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Synthesis and Characterization of Novel Nitroaniline-Based Azo Compounds as Acid-Base Indicators

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ABSTRACT

Nine new azo compounds (Y1-Y9) were synthesized in this work by diazotizing ortho-, meta-, and para-nitroaniline derivatives and then coupling them with either 2,7-dihydroxynaphthalene, 8-hydroxyquinoline, or α-naphthol. The reactions were carried out in an ice-bath at 0-5 °C under strictly regulated basic conditions. Using DMSO-d_6 as the solvent, Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy (^{1}H and ^{13}C) were used to characterize the structures of all produced compounds definitively. UV-Vis spectral shifts in DMSO solutions across a wide pH range (1-14) were examined to measure their effectiveness as acid-base indicators. Both protonation and deprotonation caused noticeable bathochromic shifts in the compounds. The cationic form (pH 1-7) exhibited absorption maxima (λmax) at 391-483 nm, whereas the anionic form (pH 8-14) absorbed at 448-587 nm. These sharp and reversible color changes, which correspond to pH ranges of 7-10, demonstrate the effectiveness of the synthesized azo compounds as effective acid-base indicators in analytical chemistry, offering potential alternatives to conventional standards.

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1. INTRODUCTION

Azo compounds, characterized by the presence of the iconic chromophoric azo group (–N=N–), represent one of the most significant and extensively studied classes of synthetic dyes, accounting for over 70% of all commercial dyes [1]. Their prominence stems from versatile synthesis, remarkable colorfastness, and a broad spectrum of vibrant colors ranging from yellow to deep blue, dictated by an extensive π-conjugation system and the nature of substituents on the aromatic rings [2, 3]. Beyond their traditional role in coloring textiles, leather, and plastics, azo compounds find applications in diverse fields, including organic photonics, molecular sensors, and biomedical studies [4].The color properties of azo dyes can be finely tuned by introducing auxochromic groups (e.g., –OH, –NH_2, –COOH), which influence the electron density and, consequently, the compound's absorption characteristics and solubility [5]. Additionally, their use as acid-base indicators demonstrates their structural adaptability [6]. These indicators are weak organic acids or bases that exhibit a distinct and reversible color change due to protonation or deprotonation events, which alter their electronic structure and hence their absorption spectra in the visible region [7]. The dissociation constant (pKa) of the indicator dictates its effective pH transition range, which is crucial for determining the endpoint in acid-base titrations [8]. While classical indicators like phenolphthalein and methyl orange are widely used, they possess fixed and sometimes limited pH ranges. There is continuous research interest in developing novel azo-based indicators with tailored pKa values, improved solubility in various solvents, and more distinct color changes to cover different titration ranges and modern applications [9, 10]. Furthermore, studying the relationship between the structure of azo compounds (e.g., the position of the nitro group – ortho, meta, or para) and their acid-base sensing properties provides valuable insights into their spectroscopic behavior [11]. Motivated by this, the objective of the present study is to synthesize and characterize a new series of azo compounds (Y1–Y9) derived from nitroaniline isomers coupled with naphthol and quinoline derivatives.

The core aim is to systematically investigate their spectroscopic properties and evaluate their potential as novel acid-base indicators by determining their ionization constants and precise pH transition ranges using UV-Vis spectroscopy, thereby identifying their suitability for analytical applications [12]. The main goal is to use UV-Vis spectroscopy to determine their ionization constants and precise pH transition ranges in order to systematically examine their spectroscopic properties and assess their potential as novel acid-base indicators and determine their suitability for analytical applications [13].

