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Synthesis, Characterization and Analytical Study of New Azo Compounds for using as acid-base indictors

Hussain Saleem Jabbar[1], Ahmed Dhary Saleh[2], Abdullah Hussein Kshash[3]
Department of Chemistry, Education College for Pure Science (CS),
University of Anbar (UoA), Anbar, Iraq.

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ABSTRACT

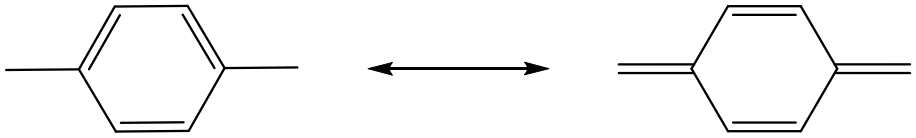
A diazotization method was used to synthesize new azo compounds, to which phenol was subsequently added to diazonium salt solution in basic medium at temperatures ranging from 0 to 5 °C and compounds were characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. The potential of the compounds as acid-base indicators was tested by determining their ionization and protonation constants at different pH levels (1 to 14) using a DMSO solution of the synthesized compounds. UV-Vis spectra shown as maximum wavelength (380-390 nm) observed at pH 1-7 occurs, indicating the cationic formula (protonated form of compound H2 and H4), another peak (470-530 nm) appears at pH 8-13, indicating the ionic formula (deprotonated form of compound H2 and H4), where for compound H5 observed at 560 nm at pH 1-7. Another peak appears 505 nm at pH 8-13 attributable to absorption the ionic formula (deprotonated form of compounds H5). Molecules H2, H4, and H5 showed distinct color changes when shifted to acidic and basic conditions. Furthermore, these compounds showed exceptional accuracy in drawing conclusions about the phenomenon.

Corresponding Author:

Abdullah Hussein Kshash
Department of Chemistry, Education College for Pure Science
University of *Anbar*
Ramadi *City*, Anbar, Iraq.
Email: drabdullahkshash@gmail.com

1. INTRODUCTION

AZO compounds are a class of organic molecules which have a functional group R-N=N-R. R and R' are usually Aromatic rings homogeneous or heterogeneous [1]. Azo dye was discovered in 1862 by chemist Johann Peter Griess which was synthesized the dye by combining diazotized sulphanilic acid with aniline [2]. Azo compounds were prepared in two steps: firstly, the preparing of the diazonium salt, followed by coupling the diazonium salt with phenols to produce the azo compounds. Both steps are carried out with a temperature range of 0-5^{o}C [3]. There are several factors are affected on diazotization as temperature (0-5 ^{o}C), acid concentration, pH of $NaNO_2$, reaction time and concentration of sodium nitrite [4]. Azo compounds are classified depending on nature of auxochrome associated into acidic if it contains of an acidic group, such as (SO_3H, OH, COOH) and basic if it contains of a basic group, such as (NR, NRH, NH_2) [5]. Azo compounds have diverse structures and unique properties therefor it used in various fields, such as pharmaceuticals, antifungal activity, food additives and anti-corrosion [6-9]. In addition, azo-compounds were used as acid-base indicators which are undergo change in color due to the conversion in their internal structure when the concentration of hydronium ions change [10]. Acid-base indicators are used in titrations to determine the endpoint of acid-base reactions, and used to measure pH values [11]. The quinonoid theory was explained the color change of indicators depending on the structural change of the indicator, this theorem defines the indicator as tautomer that can occur in a compounds benzenoid and quinonoid forms, the indicators light colour corresponds to the benzenoid form and their dark color corresponds to the quinonoid form, both of which rely on the medium's pH.



Benzenoid form Quinonoid form

One of the forms found in alkaline media while other is in acidic media as a result, the medium changes during the titration from alkaline to acidic or vice versa, causing the loss or gain of a proton [12],[13] Also, the color fastness of the chemical indicator are affected by light and temperature [14].

