efficient method. The structures of synthesized compounds were confirmed using spectroscopic technique IR, <sup>1</sup>H-NMR, Mass spectra. UV absorption study of the synthesized compounds and interaction of 1-naphthyl-azo-2-naphthanol with different transition metal ion in basic and acidic solutions.

**Keywords:** Azo coupling, Diazotization, Naphthylamine.

### Introduction

In 1856 W. H. Perkin discovered Mauveine<sup>1</sup>, the first synthetic organic dye. Since then literally thousands of synthetic dyes have been prepared; for example azo benzothiazolyl dyes<sup>2</sup> and acridine dyes<sup>3</sup>. In 1987 Zollinger reported that over 7 x 10<sup>5</sup> tonnes of synthetic dyes are produced annually<sup>4</sup>. These days, dyes are widely used in environmental<sup>11</sup>, biological and analytical sciences<sup>6</sup>. Most dyes are classified according to their chemical structure or application method. The largest single group of dyes which have been developed are the azo dyes, all of which incorporate the -N=N- functional group attached directly to aromatic rings<sup>7,8</sup>. Azo compounds are a very important chemical compounds<sup>9</sup> receiving attention in many areas of research. They are colored, used as dyes and pigments for a long time<sup>10</sup>. These are the Azo dyes have various interest of application in titrations and in analytical chemistry<sup>7-9</sup>. They are also used in waxes, plastics, oils<sup>10</sup>. Although some azo dyes are reported to be toxic, many of additional monoazo dyes are permitted in chemotherapeutic drugs and cosmetics<sup>11-13</sup>. Azo dyes are easily prepared using the coupling reactions<sup>14</sup>.

### Materials and Methods

The organic materials were purchased from SdFine and Merck and were used without any additional purification. Merck, precoated Silica gel 60 F<sub>254</sub> (Aluminum sheet) plates were used for analytical TLC. IR spectra were recorded on FTIR spectrophotometer, <sup>1</sup>H-NMR spectra of all the synthesized compounds were recorded in (CDCl<sub>3</sub>/DMSO-d<sub>6</sub>) on Bruker Avance-2 400MHz NMR Spectrophotometer using TMS as an internal standard. The melting point was determined in open capillary tubes.

### General experimental procedures: Step1- Preparation of diazonium salt:

Take 2gm of substituted aniline in acidic water (1ml of conc. HCl and 10ml water) cool this solution at 0°C. Take 0.5gm sodium nitrite solution, cool this solution in ice bath to 0°C. Add NaNO<sub>2</sub> solution in above naphthalene solution drop wise with constant stirring, then filter the solution and collect the filtrate, which is the diazonium salt solution.

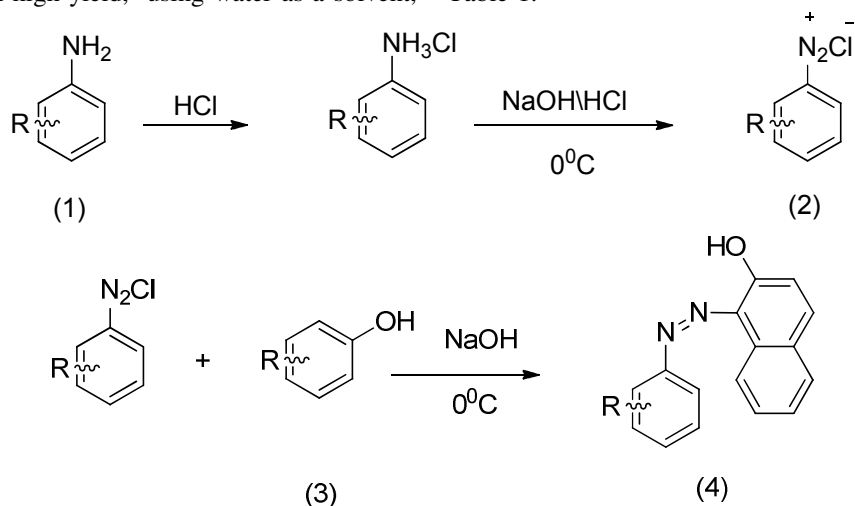
**Step2- Coupling reaction:** Dissolve 1.5gm β-naphthol in 10ml NaOH (10%) solution. Cool the solution 0°C in ice bath, add drop wise ice cold solution of the diazonium salt solution (step1) into an ice cold solution of β-naphthol in NaOH with constant stirring after complete addition allow the reaction mixture to stand for 10min in ice bath. Filter the red dye and wash with cold water, dry the product.