2. Experimental Methodology

2.1 Materials and Instrumentation.

All chemicals and solvents,including nitroaniline isomers, 8-hydroxyquinoline, α-naphthol, and 2,7-dihydroxynaphthalene, were of analytical reagent grade (purity ≥ 99%) and were purchased from Merck, Sigma-Aldrich, and CDH. They were used without further purification. Melting points were determined in open capillary tubes using an SMP10 melting point apparatus and are uncorrected. Fourier Transform Infrared (FT-IR) spectra were recorded using the Attenuated Total Reflectance (ATR) technique on a Bruker Tensor 27 spectrometer. UV-Visible absorption spectra were measured using a Jenway 6800 double-beam spectrophotometer equipped with 1 cm matched quartz cells. The pH measurements were carried out using an EZDO PL-700AL pH meter. Nuclear Magnetic Resonance (NMR) spectra (^{1}H and ^{13}C) were recorded on a Bruker Avance spectrometer operating at 400 MHz at the University of Basrah. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as the solvent for all NMR measurements, and chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard.

2.2 Synthesis of Azo Compounds

Nitroaniline derivative (3.6 mmol) was dissolved in a mixture of distilled water (10 mL) and concentrated hydrochloric acid (5 mL) in a 100 mL round-bottom flask. The solution was cooled and maintained at 0–5 °C in an ice-bath under constant stirring. A pre-cooled aqueous solution of sodium nitrite (0.25 g, 3.6 mmol in 10 mL H_2O) was added dropwise to the reaction mixture over 15 minutes, ensuring the temperature did not exceed 5 °C. The resulting diazonium salt solution was stirred for an additional 60 minutes at this low temperature to complete the diazotization reaction. In a separate beaker, the coupling component (naphthol or quinoline derivative, 3.6 mmol) was dissolved in a 25% aqueous sodium hydroxide solution (10 mL) and cooled to 0–5 °C. The freshly prepared diazonium salt solution was then added gradually to the cold alkaline solution of the coupling component with vigorous stirring. The reaction mixture was stirred for a further 30 minutes in the ice bath to facilitate azo coupling. The pH of the mixture was then carefully adjusted to approximately 7 using dilute HCl. The precipitated crude azo dye was collected by filtration, washed thoroughly with cold distilled water to remove inorganic salts, and recrystallized from hot ethanol to obtain the pure product [13]. All synthetic procedures were performed in triplicate to ensure reproducibility, and the reported yields represent the average of these runs.

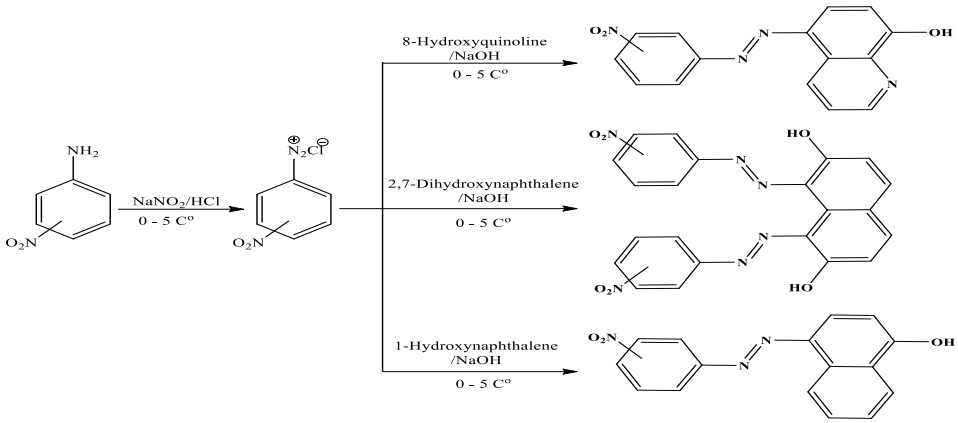
2.3 Study of Acid-Base Indicator Properties

Buffer solutions covering a broad pH range(1–14) were prepared using standard methods. A stock solution of each synthesized azo compound (Y1–Y9) was prepared in dimethyl sulfoxide (DMSO) at a concentration of 6.79×10^{-4} M. An aliquot of the stock solution was added to each buffer solution to maintain a consistent concentration for spectral measurements. The UV-Vis absorption spectra of these solutions were recorded immediately after preparation in the range of 200–800 nm using a 1 cm quartz cell. The corresponding buffer solution containing an equal volume of DMSO was used as a blank for baseline correction [14]. The measurements for each compound at each pH were repeated three times to confirm the reproducibility of the spectral shifts.

