

Synthesis and Analytical Studies of 3-(4-Acetyl-3-Hydroxyphenyl) Diazenyl)-4-Amino-N-(5-Methylisoxazol-3-Yl)Benzene Sulfonamide with Some Metals

Mohauman Mohammad Al-Rufaie*

Department of Chemistry, College of Science, Kufa University, Iraq

Abstract

Synthesis new organic azo dye as reagent 3-((4-acetyl-3-hydroxyphenyl) diazenyl)-4-amino-N-(5-methylisoxazol-3-yl)benzene sulfonamide (SDA) and Analytical Study of Co(II), Ni(II) and Cu(II), metals complexes. The reagent and its complexes were characterized by elemental analysis, UV-Vis, and molar conductivity measurements. The data show that the complexes have the composition of $[MR]X_2$ type. The conductivity data for all complexes are consistent with those expected for an electrolyte. Octahedral environment is suggested for metal complexes.

Keywords: New azo compound; Analytical studies; Metals complexes; Sulfonamide (SDA)

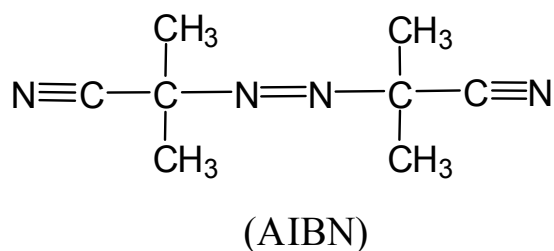
Introduction

Azo compounds are compounds bearing the functional group ($R-N=N-R'$), in which R and R' can be either alkyl or aryl [1]. Aryl azo compounds are more stable than alkyl azo compounds (R and R' aliphatic) [2]. One example is diethyldiazene ($Et-N=N-Et$). At elevated temperatures, the carbon-nitrogen (C-N) bonds in certain alkyl azo compounds cleave with loss of nitrogen gas to generate radicals like azo bisisobutyl nitrile (AIBN) (Scheme 1) [3].

Aryl azo compounds are stable and have a broad range of colors [4], including yellow, orange, red, brown, and blue. The colors differences are caused by different substituents on the aromatic rings which lead to differences in the extent of conjugation of the π -system in the azo compound. In general, the less extensive the conjugated π -system of a molecule, the shorter the wavelength of visible light it will absorb as shown below:

Colorless \rightarrow yellow \rightarrow orange \rightarrow red \rightarrow green \rightarrow blue
(Shortest wavelength) (Longest wavelength)

Azo compounds constitute one of the largest classes of industrially synthesized organic compounds, for their widespread applications in many areas of dye-stuff industry, pharmacy and dissymmetry due to the presence of azo ($-N=N-$) linkage 1-3 [1,2]. It can simply be defined as any class of artificial dyes that contains the azo group ($-N=N-$). Describing a dye molecule as nucleophiles will be known as auxochromes, while the aromatic groups are called chromospheres. The dye molecule is often described as a chromogen [3]. Azo compounds are highly colored and have been used as dyes and pigments for a long time. A large number of (N,N')-donor reagent azo compounds have been prepared in the last years [4]. These are the largest group of organic dyes [5]. A number of these azo dyes have been used as chelating reagents in addition



Scheme 1: Azo bisisobutyl nitrile.

of the uses as reagents in analytical chemistry [6]. The present study reports the preparation, spectral characterization and analytical study of new azo reagent (SDA) and metal complexes. Synthesis of most azo dyes involves diazotization of primary aromatic amines, followed by coupling with one or more nucleophiles [7] (Scheme 2).

Azo compounds are important structures in the medicinal and pharmaceutical fields. Furthermore, azo dye compounds also have a lot of applications in industry and photodynamic therapy as well as photosensitive species in photographic or electro photographic systems and they are dominant organic photoconductive materials [8].