**Spectral data (4e):** IR (KBr) cm<sup>-1</sup>: 1142 (C-O), 1604 (C=C), 3082 (C=CH), 3240 (phenolic O-H), 1342 (C-N), <sup>1</sup>H NMR (DMSO- d<sub>6</sub>): 17 (s, 1H, Ar-OH), 8.6 (d, 1H, Ar-H), 8.2 (dd, 1H, Ar-H), 8.07 (d, 1H, Ar-H), 7.9 (m, 1H, Ar-H), 7.7 (m, 2H, Ar-H), 7.5(m, 2H, Ar-H), 7.4 (d, 1H, Ar-H), 7.3 (m, 2H, Ar-H), 6.9 (d, 1H, Ar-H) (Yield- 89%) (m.p. 182°C).

### Results and Discussion

1-naphthylamine is reacted with NaNO<sub>2</sub> crystals under extremely acidic solutions using HCl in a very low (0°C) temperature. The naphthyl diazonium intermediate easily decomposes back into its 1-naphthylamine counterpart at slightly higher temperature, thus the solution is maintained in an ice bath a constant temperature of 0°C. The phenyl diazonium salt by the product then undergoes diazonium-coupling reaction. β-naphthol couples with the diazonium salt. The attack of the diazonium salt on the carbon next to the -OH in the β-naphthol is favored. Completion of the

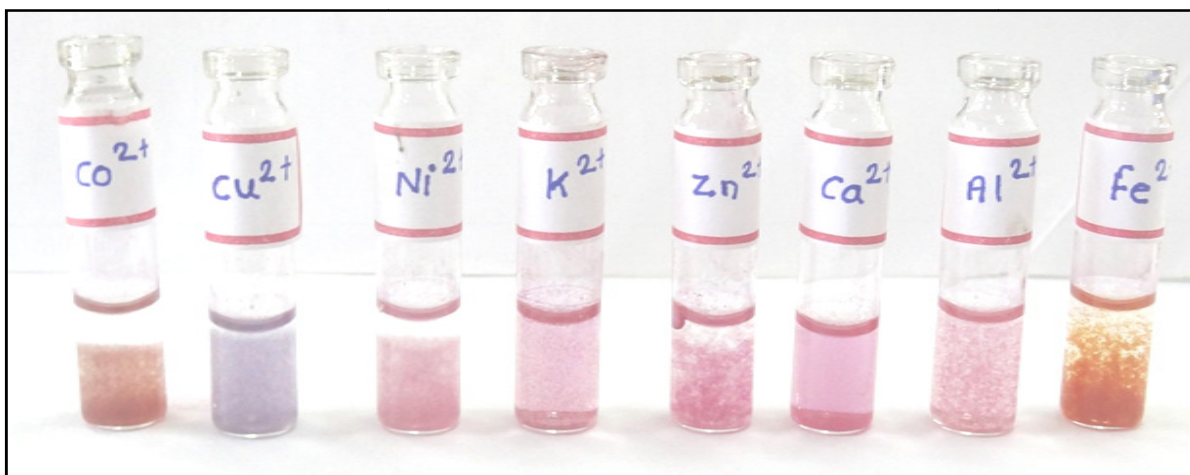
reaction was monitored by TLC ethylacetate : hexane =70:30) a short time and low temperature (Scheme-1). Different derivatives of azo dye were synthesized which are depicted in Table-1.



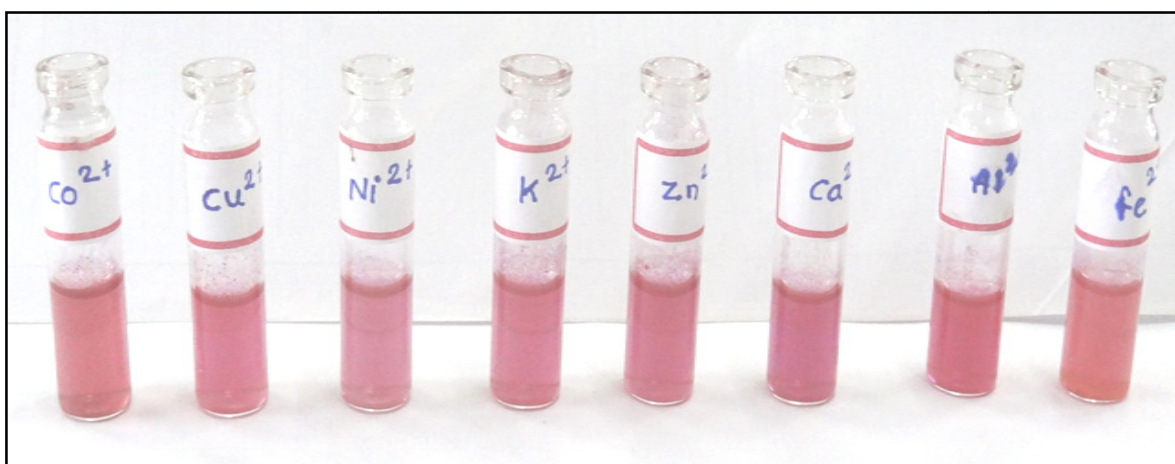
Scheme-I

Table-1  
 Different derivatives of azo dye

Sr. No.	Derivative	MP <sup>0</sup> C	Yield
4a		112	76
4b		80	78
4c		109	68
4d		118	72
4e		182	86