3. RESULTS AND DISCUSSION

3.1. Synthesis of the Compounds (Y1-Y9)

Naphthol, quinoline, and nitro-substituted aniline derivatives were utilised for the synthesis of azo compounds in a two-step process. The first step involved the preparation of diazonium salt via diazotization of the aromatic amine with sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl) while maintaining a temperature between 0–5 °C. The second step involved coupling the diazonium salt with naphthol and quinoline derivatives dissolved in sodium hydroxide solution. The reaction mixture was stirred for at least 30 minutes, and the pH was subsequently adjusted to 7. The synthetic pathway for azo compounds is illustrated in Scheme 1.



SCHEME 1. Synthetic route of (Y1-Y9) compounds

(E)-5-((4-nitrophenyl)diazenyl)quinolin-8-ol Y1

Following the general procedure, p-Nitroaniline (0.5 gm, 3.6 mmol) and 8-Hydroxyquinoline (0.5 gm, 3.6 mmol) were reacted to obtain Y1, M.F ($C_{15}H_{10}N_4O_3$), (0.9 gm, 84.9 %), M.P (239-242 °C), R_f 0.3(Methanol:Benzene 3:7), as Reddish-Orange powder. **FT-IR** (cm^{-1}, ν) 3246 (O-H), 3046-3085 (C-H ar.), 1468-1628 (C=C ar.), 1468 (N=N), 1333-1548 (NO_2). **^{1}H-NMR** (400 MHz, DMSO-d_6 , δ= ppm) δ 9.07 (s, 1H), 8.58 (s, 1H), 8.39 (s, 1H), 8.20 – 8.08 (m, 2H), 8.00 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.50 (s, 1H), 7.40 – 7.33 (m, 1H). **^{13}C-NMR** (101 MHz, DMSO-d_6, δ= ppm) δ 165.63, 154.03, 150.10, 134.31, 127.88, 125.66, 124.70, 113.56, 112.85, 110.81.

(E)-5-((2-nitrophenyl)diazenyl)quinolin-8-ol Y2

Following the general procedure, o-Nitroaniline (0.5 gm, 3.6 mmol) and 8-Hydroxyquinoline (0.5 gm, 3.6 mmol) were reacted to obtain Y2, M.F ($C_{15}H_{10}N_4O_3$), (0.76 mg, 71.7%), M.P (216-219 °C), R_f 0.2(Methanol:Benzene 3:7) , as Brown powder. **FT-IR** (cm^{-1}, ν) 3215 (O-H), 3059 (C-H ar.), 1476-1602 (C=C ar.), 1476 (N=N), 1340-1510 (NO_2). **^{1}H-NMR** (400 MHz, DMSO-d_6 , δ= ppm) δ 9.11 (s, 1H), 8.94 (d, *J* = 4.3 Hz, 1H), 8.47 (d, *J* = 7.7 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 3.1 Hz, 1H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 9.3 Hz, 1H). **^{13}C-NMR** (101 MHz, DMSO-d_6 , δ= ppm) δ 157.24, 147.97, 147.40, 144.75, 140.67, 138.75, 133.96, 131.75, 128.57, 124.58, 124.39, 119.85, 117.87, 114.33.

(E)-5-((3-nitrophenyl)diazenyl)quinolin-8-ol Y3

Following the general procedure , m-Nitroaniline (0.5 gm, 3.6 mmol) and 8-Hydroxyquinoline (0.5 gm, 3.6 mmol) were reacted to obtain Y3, M.F ($C_{15}H_{10}N_4O_3$), (0.92 mg, 86.8%), M.P (227-230 °C), R_f 0.4(Methanol:Benzene 3:7), as Dark Golden Brown powder. **FT-IR** (cm^{-1},ν) 3275 (O-H), 3090 (C-H ar.), 1447-1611 (C=C ar.), 1447 (N=N), 1346-1528 (NO_2). **^{1}H-NMR** (400 MHz, DMSO-d_6 , δ= ppm) δ 9.03 (s, 1H), 8.75 (s, 1H), 8.72 (d, *J* = 8.6 Hz, 1H), 8.56 (s, 1H), 8.37 (d, *J* = 8.1 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 8.09 (t, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 11.6 Hz, 1H), 7.33 (d, *J* = 11.5 Hz, 1H), 7.00 (s, 1H). **^{13}C-NMR** (101 MHz, DMSO-d_6 , δ= ppm) δ 159.78, 149.15, 148.88, 138.55, 136.74, 129.69, 125.16, 124.30, 119.17, 116.69.

