

Synthesis of New Azo Dyes Derived from 2,7-Dihydroxynaphthalene

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Abstract: Two novel azo dyes were synthesized by coupling of diazonium salts of 2-aminophenol and 1-amino-2-hydroxynaphthalene-4-sulphonic acid diazonium salts with the title compound 2,7-dihydroxynaphthalene. The resultant dyes 1-(2-hydroxyphenylazo)-2,7-dihydroxynaphthalene (dye I) and 1-(2,7-dihydroxy-naphthylazo)-2-hydroxy-4-naphthalenesulfonic acid (dye II) respectively were characterized by IR, HPLC-MS, ¹HNMR and ¹³C-NMR spectroscopies. Some of physical constants, e.g. ionization constants and melting point were calculated, there was $pK_1=4.32$, $pK_2=8.26$, $pK_3=10.58$, m. p. $220\pm 2^\circ\text{C}$, and $pK_1=7.62$, $pK_2=8.69$, $pK_3=9.65$, m. p. $289\pm 2^\circ\text{C}$ for dye I and dye II, respectively.

Keywords: Azo dyes synthesis; diazotization; ionization constants; 2, 7-dihydroxynaphthalene; 2-aminophenol; 1-amino-2-hydroxynaphthalene-4-sulphonic acid.

1. INTRODUCTION

Azo colorants are the most important class of synthetic dyes and pigments, representing 60-80% of all organic colorants [1], so they occupy an important position in organic chemistry especially from their industrial, medicinal and analytical point of view [2]. They do not occur in nature and produce only through chemical synthesis [3]. Their uses as light absorbance for plastics [2], and as substrates for many industrial applications such as textile fibers, leather, paper, hair, mineral oils, waxes, foodstuffs and cosmetics [1]. Furthermore, they have medicinal importance [4,5] as anti-inflammatory drugs [2]. In addition, it involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation [6]. On other hand, their use as electro-analytical reagent for detection of trace metals [2]. Recently, used as sensitized solar cells due to their efficient conversion of solar energy to electricity at a low cost [7].

2. EXPERIMENTAL

2.1 Instruments and Apparatus

UV/VIS spectrophotometer V-630 (JASCO, Japan); FT/IR spectrophotometer 4100 (JASCO, Japan); ¹H-NMR spectrometer AC-400MHz (BRUKER, USA) using TMS as internal standard and DMSO-d₆ as solvent; LC-MS spectrophotometer 2010 (SHIMADZU, Japan); pH-meter 744 (METROHM, Swiss); electro-thermal melting point (ELECTROTHERMAL, England); electro-magnetic stirrer L32 (LABINCO, Poland); analytical balance 3432 (SARTORIUS, Germany), with accuracy $\pm 0.1\text{mg}$; drying oven E28 (HERAEUS, Germany); UV lamp (DESAGA, Germany) with 245nm and 336nm wave-lengths; bi-distill water apparatus (JANAT, Syria).

2.2 Chemicals

- Organic solvents: methanol ($\geq 99.5\%$, Extra Pure, MERCK, Germany), acetone ($\geq 99.0\%$, For Synthesis, MERCK, Germany), *N,N*-dimethylformamide (DMF) ($\geq 99.9\%$, Extra Pure, RIEDEL-de HAËN, Germany), ethyl acetate ($\geq 99.0\%$, Extra Pure, SOLVAY, USA), toluene ($\geq 99.0\%$, GR for Analysis, MERCK, Germany).
- Organic materials: 2,7-dihydroxynaphthalene ($\geq 98.0\%$, FOR SYNTHESIS, MERCK, Germany),

2-aminophenol ($\geq 99.0\%$, For Synthesis, MERCK, Germany), 1-amino-2-hydroxynaphthalene-4-sulphonic acid ($\geq 99.0\%$, For determination of Phosphate, MERCK, Germany).

- Inorganic materials: sodium nitrite ($\geq 99.0\%$, GR FOR ANALYSIS, MERCK, Germany), copper nitrate ($\geq 99.0\%$, EXTRA PURE, HIMEDIA, India), hydrochloric acid ($\geq 37\%$, GR for Analysis, MERCK, Germany), sodium hydroxide ($\geq 97.0\%$, EXTRA PURE, RASAYAN, India), Potassium Bromide (Uvasol, for IR spectroscopy, MERCK, Germany).
- TLC plates: TLC aluminum sheets silica gel 60 F₂₅₄ (MERCK, Germany).