2. METHOD

Chemicals were purchase from Merck, BDH, Sigma Aldrich, and Fluka. Melting points were determined using SMP10 tool. The UV-Vis absorption spectra were measured using Jenway 6800 Double-Beam Spectrophotometer. Infrared spectra were recorded using ATR method using a Bruker-Tensor 27 spectrometer. The pH data were measured using a pH meter EZDO PL-700AL capable of measuring pH, mV, ION, °F, and °C. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer at University of Basra, the solvent used was DMSO-d_6.

2.1. Synthesis of Azo compounds:

Azo compounds were synthesized by adding (4 mmol) of amine to solution of 5 mL distilled water and 5 mL of hydrochloric acid at 0-5 °C in round bottom flask 100 mL, after that (0.3g, 4 mmol in 10 mL of distilled water) of sodium nitrite was added dropwise and the mixture left for 30 minutes with stirring, followed by adding solution of phenol (4 mmol) dissolved in 10mL of a 25% NaOH at 0-5 °C. pH of solution was adjusted to pH=7. The product was washing by water and purified by column chromatography [15].

2.2. Study of properties of azo compounds as Acid-Base indicators:

A study was performed by using, 6.2 x 10^{-3} M concentration of prepared compounds in different buffer solutions ranged between (pH 1-14). Absorption spectra of all compounds were measured between 200 and 900 nm by using a 1 cm quartz cell. The blank solutions were synthesized from buffer solution and solvent. The ionization and protonation constants were calculated using the half-height technique [16].

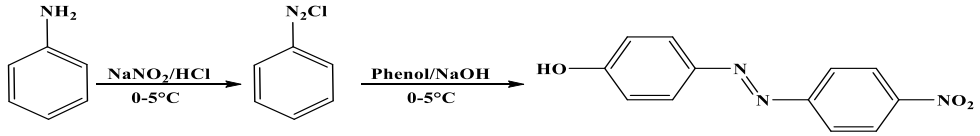
2.3. Indicator test:

The indicator test was performed by titrating of HCl (0.1 M) against NaOH (0.1 M).

3. RESULTS AND DISCUSSION

3.1. Synthesis of the compounds (H1-H5)

Azo compounds were synthesized by coupling of phenol(4-hydroxybenzoic acid, 2-((4-hydroxybenzylidene)amino)-4-methylphenol,(E)-4-((naphthalen-1-ylimino)methyl)phenol, 3,5-dihydroxybenzoic acid)and amine(benzidine , 4-nitroaniline, 2-amino-4-methylphenol, naphthalen-1-amine) in distilled water and hydrochloric acid as a solvent at 0-5 °C. as shown in scheme 1. Some physical and chemical properties of the synthesized H1-H5 compounds were shown in Table (1).



anilines = benzidine , 4-nitroaniline, 2-amino-4-methylphenol, naphthalen-1-amine

phenols = 4-hydroxybenzoic acid, 2-((4-hydroxybenzylidene)amino)-4-methylphenol,(E)-4-((naphthalen-1-ylimino)methyl)phenol, 3,5-dihydroxybenzoic acid

Scheme 1. Synthetic route of (H1-H5) compounds

Table 1. The physical properties, chemical of the prepared (H1-H5) compounds.

Comp.	M.F.	M.P °C	Color	Yield%	R_f
H_1	$C_{26}H_{18}N_4O_8$	211-213	colorless	61	0.589
H_2	$C_{26}H_{18}N_4O_6$	>300	Yellow	57	0.460
H_3	$C_{17}H_{12}N_2O_4$	245-247	Brown	70	0.443
H_4	$C_{20}H_{16}N_4O_4$	207-209	Yellow	53	0.561
H_5	$C_{24}H_{19}N_3O_2$	187-189	light brown	50	0.732