1,8-bis((E)-(4-nitrophenyl) diazenyl) naphthalene-2,7-diol Y4

Following the general procedure, p-Nitroaniline (0.5 gm, 3.6 mmol) and 2,7-Dihydroxynaphthalen (0.29 gm, 1.8 mmol) were reacted to obtain Y4, M.F ($C_{22}H_{14}N_6O_6$), (0.73 mg, 88.5%), M.P (256-259 °C), R_f 0.34(Methanol:Benzene 3:7), as Dark Brown to Blackish powder.

FT-IR (cm^{-1},ν) 3392 (O-H), 3071 (C-H ar.), 1603-1481 (C=C ar.), 1481 (N=N), 1318-1571 (NO_2). **^{1}H-NMR** (400 MHz, DMSO-d_6, δ= ppm) δ 10.24 (s, 1H), 8.33 (d, *J* = 9.1 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 9.4 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H). **^{13}C-NMR** (101 MHz, DMSO-d_6 , δ= ppm) δ 159.91, 148.55, 144.46, 131.97, 126.87, 126.14, 122.59,121.19, 117.40, 116.72, 112.83.

1,8-bis((E)-(2-nitrophenyl) diazenyl)naphthalene-2,7-diol Y5

Following the general procedure, o-Nitroaniline (0.5 gm, 3.6 mmol) and 2,7-Dihydroxynaphthalen (0.29 gm, 1.8 mmol) were reacted to obtain Y5, M.F ($C_{22}H_{14}N_6O_6$), (0.68 gm, 82.4%), M.P (244-247 °C), R_f 0.22(Methanol:Benzene 3:7), as Light Black powder. **FT-IR** (cm^{-1} ,ν) 3301 (O-H), 3081 (C-H ar.), 1451-1603 (C=C ar.), 1451 (N=N), 1363-1524 (NO_2). **^{1}H-NMR** (400 MHz, DMF-d_7, δ=ppm) δ 10.63 (s, 1H), 8.76 (d, *J* = 8.5 Hz, 1H), 8.68 (d, *J* = 6.9 Hz, 1H), 8.31 (t, *J* = 7.8 Hz, 1H), 8.21 – 8.11 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 5.9 Hz, 1H). **^{13}C-NMR** (101 MHz, DMF-d_7, δ=ppm) δ 160.34, 145.18, 139.60, 137.16, 136.11, 135.69, 133.08, 132.40, 126.89, 125.05, 123.50, 122.43, 118.13, 117.25, 109.34.

1,8-bis((E)-(3-nitrophenyl)diazenyl)naphthalene-2,7-diol Y6

Following the general procedure, m-Nitroaniline (0.5 gm, 3.6 mmol) and 2,7-Dihydroxynaphthalen (0.29 gm, 1.8 mmol) were reacted to obtain Y6, M.F ($C_{22}H_{14}N_6O_6$), (0.7 mg, 84.8%), M.P (194-197 °C), R_f 0.59(Methanol:Benzene 3:7), as Earthy Red powder. **FT-IR** (cm^{-1} ,ν) 3304 (O-H), 3069-3094 (C-H ar.), 1618-1489 (C=C ar.), 1351-1567 (NO_2). **^{1}H-NMR** (400 MHz, DMSO-d_6 , δ= ppm) δ 10.10 (s, 0H), 8.43 (d, *J* = 8.1 Hz, 1H), 8.27 (dd, *J* = 13.9, 7.9 Hz, 3H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 9.1 Hz, 1H), 7.76 (t, *J* = 5.7 Hz, 1H), 7.62 (d, *J* = 9.3 Hz, 1H), 7.10 (d, *J* = 19.7 Hz, 1H). **^{13}C-NMR** (101 MHz, DMSO-d_6 , δ= ppm) δ 160.36, 149.63, 141.66, 135.46, 134.77, 134.54, 134.34, 132.98, 130.21, 129.56, 128.98, 128.65, 127.81, 127.22, 127.10, 126.87, 126.30, 125.99, 125.81, 124.41, 123.58, 117.69, 114.61.