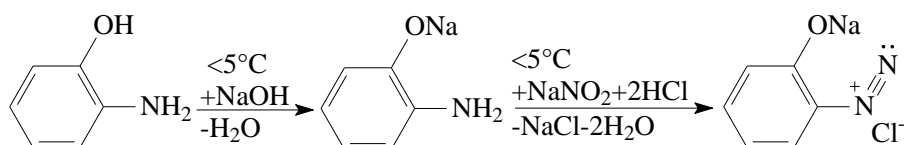
2.3 Methods

2.3.1 Synthesis of Dye I

The dye I was synthesized through two main steps, they are diazotization and coupling reactions.

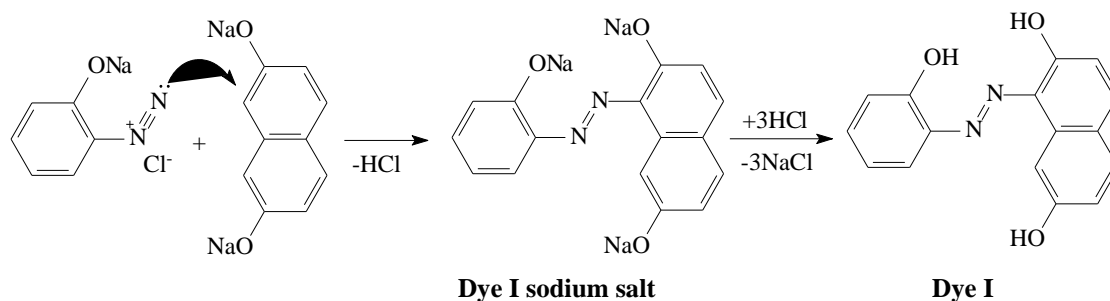
a. Diazotization Reaction

- 2-Aminophenol (C₆H₇NO, 5.4565g, 50mmol) was dissolved in saturated aqueous solution of sodium hydroxide (NaOH, 2.2000g, 55mmol) and cooled down to $\leq 5^\circ\text{C}$.
- Saturated aqueous solution of sodium nitrite (NaNO₂, 3.7950g, 55mmol) was added with continues stirring to cold ($\leq 5^\circ\text{C}$) aqueous solution of sodium 2-aminophenolate.
- The mixture was added drop wise to cool hydrochloric acid (HCl_{37%w/w}, 10.8514g, 9.15mL, 110mmol) with continues stirring and temperature maintained at $\leq 5^\circ\text{C}$.
- Continues the stirring and cooling ($\leq 5^\circ\text{C}$) for 30 minutes will produce 2-diazophenol hydrochloric salt.



b. Coupling Reaction

- 2,7-Dihydroxynaphthalene (C₁₀H₈O₂, 8.0085g, 50mmol) was dissolved in aqueous solution of sodium hydroxide (NaOH, 4.4000g, 110mmol) and cooled down to $\leq 5^\circ\text{C}$.
- Cold ($\leq 5^\circ\text{C}$) aqueous solution of the 2-diazophenol hydrochloric salt was added drop wise to cool ($\leq 5^\circ\text{C}$) aqueous solution of disodium 2,7-dihydroxynaphthalenolate with continues stirring and cooling.
- Continues stirring and cooling ($\leq 5^\circ\text{C}$) for 30 minutes will produce trisodium 2,7-dioxy-1-[(2-oxy-1-phenylazo)]naphthalene (dye I sodium salt).
- Solution left to rise to room temperature and then acidified by hydrochloric acid (HCl_{37%w/w}, 16.2771g, 13.70mL, 110mmol) solution to yield 2,7-dihydroxy-1-[(2-hydroxy-1-phenylazo)]naphthalene (dye I) precipitate.



- Dye I was filtrated and washed twice with about 10 mL of cold water thereafter was dried completely at $55 \pm 5^\circ\text{C}$ to prevent dissolving inorganic salts.

c. Crystallization

Saturated methanolic dried dye I solution was filtrated out from inorganic materials which are insoluble in dried methanol. Bi-distilled water was added to filtrate drop wise with stirring until dye I start to precipitate. The mixture was left over-night to complete precipitation process. The crude dye I was filtrated and dried out then kept away from air, light and heat to afford 75%. Recrystallization was done using the above-mentioned method of crystallization.