3.2 Characterization

3.2.1. FTIR of (H1-H5):

The FTIR spectra of azo compounds (H1-H5) indicated the disappear of stretching vibration for the NH2 group and the appearance of absorption band for azo groups (N=N) within range of (1397--1438) cm^{-1}. The absorption band for hydroxyl Carboxylic groups was found at a range (2480-3400) cm^{-1} for H1-H3, whiles the absorption band for hydroxyl groups for H4 and H5 appeared at 3427 cm^{-1} and 3414cm^{-1} for H5 . The spectra exhibited aromatic C-H absorption bands at the range (3027-3105) cm^{-1}. Additionally, medium absorption bands appeared at range (1590-1593) cm^{-1} for attribution of C=N group for H4 and H5 compounds. [17]. Data were shown in table 2 and figure 1.

Table 2. FTIR data (cm^{-1}) for synthesized H1-H5 compounds

Comp.	ν C-H $_{ar}$	ν C-H $_{alph.}$	ν N=N	ν O-H	ν C=N	ν C=O	ν NO_2
H1	3027	-	1397	2602-3400	-	1712	-
H2	3063	-	1438	2550-3380	-	1753	-
H3	3062	-	1402	2480-3350	-	1694	-
H4	3105	2901-2986	1403	3427	1590	-	1375-1521
H5	3042	2912-2988	1408	3414	1593	-	-

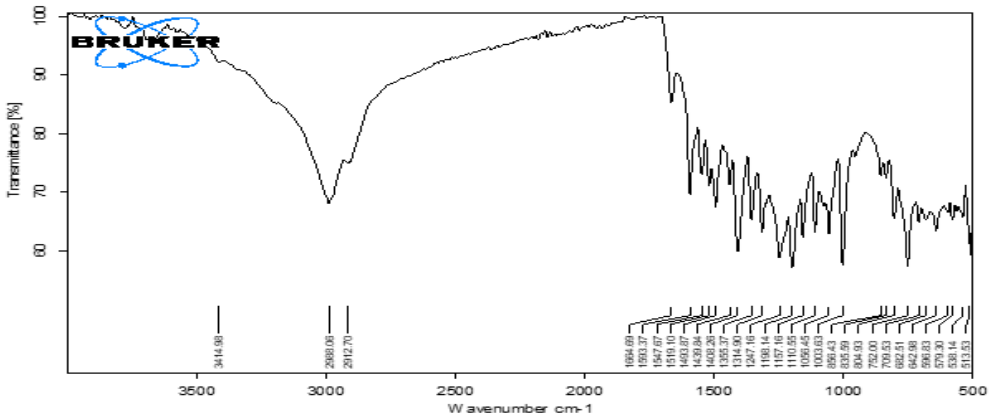


Figure 1: FT-IR spectrum for compound H_5

3.2.2. Characterization of H_1-H_5 compounds using ^{1}H-NMR and ^{13}C-NMR

The 1H-NMR spectra of compounds H1 – H3 reveal a singlet signal within the range (12.47-13.24) ppm attributable to protons of (COOH) group. A singlet signal was observed at (10.25-11.35) ppm due to the proton of hydroxyl group. Aromatic protons were observed at (6.20-8.77) ppm. Figure 2 shows the 1H-NMR spectrum for compound H3. In addition, a distinct singlet signal was observed in the (8.44-8.45) ppm for attributing a proton of azomethine group (H-C=N), in compounds H4 and H5[20]. The structures of (H1-H5) compounds were confirmed by analysis of 13C-NMR spectrum. These spectra

of aromatic carbon signals were appeared at (104.12-167.23) ppm. Signals in the (152.00-161.16) ppm were attributed to (HC=N) in compounds H4 and H5, and signals during (168.58-177.93) ppm corresponding to the carbon of the carbonyl carboxylation group. Data were given in **table 3**. The 13C-NMR spectrum for the compound H5 was shown in **Figure 3**