(E)-4-((4-nitrophenyl)diazenyl)naphthalen-1-ol Y7

Following the general procedure, p-Nitroaniline (0.5 gm, 3.6 mmol) and α-Naphthol (0.5 gm, 3.6 mmol) were reacted to obtain Y7, M.F ($C_{16}H_{11}N_3O_3$), (0.93 mg, 87.7%), M.P (277-280 °C), R_f 0.68(EtOAC:Hexane 2:8), as Deep Red powder. **FT-IR** (cm^{-1} ,ν) 3268 (O-H), 3072 (C-H ar.), 1457-1627 (C=C ar.), 1457 (N=N), 1316-1502 (NO_2). **^{1}H-NMR** (400 MHz, DMSO-d_6 , δ= ppm) δ 10.19 (s, 1H), 8.49 (d, *J* = 29.2 Hz, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 2H), 7.73 (t, *J* = 8.6 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 6.8 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H). **^{13}C-NMR** (101 MHz, DMSO-d_6 , δ= ppm) δ 159.48, 150.57, 149.24, 149.16, 145.94, 142.45, 135.19, 131.58, 131.46, 130.37, 130.17, 124.78, 121.89, 121.16, 121.01, 120.39, 116.51, 112.32, 110.19, 107.43, 106.68.

(E)-4-((2-nitrophenyl)diazenyl)naphthalen-1-ol Y8

Following the general procedure, o-Nitroaniline (0.5 gm, 3.6 mmol) and α-Naphthol (0.5 gm, 3.6 mmol) were reacted to obtain Y8, M.F ($C_{16}H_{11}N_3O_3$), (1 gm, 94.3%), M.P (243-246 °C), R_f 0.6(EtOAC:Hexane 2:8), as Reddish Brown powder. **FT-IR** (cm^{-1} ,ν) 3283 (O-H), 3071 (C-H ar.), 1456-1645 (C=C ar.), 1456 (N=N), 1355-1537 (NO_2). **^{1}H-NMR** (400 MHz, DMF-d_7, δ=ppm) δ 9.23 (s, 1H), 8.83 (d, *J* = 8.5 Hz, 1H), 8.68 (d, *J* = 9.1 Hz, 1H), 8.48 (t, *J* = 9.9 Hz, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.28 (t, *J* = 8.1 Hz, 1H), 8.18 – 8.11 (m, 1H), 8.04 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 9.5 Hz, 1H), 7.23 (d, *J* = 10.3 Hz, 1H). **^{13}C-NMR** (101 MHz, DMF-d_7, δ=ppm) δ 160.71, 155.59, 147.63, 145.61, 140.53, 134.25, 131.37, 129.34, 128.52, 128.24, 126.64, 125.19, 124.88, 123.45, 123.26, 120.53, 118.09, 116.61, 112.98, 109.66.