Experimental

Apparatus and materials

All reagents and solvents were obtained from Fluke, The Merck and BDH. The melting points were determined on an Electro thermal, melting point 9300. Elemental analyses were carried out by means of Micro analytical unit of 1108 C.H.N.S Elemental analyzer while the UV-Vis. Spectra recorded in ethanol on Shimaduz model 1650PC. Molar conductance measurements were determined in DMF by using an Alpha Digital conductivity meter model 800. pH measurements were carried out using pH-meter Hanna. The metal content of the complex was measured by using atomic absorption technique by Perkin-Elmer model 2280.

Preparation of the reagent (SDA)

The reagent (SDA) was prepared according to the following general procedure [9,10] 4-amino-2-Hydroxy acetophenone (0.01 mol) (1.511 g) was dissolved in (3 ml) concentrated hydrochloric acid and (15 ml) distilled water. The mixture was cooled at (0-5°C) in ice-water bath. Then a solution of sodium nitrite (0.01 mol) dissolved in (5 ml) of distilled water was cooled at (0-5°C). This solution was added a drop wise to the mixture with stirring at the same temperature. The resulting

*Corresponding author: Mohauman Mohammad Al-Rufaie, Department of Chemistry, College of Science, Kufa University, Iraq, Tel: 07809086646; E-mail: mohaumanmajeed@yahoo.com

Received January 23, 2016; Accepted February 12, 2016; Published February 16, 2016

Citation: Al-Rufaie MM (2016) Synthesis and Analytical Studies of 3-(4-Acetyl-3-Hydroxyphenyl) Diazenyl)-4-Amino-N-(5-Methylisoxazol-3-Yl)Benzene Sulfonamide with Some Metals. Mod Chem appl 4: 175. doi:10.4172/2329-6798.1000175

Copyright: © 2016 Al-Rufaie MM. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

diazonium chloride solution was mixed with Sulfamethoxazole (2.5 g, 0.01 mol) dissolved in (200 ml) alkaline ethanol cooled below 0°C. After leaving in the refrigerator for 24 hr, the mixture was acidified with dilute hydrochloric acid until pH=5. The precipitate was filtered off, and re-crystallized twice from hot ethanol, and dried in a vacuum desiccator and shown in the following Scheme 3 [11].

Preparation of metal complexes

The metal complexes were prepared by the mixing of 50 ml ethanolic solution of (CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O) with the 50 ml of ethanolic solution of reagent in (1:1) (metal:reagent) ratio. The resulting mixture was refluxed for 2 h. Colored product appeared on standing and cooling the above solution. The precipitated complexes were filtered, washed and re-crystallized with ethanol several times and dried over anhydrous CaCl₂ in desiccators [12,13].

Results and Discussion

The analytical data for the reagent and complexes together with some physical properties are summarized in Table 1 [14]. The analytical data of the complexes correspond well with the general formula [MR] X₂ where M= Co(II), Ni(II), and Cu(II), R=(SDA).

Absorption spectra

The absorption spectra in aqueous ethanolic solution 50% (V/V) were studied for the prepared complexes showed a bath chromic shift

ranging about (84-207) nm. The absorption spectra of reagent (SDA) and Co(II), Ni(II) and Cu(II) chelat complexes is shown in Figures 1-4 [15].

Effect of pH

The effect of acidity of the absorbance values of the complexes was studied in the 50%(v/v) ethanolic by changing the pH value of the solution and the results is shown in Figures 5-7, where demonstrated that the best absorbance of Co(II), Ni(II) and Cu(II) (SDA) system is in the range (6.5-8). The reagent formed stable complexes with metal ions at same pH.

Effect of time

Also the reaction is complete in 5 min at room temperature and remains stable for about 180 min. This show the reagent (SDA) strong coordination with metal ions in this time. The results are shown in Figure 8.