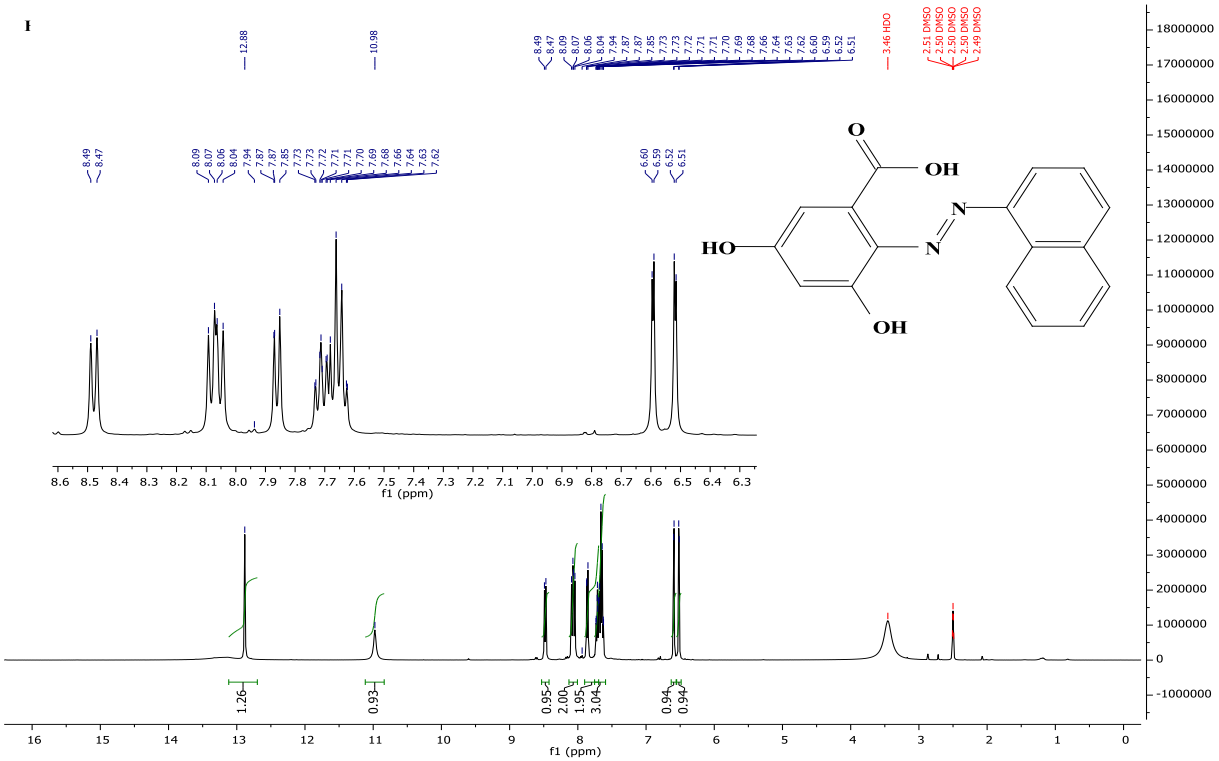


Figure 2. ^{1}H-NMR spectrum of compound H_3.