(E)-4-((3-nitrophenyl)diazenyl)naphthalen-1-ol Y9

Following the general procedure , m-Nitroaniline (0.5 gm, 3.6 mmol) and α-Naphthol (0.5 gm, 3.6 mmol) were reacted to obtain Y9, M.F ($C_{16}H_{11}N_3O_3$), (0.75 mg, 70.8%), M.P (249-251 °C), R_f 0.8(EtOAC:Hexane 2:8), as Reddish Brown powder. **FT-IR** (cm^{-1} ,ν) 3258 (O-H), 3070 (C-H ar.), 1525-1625 (C=C ar.), 1477 (N=N), 1347-1525 (NO_2). **^{1}H-NMR** (400 MHz, DMSO-d_6 , δ= ppm) δ 8.90 (d, *J* = 8.6 Hz, 1H), 8.59 (s, 1H), 8.38 (s, 1H), 8.26 – 8.16 (m, 1H), 7.98 (d, *J* = 11.3 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 16.5 Hz, 1H), 7.38 (d, *J* = 10.0 Hz, 1H), 7.21 (t, *J* = 8.9 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H). **^{13}C-NMR** (101 MHz, DMSO-d_6) δ 159.53, 153.46, 149.16, 139.78, 132.72, 131.38, 131.36, 129.50, 128.79, 127.29, 126.22, 124.76, 124.74, 122.95, 122.93, 122.41, 120.69, 116.85, 115.57, 109.05.

(E)-2,3-dimethyl-4-(phenyldiazenyl)phenol Ystandard

^{1}H-NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 7.81 (d, J = 9.5 Hz, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 1H), 2.62 (s, 3H), 2.16 (s, 3H). **^{13}C-NMR** (101 MHz, DMSO-d_6) δ 159.23, 153.07, 143.79, 140.12, 130.56, 129.77, 123.68, 122.62, 114.06, 113.46, 13.86, 12.12.

3.2. R Characterization

3.2.1. FT-IR of (Y1-Y9)

The successful formation of the target azo compounds(Y1–Y9) was initially corroborated by FT-IR spectroscopy. The definitive disappearance of the characteristic N–H asymmetric and symmetric stretching vibrations of the primary amino group (NH_2) in the range of 3500–3300 cm^{-1}, present in the starting nitroaniline precursors, confirmed their consumption in the diazotization reaction. Subsequently, the spectra exhibited broad absorption bands in the range of 3215–3392 cm^{-1}, which are attributable to the O–H stretching vibrations of the phenolic hydroxyl groups. Characteristic aromatic C–H stretching vibrations were observed between 3046 and 3104 cm^{-1}. The signature absorption band for the azo group (–N=N–) manifested as a strong peak within the range of 1447–1501 cm^{-1}. Furthermore, the asymmetric and symmetric stretching vibrations of the nitro group (–NO_2) were distinctly observed as two strong bands in the ranges of 1316–1571 cm^{-1} and 1510–1571 cm^{-1}, respectively [15]. The FT-IR spectrum of compound Y1 is provided as a representative example in Figure 1.