Metal: Reagent ratio

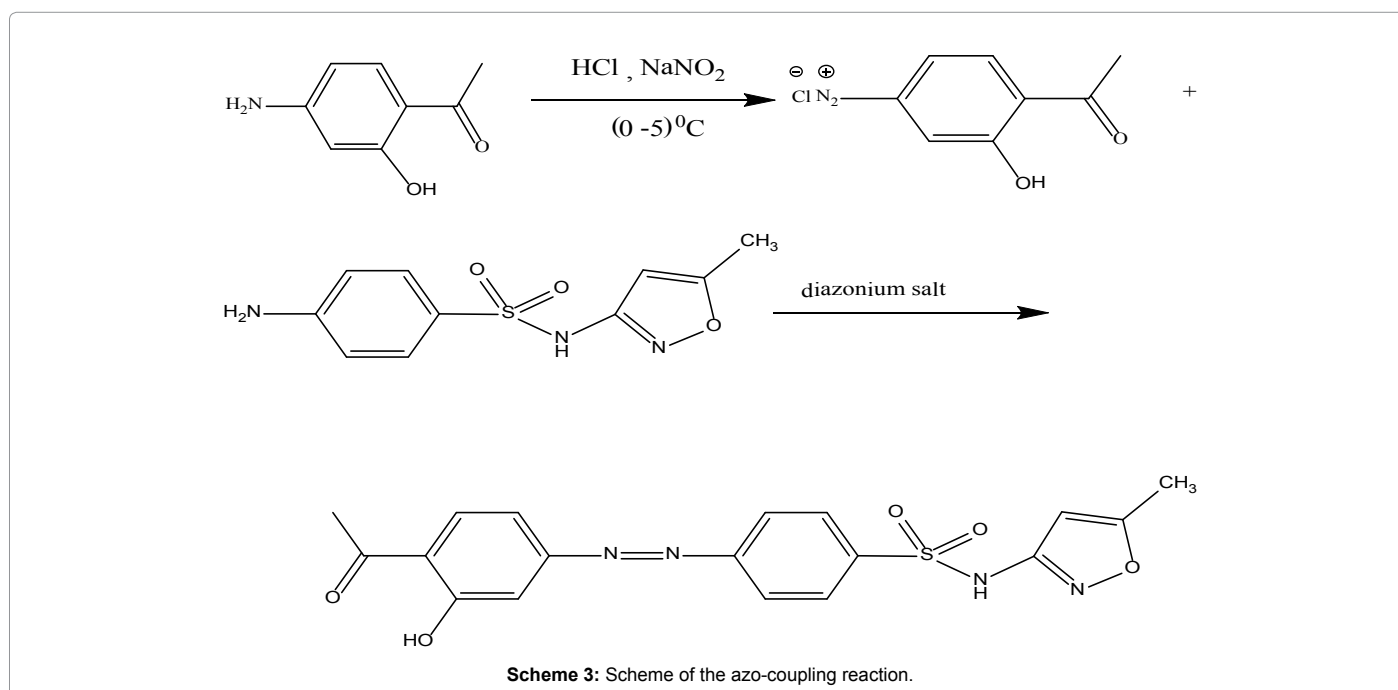
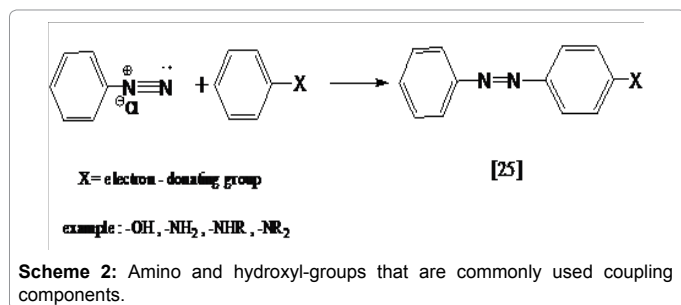
The (metal: reagent) ratios of complexes were determined by molar ratio method at fixed concentration and pH at wavelengths of maximum absorption. The results are given in Table 2, the reagent was found to form (2: 1) chelates with all metal ions.