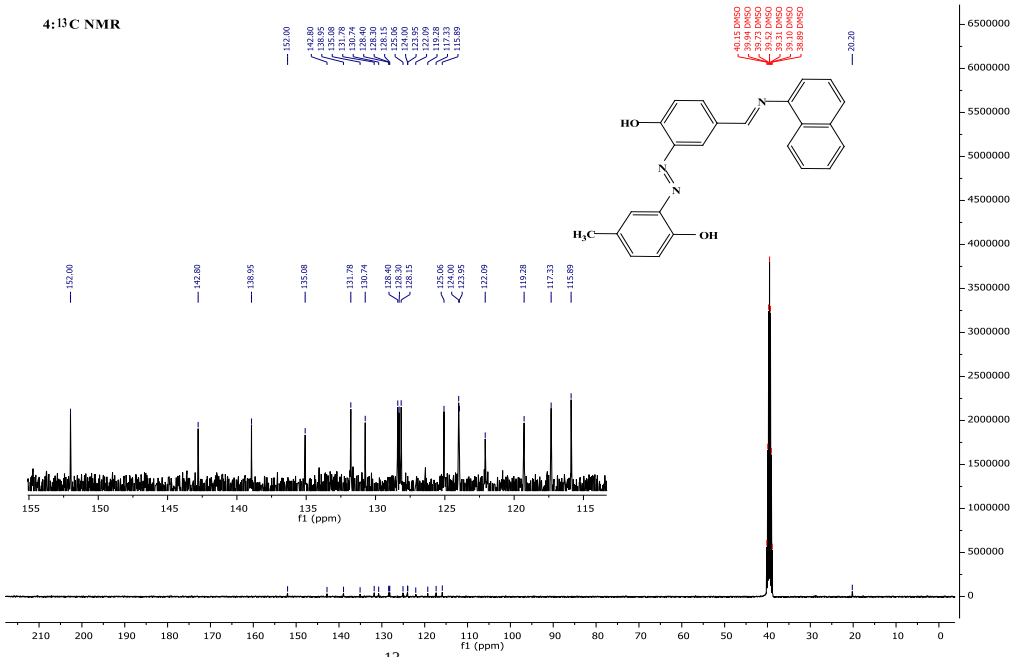
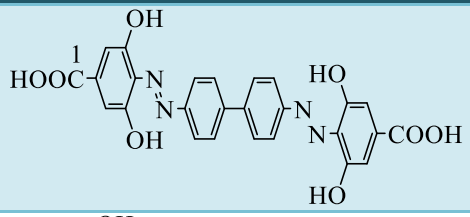
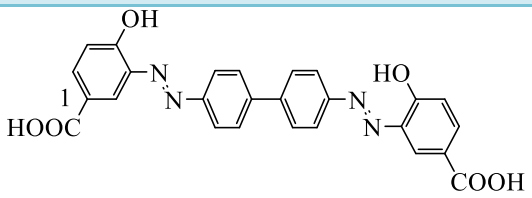
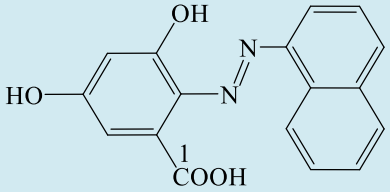
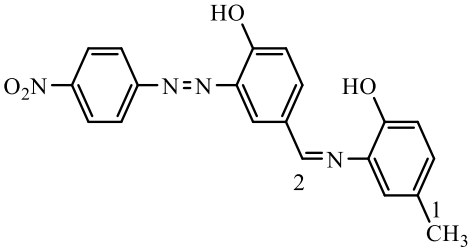
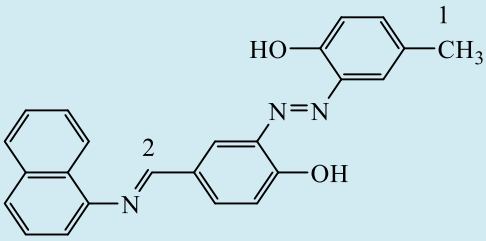


Figure 3. ^{13}C-NMR spectrum of compound H_5

Table 3. ^{1}H-NMR and ^{13}C-NMR chemical shift (ppm) for synthesized H_1-H_5 compounds.