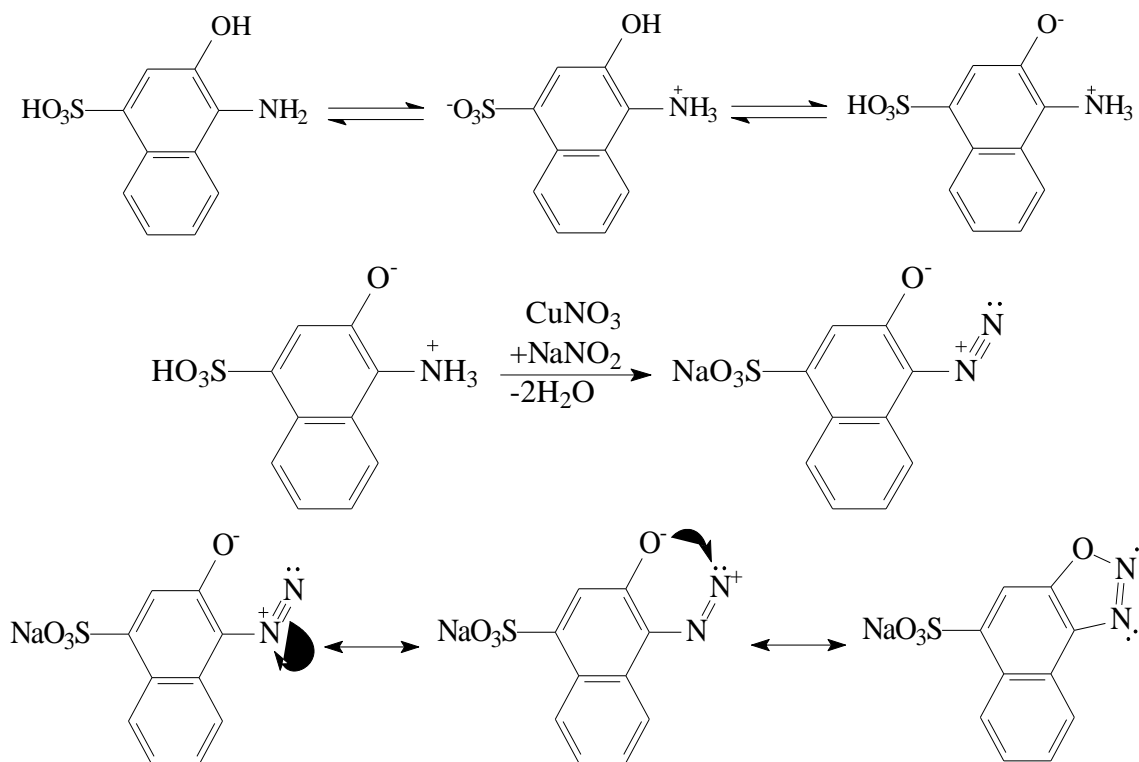
The purity of dye I confirmed initially by TLC on silica gel 60 - F₂₅₄ using toluene:ethyl acetate (9:1) as eluent. No accompanying spots were observed in resulting chromatogram.

2.3.2 Synthesis of Dye II

1-Amino-2-hydroxynaphthalene-4-sulphonic acid was diazotized in presence of copper nitrate as catalyst at temperature 15°C [8].