Calculation of the metal complexes stability constant

Stability constants are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength λ_{max} and pH values. The degree of formation of the complexes is obtained according to the relationship [16], $\beta=(1-\alpha)/(4\alpha^3c^2)$, and $\alpha=(Am-As)/Am$, where As and Am are the absorbance's of the partially and fully formed complex respectively at optimum concentration. The calculated β and Log β values for the prepared complexes are recorded in Table 2.

Conclusions

In this present study we report the preparation characterization

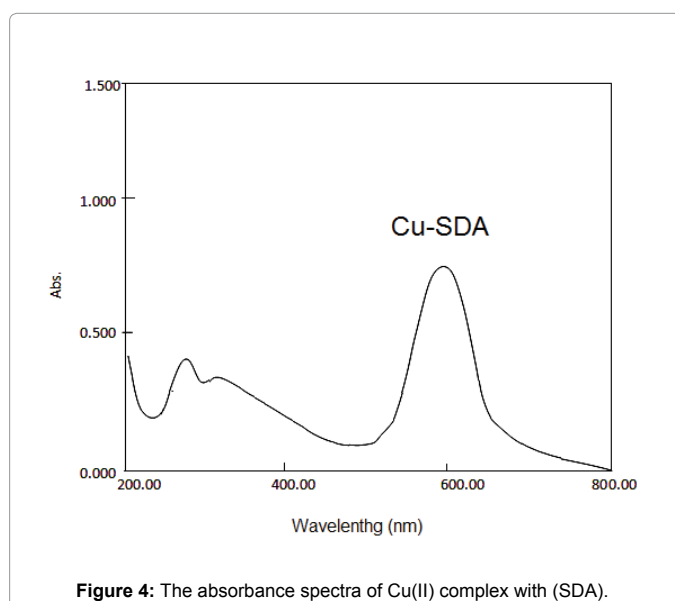
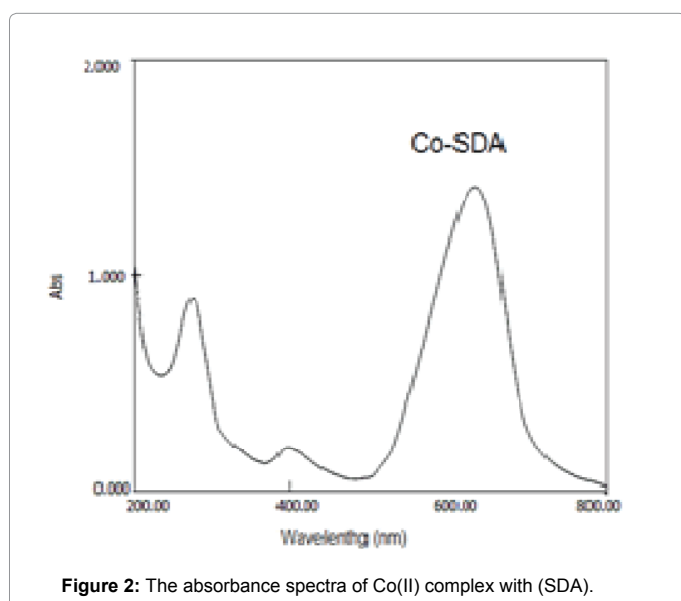
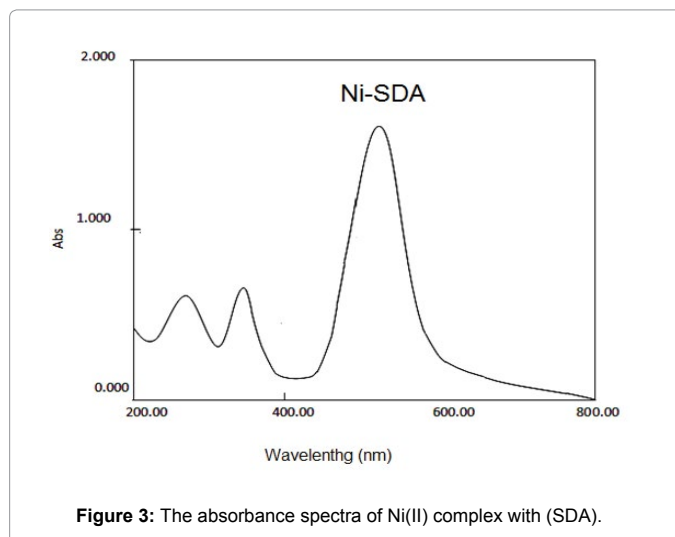
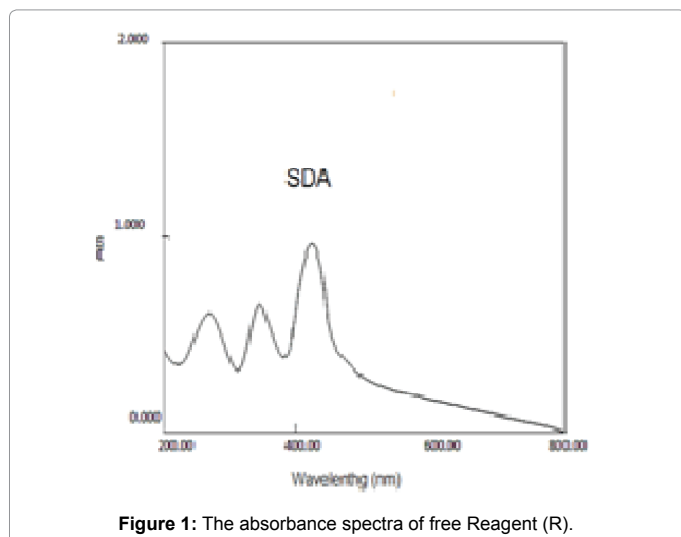