Comp.	Structure	^{1}H-NMR	^{13}C-NMR
H1		6.44-7.99 (m,12H, Ar-H) 11.04(s,1H, OH) 13.24 (s,1H, COOH)	104.22-162.71 (C-H $_{arom}$.) 168.58 (C_1)
H2		6.82-8.14 (m,14H, Ar-H) 10.32(s,1H, OH) 12.47 (s,1H, COOH)	115.18-167.23 (C-H $_{arom}$.) 177.93 (C_1)
H3		6.51-8.49(m,9H, Ar-H) 10.98 (s,1H,OH) 12.88 (s,1H, COOH)	104.12-162.69 (C-H $_{arom}$.) 169.03 (C_1)
H4		6.20-8.77 (m,10H, Ar-H) 8.45 (s,1H, HC=N) 10.63-11.35 (s,1H, OH) 2.23 (s,3H, alph-H)	114.31-158.97 (C-H $_{arom}$.) 20.29 (C_1) 161.16 (C_2)
H5		7.06-7.94 (m,14H, Ar-H) 8.44 (s,1H, HC=N) 10.25 (s,1H, OH) 2.29 (s,3H, alph-H)	115.99-142.80 (C-H $_{arom}$.) 20.20 (C_1) 152.00 (C)

3.3. Acid-Base Properties:

The absorbance of dilute solutions of synthesized compounds (H1-H5) was measured within (200-900 nm). The maximum wavelength was found (380-390 nm) with pH 1-7 because attribution of the cationic formula (protonated form of H2 and H4 compounds), while another peak appearance within (470-530 nm) with pH 8-13 as to attribution of the anionic formula (deprotonated form of H2 and H4 compounds). But the compound H5 gave the maximum wavelength at 560 nm with pH 1-7, which attributable to the absorption of the cationic formula (protonated form of compounds), while another peak was found at 505 nm with pH 8-13 for attributing the absorption of the anionic formula (deprotonated form of compounds) [18]. The compounds H2, H4, and H5 were shown sharp color changes when moving from acidic condition to the basic condition or vice versa. These compounds were also able to determine the end point of the reaction with high accuracy, except compounds H1, H3 which showed no color change with the change the acid or base condition of solution. **Figure 4**. shown absorption spectra of the compounds H2, H4 and H5 in different pH solutions.

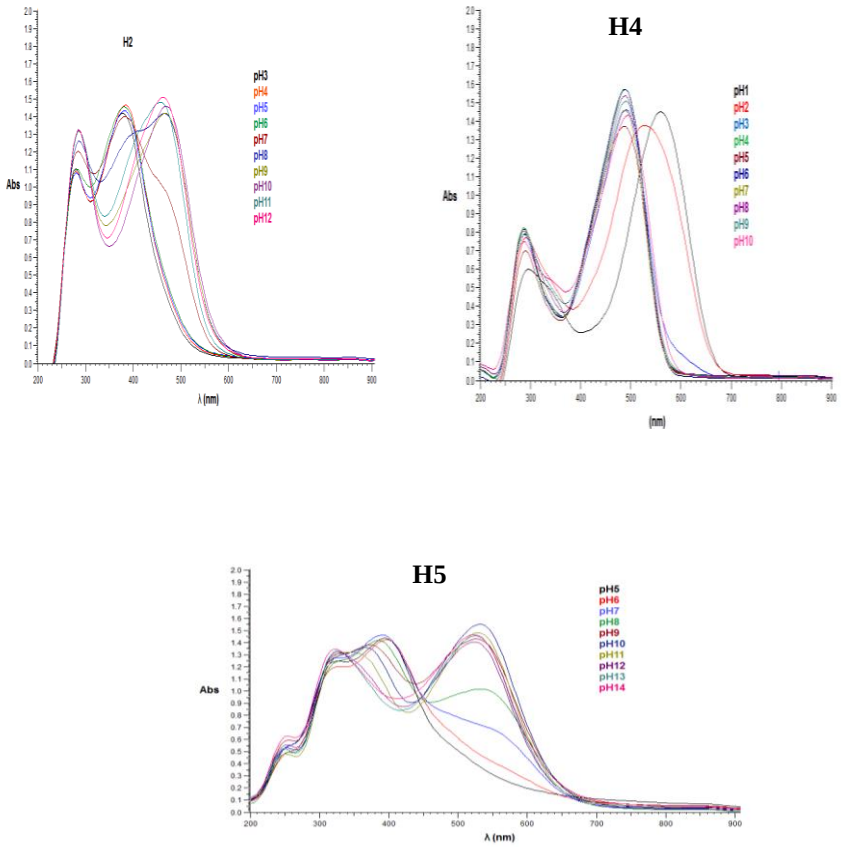


Figure 4. The visible absorption spectra of the compounds H2, H4 and H5 in different pH solutions