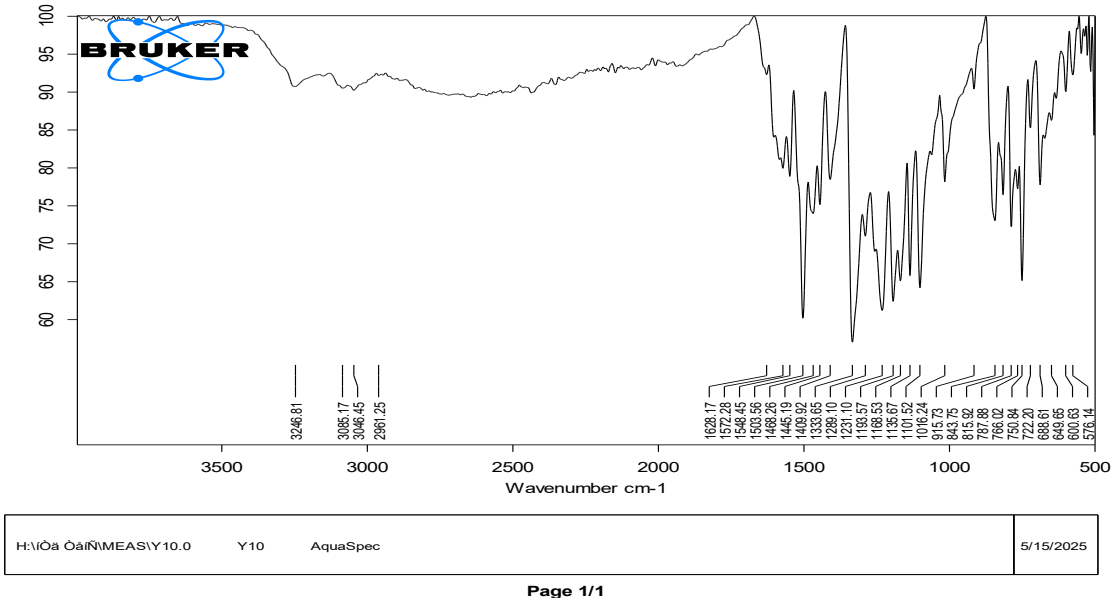


Figure 1. FT-IR spectrum for compound Y1

3.2.2. Nuclear Magnetic Resonance (NMR) Spectroscopy

The molecular structures of the synthesized azo compounds (Y1–Y9) were unambiguously confirmed by comprehensive NMR spectroscopic analysis (^1H and ^{13}C), performed in deuterated dimethyl sulfoxide (DMSO-d_6).

^{1}H-NMR Analysis: The ^{1}H-NMR spectra of all compounds consistently displayed a distinctive downfield-shifted singlet signal in the range of δ 8.90–10.63 ppm. This notable deshielding is a definitive characteristic of the phenolic proton (–OH). Additional signals corresponding to the aromatic protons appeared as a complex multiple in the range of δ 6.68–8.94 ppm. Specifically, the protons located ortho to the strongly electron-withdrawing nitro group were observed as doublets in the lower field region of this range (δ ~8.43–8.94 ppm), due to the combined electron-withdrawing effect and magnetic anisotropy of the –NO_2 group [16]. The ^{1}H-NMR spectrum of compound Y4 is depicted in Figure 2.

^{13}C-NMR Analysis: The ^{13}C-NMR spectra provided further conclusive evidence for the proposed structures. Key signals were observed for the carbon atoms directly bonded to the hydroxyl group (–C–OH), which resonated significantly downfield in the range of δ 150.57–165.63 ppm. The carbon atoms of the nitro groups (–C–NO_2) were identified within the range of δ 140.53–149.16 ppm. The remaining carbon atoms of the aromatic rings generated signals spanning the range of δ 109.05–144.75 ppm. The ^{13}C-NMR spectrum of compound Y7 is presented in Figure 3.

Comparative Analysis with Reference Compound (Ystandard): To further validate the structural assignments and to provide a benchmark for the spectroscopic properties,a known azo compound, (E)-2,3-dimethyl-4-(phenyldiazenyl)phenol (Ystandard), was synthesized and characterized. The ^{1}H-NMR spectrum of Ystandard (Figure 4) exhibited a sharp singlet at δ 10.26 ppm for the phenolic proton, alongside aromatic proton signals in the range of δ 6.84–7.81 ppm and two sharp singlets for the methyl groups at δ 2.16 ppm and δ 2.62 ppm. The ^{13}C-NMR spectrum (Figure 5) confirmed the structure, showing signals for the phenolic carbon at δ 159.23 ppm, aromatic carbons between δ 113.46–153.07 ppm, and the methyl carbons at δ 12.12 ppm and δ 13.86 ppm. The stark contrast between the NMR spectra of Ystandard (lacking a nitro group) and the nitro-containing compounds Y1–Y9 is pivotal. The significant downfield shift observed for the aromatic protons ortho to the nitro group in Y1–Y9 (δ ~8.4–8.9 ppm), compared to their counterparts in Ystandard, is a direct consequence of the powerful electron-withdrawing effect and magnetic anisotropy of the –NO_2 group. This comparative analysis not only confirms the structures of the new compounds but also provides a clear spectroscopic rationale for the effect of substituents on the chemical shifts.