S No	Compound color	MP (°C)	Yield%	Molecular formula	Found (Calc.) %				
					C	H	N	S	M
1	R=(SDA) Brown	250-255	91	$C_{18}H_{16}N_4O_5S$	52.287 (52.42)	3.838 (3.91)	20.025 (20.38)	7.57 (7.77)	-
2	Co-SDA Brown-Red	272-264	82	$C_{18}H_{16}N_4O_5S Cl_2Co$	45.101 (45.39)	3.091 (3.17)	17.469 (17.64)	6.523 (6.73)	5.97 (6.19)
3	Ni-SDA Green	206-218	89	$C_{18}H_{16}N_4O_5S Cl_2Ni$	45.211 (45.40)	3.03 (3.17)	17.512 (17.65)	6.52 (6.73)	6.021 (6.16)
4	Cu-SDA Blue	223-211	75	$C_{18}H_{16}N_4O_5S Cl_2Cu$	44.873 (45.17)	2.98 (3.16)	17.441 (17.56)	6.49 (6.70)	6.28 (6.64)

Table 1: Analytical data and physical properties of the reagent (SDA) and complexes.

S No	Metal ions and color	pH	wave length (λ_{max}) nm	molar conc. $\times 10^{-5}$ M	β $L^2 \cdot mol^{-2}$	log β	Molar conduc. $S \cdot mol^{-1} \cdot cm^2$
1	Co-SDA Brown-Red	8	625	1	6.83×10^{10}	10.83	66.23
2	Ni-SDA Green	7.5	510	3.4	6.39×10^{10}	10.80	63.91
3	Cu-SDA Blue	6.5	608	5	9.83×10^{11}	11.99	69.21

Table 2: Metal: reagent stability constant value (β), molar conductivity, optimal concentration and wave length.