The half-height curve approach was used to calculate the ionization and protonation constants of H1-H5 compounds by collecting the absorbance of synthesized compounds at' a maximum wavelength with varying pH 1-14, after that, plotting the absorbance against pH as shown in **Figure 5**. Finally, the pK values were calculated by using equations 1 and 2. All results were put in Table 4.

$$pK = pH \text{ (at } A_{1/2}) \quad (1)$$

$$A_{1/2} = (Amax + Amin)/\,2 \quad (2)$$

AL= limiting absorption, Am= minimum absorption, Amax=maximum absorption [19].

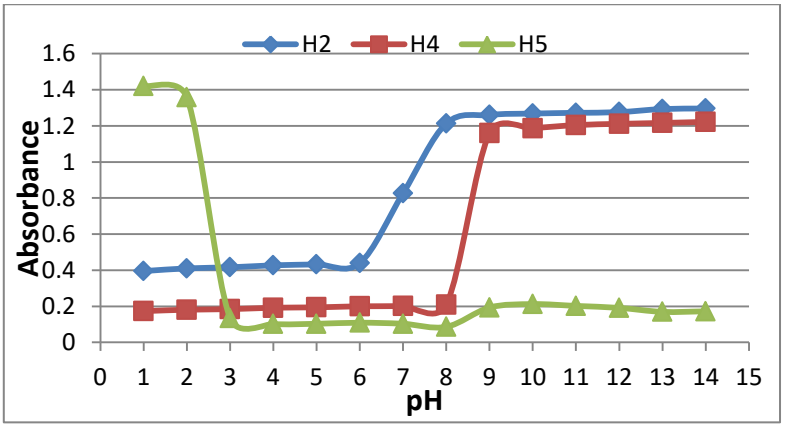


Figure 5. absorption curve of the compound H_2, H_4, H_5 at the maximum.

Table. 4: Protonation and Ionization constants and indicator range of H1- H5 compound.

No.	Am	AL	$A_{1/2}$	Pka	pH range
H2	0.395	1.296	0.8455	7.1	6.1 – 8.1
H4	0.173	1.222	0.697	8.6	7.6-9.6
H5	0.086	1.421	0.753	2.5	1.5-3.5

Am: minimum, AL: limiting absorption

The color change of the compounds H2 , H4 , H5 were determined by using acid solution and base solution. Figure 6. Furthermore, the test color change accuracy of the synthesized chemical toward a change in pH was done by titration 0.1M of HCl versus 0.1M of NaOH by comparation with phenolphthalein as reference indictor [20]. The obtining results were shown in Table 5.