a. Diazotization Reaction

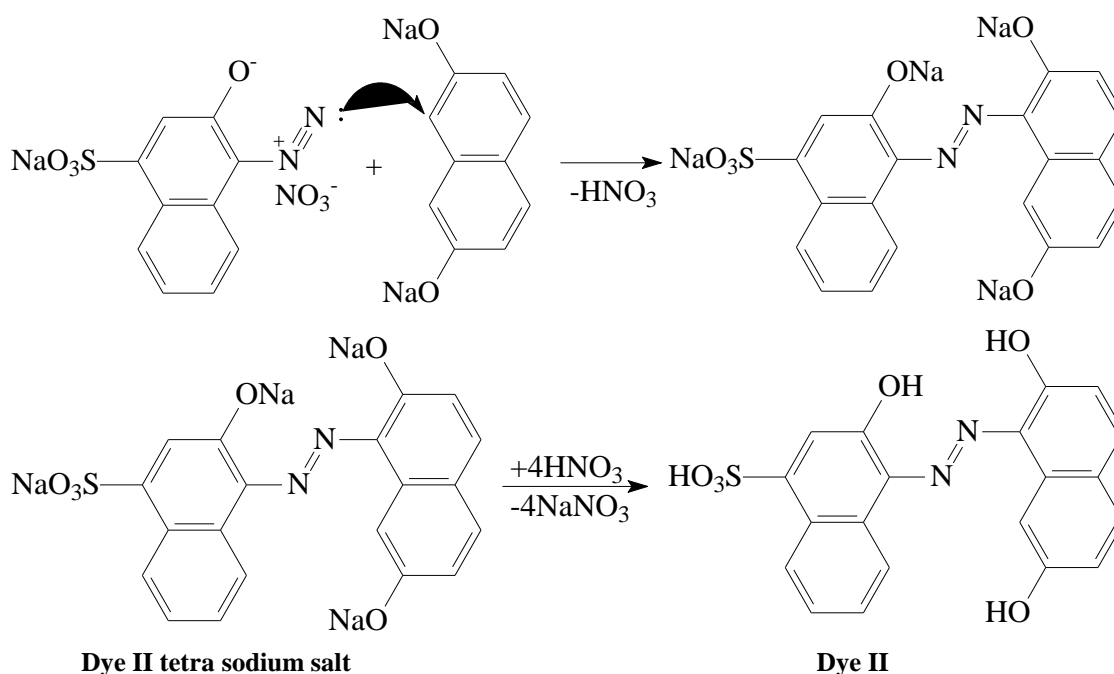
- 1-Amino-2-hydroxynaphthalene-4-sulphonic acid (C₁₀H₉NO₄S, 11.9625g, 50mmol), sodium nitrite (NaNO₂, 3.7950g, 55mmol) and catalytically amount of Cu(NO₃)₂·9H₂O were dispersed in 40mL of water and stirred until reaction mixture convert to soluble diazonium salt. The release of nitrogen gas indicates to the decomposition of diazonium salt. The sodium 1-diazo-2-hydroxynaphthalene-4-sulphonate salt is soluble in water and stable at room temperature, due to tautomerism with pentagonal cyclic isomer formed between hydroxyl and diazo groups.



b. Coupling Reaction

- 2,7-Dihydroxynaphthalene (C₁₀H₈O₂, 8.0085g, 50mmol) was dissolved in saturated aqueous solution of sodium hydroxide (NaOH, 4.4000g, 110mmol).
- Aqueous solution of sodium 1-diazo-2-hydroxynaphthalene-4-sulphonate was added drop wise to aqueous solution of disodium 2,7-dihydroxynaphthalenate with continues stirring at room temperature.
- Continuous stirring for 30 minutes will produce tetrasodium 2-oxy-1-(2,7-dioxy-1-naphthalenyl)-

azo)naphthalene-4-sulphonate (dye II tetra-sodium salt).



- The solution was acidified by hydrochloric acid ($\text{HCl}_{37\% \text{ w/w}}$, 24.4157g, 20.55mL, 165mmol) solution to yield 2-hydroxy-1-(2,7-dihydroxy-1-naphthylazo)naphthalene-4-sulphonic acid (dye II) precipitate.
- Dye II was filtered out and washed twice with about 10 mL of cold water, thereafter was dried completely at $55 \pm 5^\circ\text{C}$ to prevent dissolving inorganic salts.

c. Crystallization

Dried dye II *N,N*-dimethylformamide (DMF) saturated solution was filtered from inorganic materials which are insoluble in DMF. Acetone was added drop wise to filtrate with stirring until dye II start to precipitate. The mixture was left over-night to complete precipitation process. The crude dye II was filtered, dried out and kept away from air, light and heat to afford 60%. Recrystallization was done using the above-mentioned method of crystallization. The purity of dye II was confirmed initially by TLC on silica gel 60 - F₂₅₄ using ethyl acetate:methanol:DMF (8:1:1) as eluent. No accompanying spots observed in resulting chromatogram.

2.3.3 Melting Points of Dyes I and II

Melting points of two dyes were measured. They were $220 \pm 2^\circ\text{C}$ and $289 \pm 2^\circ\text{C}$ for dye I and dye II, respectively.

2.3.4 Ionization Constants of Dyes I and II

The ionization constants of dye I and dye II were calculated spectrophotometrically according to the common methods: half-height [9-11], limited absorbance [9-11] and COLLÉTER's [12]. Table (1) shows the values of ionization constants of the two synthesized dyes.