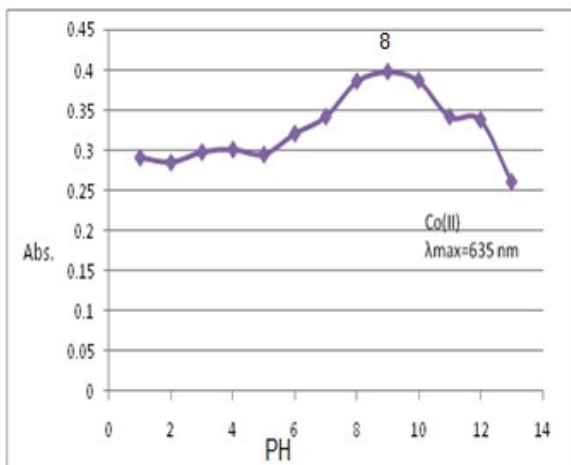


Figure 5: Effect of acidity on Co(II) complex absorbance.

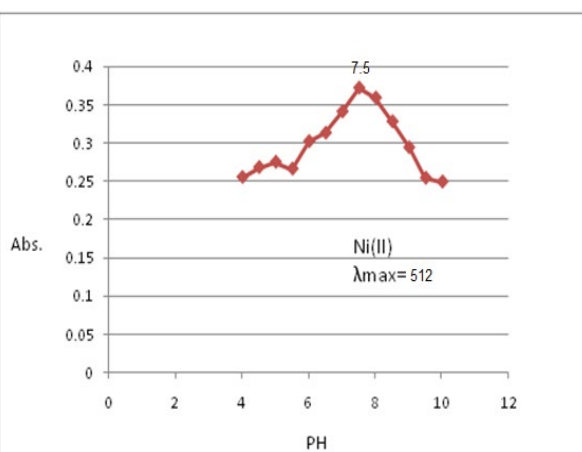


Figure 6: Effect of acidity on Ni(II) complex absorbance.

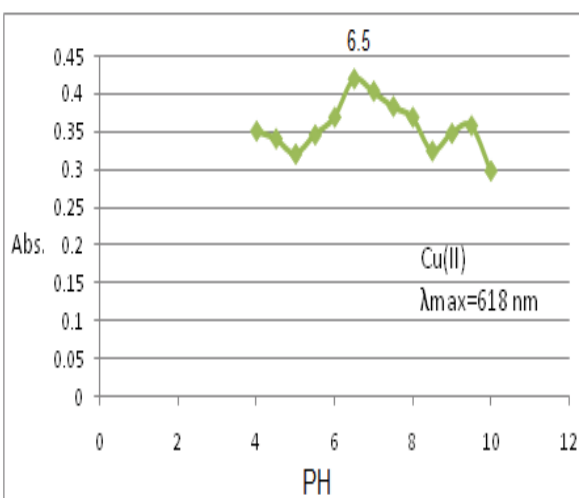


Figure 7: Effect of acidity on Cu(II) complex absorbance.

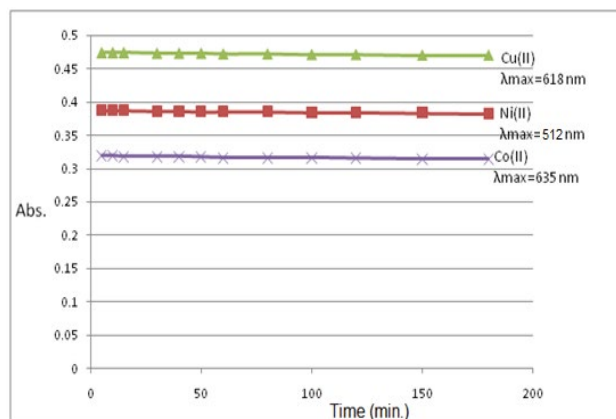


Figure 8: Effect of time on the absorbance of Co(II), Ni(II) and Cu(II) metal complexes at room temperature.

and spectroscopy study of new azo reagent derived from imidazole and its complex with Cu(II) metal ion. The isolated complex was characterized by available techniques. The aryl azo reagent (SDA) behaves as a bidentate chelating agent and coordinating through the N₂ atom of imidazole and another nitrogen atom of azo group which is the farthest of imidazole ring to form five-member metallo ring and oxygen atom for cobalt and nickel complexes. The coordination of the metal ion Cu(II) with reagent(SDA) are to give hexa coordinated show octahedral stereochemistry.