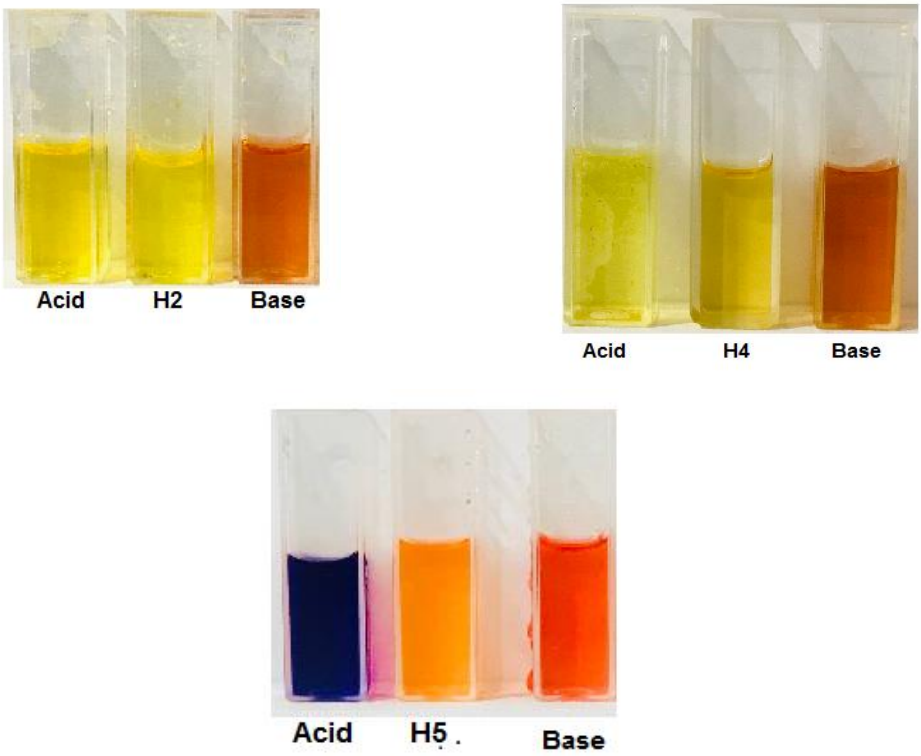


Figure 6. Colors of H_2, H4, H_5 compound in acidic, neutral and basic medium.

Table 5. Titration results using HCl (0.1M) against NaOH (0.1M)**.**

Comp.	Volume of NaOH (ml)	Mean volume of HCl (ml)	Color in acid	Color in base
H_2	5	4.2	Light yellow	Red
H_4	5	4.1	Yellow	Red
H_5	5	4.3	Light orange	Maroon
Ph.ph	5	4.26	Colorless	Dark pink

Ph.ph= Phenolphthalein

4. CONCLUSION

New Azo compounds (H1-H5) were synthesized, purified and characterized by using FT-IR,1H-NMR and 13C-NMR. The properties of acid-base indicator for compounds (H1-H5) were investigated. Ionization

and protonation constants at different pH values were calculated, and the color change was determined with pH changeable. The electronic spectra of H2, H4 compounds in different pH (1-14) solutions, exhibit a maximum absorption wavelength (380-390 nm) in acidic solutions, while (470-530 nm) in basic solution. But the compound H5 gave the maximum wavelength at 560 nm in acidic solutions, while in basic solution the peak appeared at 505 nm. The response accuracy of synthesized compounds with pH changeable was evaluated by titrating of 0.1M of HCl against 0.1M of NaOH in comparison with phenolphthalein as reference indicator. The compounds H2, H4 and H5 were shown accuracy similar to phenolphthalein. Contrasting, the compounds H1 and H3 were not shown any response to the change pH. All results indicate the possibility of using H2, H4 and H5 compounds as acid-base indicators.

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BIOGRAPHIES OF AUTHORS

Hussain Saleem Jabbar is a Master's student at the College of Education for Pure Sciences at the University of Anbar. He obtained a bachelor's degree in chemistry from College of Education for Pure Sciences (Ibn Al-Haitham) at the University of Baghdad. 2020. He can be contacted at email: hus22u4001@uoanbar.edu.iq

Dr. Ahmed Dhary Saleh is an associate professor at the College of Education for Pure Sciences at the University of Anbar. He obtained a bachelor's degree in chemistry from University of Anbar and a master's degree from the University of Baghdad, College of sciences. He obtained a doctorate from the Bangor University at UK. He can be contacted at email : eps.ahmeddhari.saleh@uoanbar.edu.iq

Dr. Abdullah Hussein Kshash is an professor at the College of Education for Pure Sciences at the University of Anbar. He obtained a bachelor's and master's degree in chemistry from University of Anbar He obtained a doctorate from the Tikrit University . He can be contacted at email : drabdullah@uoanbar.edu.iq or drabdullahkshash@gmail.com