Table (1): The average values of ionization constants of dyes I and II

	λ , nm	half height			limited absorbance			COLLÉTER			\overline{pK}_i		
		pK_1	pK_2	pK_3	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3
dye I	500	4.35	8.27	10.65	4.37	8.28	10.65	4.24	8.25	10.63	4.32	8.27	10.64
	530	4.34	8.20	10.59	4.36	8.20	10.58	4.25	8.13	10.64	4.32	8.18	10.60
	540	4.35	8.32	10.55	4.38	8.32	10.55	4.25	8.15	10.58	4.32	8.26	10.56
	550	-	8.38	10.49	-	8.39	10.50	-	8.24	10.55	-	8.34	10.51
	\overline{pK}_i	4.35	8.29	10.57	4.37	8.30	10.57	4.25	8.19	10.60	4.32	8.26	10.58
dye II	503	7.38	8.62	-	7.34	8.53	-	7.57	8.52	-	7.43	8.56	-
	545	7.64	8.85	-	7.62	8.80	-	7.82	8.86	-	7.69	8.84	-
	575	7.61	8.84	9.85	7.67	-	9.86	7.74	-	9.66	7.67	8.84	9.79
	600	7.76	-	9.67	7.73	-	9.67	7.59	-	9.48	7.69	-	9.61
	630	7.59	8.54	9.56	7.59	8.50	9.59	7.68	8.52	9.54	7.62	8.52	9.56
	\overline{pK}_i	7.60	8.71	9.69	7.59	8.61	9.71	7.68	8.63	9.56	7.62	8.69	9.65

The results in table (1) indicates to three values of ionization constants which match with the expected structures of the prepared dyes.

The color of dye I ($pT=7.8$) is changed according to pH value from orange-red in acidic media ($pH<7.3$) to violet in basic media ($pH>8.3$) through pink color.

Whereas, the color of dye II ($pT=7.3$) is changed from red in acidic media ($pH<6.5$) to marine blue ($pH>8.1$) in weak basic media through violet, with clear sharp change. So, dye II can be used as indicator at neutralization titration.

2.3.5 Identification of Dye I & II Structures

The structures of the synthesized dyes I and II were identified by the available spectroscopic methods: IR, HPLC-MS, 1H -NMR, and ^{13}C -NMR spectroscopies.

2.3.5.1 IR Spectrum

Dyes I and II were scanned through wave numbers ranged between 400-4000 cm^{-1} using KBr disk. The main absorption bands of the dyes I and II are shown in the table (2) and figure (1).

Table (2): The main absorption bands and the possible functional groups in dyes I and II

absorption bonds	wave number cm^{-1}	
	dye I	dye II
-O-H stretching	3363	3453
Aryl =C-H stretching	3051	3074
Aliphatic -C-H stretching might be caused by trace of DMF	-	2925
Aryl C=C stretching	1617	1650
-N=N- stretching	1463	1437
-S=O for -SO ₃ H	-	1047

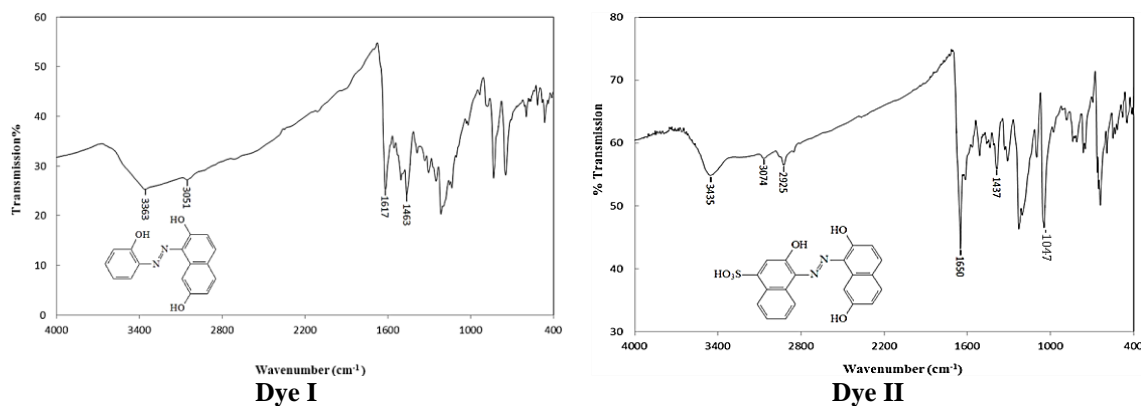


Figure (1): IR spectra of dyes I and II

2.3.5.2 HPLC-MS Spectrum

The mass spectra (positive polarity) of dyes I and II are shown in the figure (2). It shows the presence of the main peaks at m/z 279 and 409 corresponding to the radical cations $M^{+ \cdot} - 1$ (the calculated mass 280 and 410 for dye I and II, respectively), which are in agreement with the proposed structure.