References

- Rathod KM, Thaker NS (2013) Synthesis and Antimicrobial Activity of Azo Compounds Containing m-Cresol Moiety. Chem Sci Trans 2: 25-28.
- armion DM (1999) Hand book of colorant. In: Handbook of US colorants. Foods, Drugs, Cosmetics and Medical devices. 3rd edn. Wiley, New York, USA, pp: 23-26.
- Al-Rubaie LAR, Mhessn RJ (2012) Synthesis and Characterization of Azo Dye Para Red and New Derivatives. E J Chem 9: 465-470.
- Mathur T, Ray U, Baruri B, Sinha C (2005) Tetrahedral manganese(II) complexes of 1-alkyl-2-(arylo)imidazoles. X-ray crystal structure of [Mn(Haaime)₂](ClO₄)₂·DMF (Haaime = 1-methyl-2-(phenylazo)imidazole). J Coord Chem 58: 399-407.
- Mehdi RT, Ali AM (2005) Preparation and Characterization of New Azo imidazole ligand and Some Transition Metal Complexes. National Journal of Chemistry 20: 540-546.
- Ali AM, Mehdi RT (2005) Synthesis and Spectroscopic Studies of Some Transition Metal Complexes with 2-[(3-Iodophenyl) azo]-4, 5-diphenyl imidazole. Al-Mustansirya J Sci 16: 1-11.
- Dinda J, Ray U, Mostafa G, Lu TH, Usman A, et al. (2003) Copper(I)-azoimidazoles: a comparative account on the structure and electronic properties of copper(I) complexes of 1-methyl-2-(phenylazo)imidazole and 1-alkyl-2-(naphthyl-(α/β)-azo)imidazoles. Polyhedron 22: 247-255.
- Hihara T, Okada Y, Morita Z (2007) A semiempirical molecular orbital study of the photo-reactivity of monoazo reactive dyes derived from γ- and J-acids. Dyes and Pigments 73: 141-161.
- Skelton R, Dubois F, Zenobi R (2007) A MALDI sample preparation method suitable for insoluble polymers. Anal Chem 72: 1707-1710.
- Steter JR, Pontólio JO, Campos MLAM, Romero JR (2008) Modified Electrodes Prepared with Polyphenolic Film Containing Ruthenium Complex and Metal Ligand Anchored by Azo Covalent Bond. J Braz Chem Soc 19: 660-666.
- Ofomaja AE, Ho YS (2007) Equilibrium sorption of anionic dye from aqueous solution by palm kernel fibre as sorbent. Dyes and Pigments 74: 60-66.

12. Salwinska E (2009) Nitroimidazoles. Part X. Synthesis of 1-aryl-4-nitroimidazoles from 1, 4-dinitroimidazoles and primary aromatic amines. Pol J Chem 64: 813-817.
13. Das D, Sinha C (1998) Palladium azoimidazoles. Solvatochromic studies of catecholato complexes. J Trans Met Chem 23: 517-522.
14. Reddy BK, Kumar JR, Reddy KJ, Sarma LS, Reddy AV (2003) A rapid and sensitive extractive spectrophotometric determination of copper(II) in pharmaceutical and environmental samples using benzildithiosemicarbazone. Anal Sci 19: 423-428.
15. Shibata S, Furukawa M, Nakashima R (1976) Syntheses of azo dyes containing 4,5-diphenylimidazole and their evaluation as analytical reagents. Anal Chim Acta 81: 131-141.
16. Gung BW, Taylor RT (2004) Parallel Combinatorial Synthesis of Azo Dyes: A Combinatorial Experiment Suitable for Undergraduate Laboratories. J Chem Educ 81: 1630.