**Figure-1**  
Interaction of 1-naphthyl-azo-2-naphthanol with different transition metal ion in basic solution pH 10



**Figure-2**  
Interaction of 1-naphthyl-azo-2-naphthanol with different transition metal ion in acidic solution pH 2.5

## Conclusion

An efficient method for the synthesis of azo dye derivative with high yield, using water as a solvent, short time, low temperature.

## References

1. Filarowski (2010). Perkin's Mauve: The History of the Chemistry. 15(9), 850-855.
2. Pavlovic G., Racane L., Cicak H. and Kulenovic V.T. (2009). Synthesis, Spectral Properties and Applications of Some Mordant and Disperse Mono Azo Dyes Derived from 2-amino-1, 3-benzothiazole. *Dyes and Pigments*, 833, 354-362.
3. H. El Halabieh, Ozzy Mermut and C. J. Barrett. (2004). Using light to control physical properties of polymers and surfaces with azobenzene chromophores. *Pure and Applied Chemistry*, 76(7-8), 1445-1445-1465.
4. Zollinger H. (1987). Textile Dyes: Dyeing Process and Environmental Impact Colour Chemistry. *Dyes and Pigments*, 92-102, ISBN-10: 0471747955
5. Minkin V. I., Dubonsor A.D., Bren V.A. and Tsukanov V. (2008). Chemosensors with crown ether-based receptors. *ARKIVOC*, 4, 90-102.
6. Sameiro M., Maia H.L.S. and Goncalves T. (2001). A temporary marker for biological applications. *Tetrahedron Letters*, 42, 7775-7777.
7. Thomas Kerscher, Shahram Mihan and Prof. Dr. Wolfgang Beck (2011). Addition of Organometallic Nucleophiles (Carbonylmetallates) to the Allyl Ligand of  $[\eta^3\text{-C}_3\text{H}_5]\text{Pd}(\mu\text{-Cl})_2$ . Synthesis and Structure of  $(\eta^3\text{-C}_3\text{H}_5)\text{Mn}(\text{CO}_3\text{PEt}_3$ . *Zeitschrift für Naturforschung B*, 66(8), 861-564.
8. Bansal P., Singh D. and Sud D. (2010). Photocatalytic degradation of azo dye in aqueous  $\text{TiO}_2$  suspension:

- Reaction pathway and identification of intermediates products by LC/MS. *Separation and Purification Technology*, 72(3), 357-365.
- Zarei A., Hajipour A.R., Khazdooz L., Mirjalili B.F. and Chermahini A.N. (2009). Rapid and efficient diazotization and diazo coupling reactions on silica sulfuric acid under solvent-free conditions. *Dyes and Pigments*, 81, 3, 240-244.
  - Nasreen R. Jber, Rana S. Abood and Yasmeen A. Al-Dhaief (2011). Synthesis and Spectral Study of New Azo-Azomethine Dyes and its Copper (II) Complexes Derived from Resorcinol, 4-Aminobenzoylhydrazone and 4-Amino antipyrine. *Journal of Al-Nahrain University*, 14 (4), December, 50-56 .
  - Chandra U., Gilbert O., Kumara Swamy B. E., Bodke Y.D. and Sherigara B.S. (2008). Electrochemical Studies of Eriochrome Black T at Carbon Paste Electrode and Immobilized by SDS Surfactant: A Cyclic Voltammetric Study. *Int. J. Electrochem. Sci.*, 3, 1044-1054.
  - Chailapakul O., Wonsawat W., Siangproh W., Grudpan K. and Zhao Y. and Zhu (2008). Analysis of Sudan I, Sudan II, Sudan III, and Sudan IV in food by HPLC with electrochemical detection: Comparison of glassy carbon electrode with carbon nanotube-ionic liquid gel modified electrode. *Food Chemistry*, 109 (4), 876-882.
  - Eriksson A. and Nyholm L. (2001). Coulometric and spectroscopic investigations of the oxidation and reduction of some azosalicylic acids at glassy carbon electrodes. *Electrochimica Acta*, 496, 1113-1129.
  - Menek N. and Karaman Y. (2006). Polarographic and voltammetric investigation of 6'-butoxy-2,6-diamino-3,3'-azodipyridine. *Dyes and Pigments*, 68, 101-108.