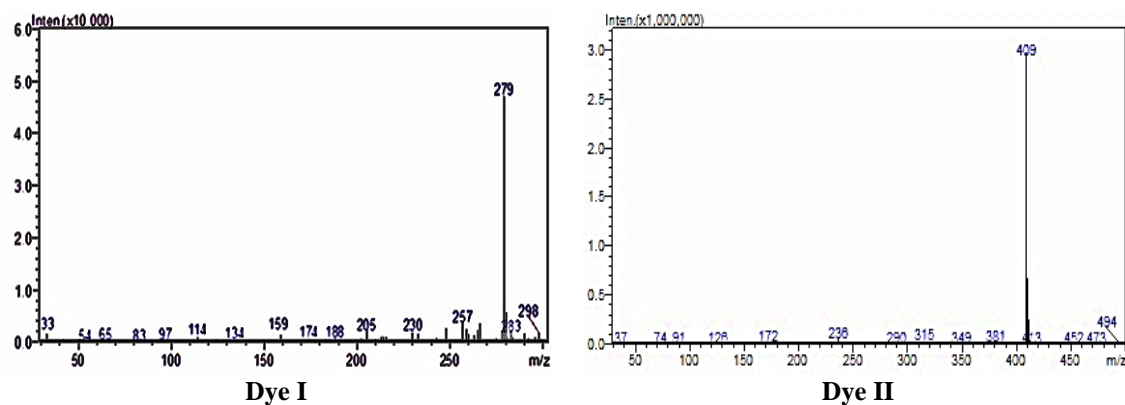


Figure (2): HPLC-MS spectra of dyes I and II

2.3.5.3 ^1H NMR Spectrum

The ^1H -NMR and ^{13}C -NMR spectral data of dyes I and II consist the following results, where the chemical shift δ are given in ppm:

- ^1H -NMR: $\delta = 10.57$ (s, 1H, O-H), 10.29 (s, 1H, O-H), 9.12 (s, 1H, O-H), 6.71 – 7.76 (m, 9H, Ar-H); ^{13}C -NMR: $\delta = 156.29$ (1C, C-OH), 154.64 (1C, C-OH), 154.52 (1C, C-OH), 138.83 – 107.32 (2C, C-N=N; 11C, C-Ar) for dye I.
- ^1H -NMR: $\delta = 11.31$ (s, 1H, SO_3H), 10.39 (s, 1H, O-H), 9.25 (s, 1H, O-H), 9.09 (s, 1H, O-H), 6.96 – 8.13 (m, 10H, Ar-H); ^{13}C -NMR: $\delta = 156.82$ (1C, C-OH), 154.47 (1C, C-OH), 153.39 (1C, C-OH), 141.28 (1C, C- SO_3H), 134.72 – 106.92 (2C, C-N=N; 14C, C-Ar) for dye II.

3. CONCLUSION

We have synthesized two azo dyes derived from 2,7-dihydroxynaphthalene, and found that the diazotization can be carried out through the common procedure at temperature $\leq 5^{\circ}\text{C}$ using 2-aminophenol. Where, at laboratory temperature using 1-amino-2-hydroxynaphthalene-4-sulfonic acid due to tautomeric structures and resonance between hydroxyl and diazo groups.

The number of observed ionizations are equal to the number of hydroxyl groups indicated in expected structures of the synthetic two dyes, which determined spectrophotometrically directly from spectrum or by COLLÉTER mathematic method. Improvement of these methods are accomplished using MATLAB R2008a and JASCO-v630 spectrophotometer programs (absorption resolution 10^{-7}). However, we could not be able to determine the ionization of sulfo-hydroxyl group proton spectrophotometrically.

The spectral methods (IR, HPLC-MS, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) proved the proposed structures of the synthesized dyes.

In our other work, we determined some transition metal ions by using the dyes I and II as chromophoric reagents. In addition, we could titrate some organic acids by neutralization-titration using the dye II as indicator.

We provided the dye II to other researchers, who use it as a reagent to determine an active pharmaceutical ingredient.

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