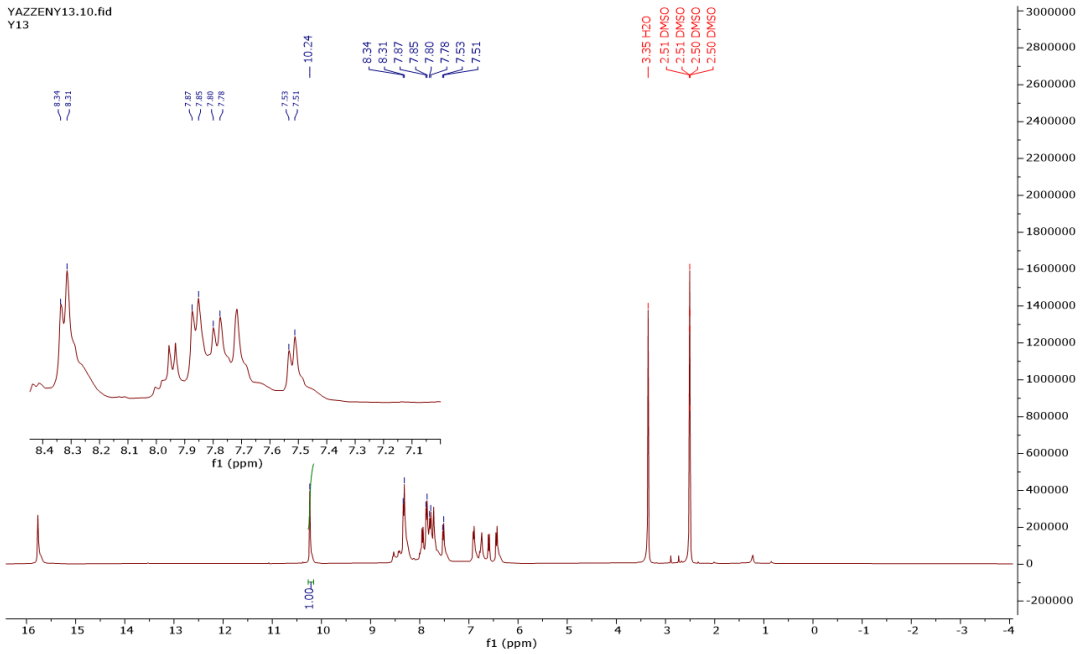


Figure 2. ^{1}H-NMR spectrum of compound Y4

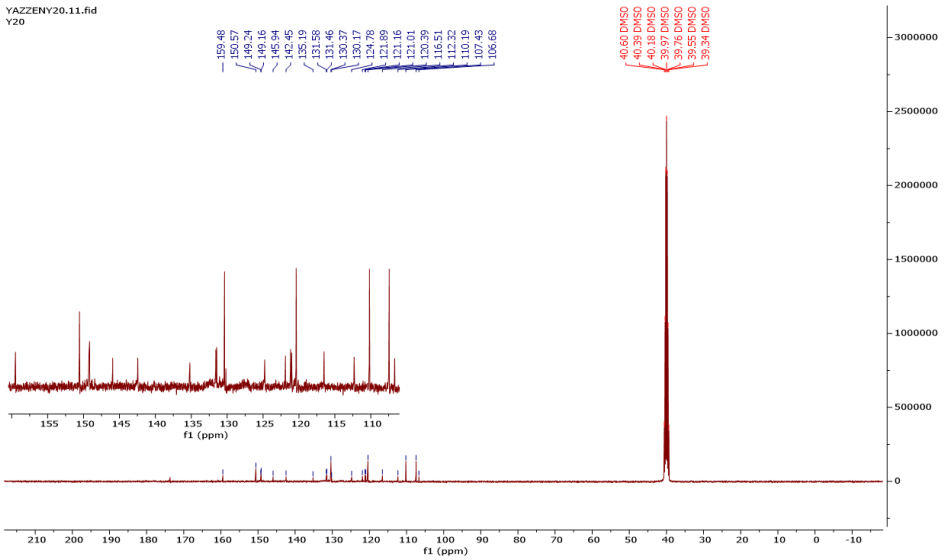


Figure 3. ^{13}C-NMR spectrum of compound Y7

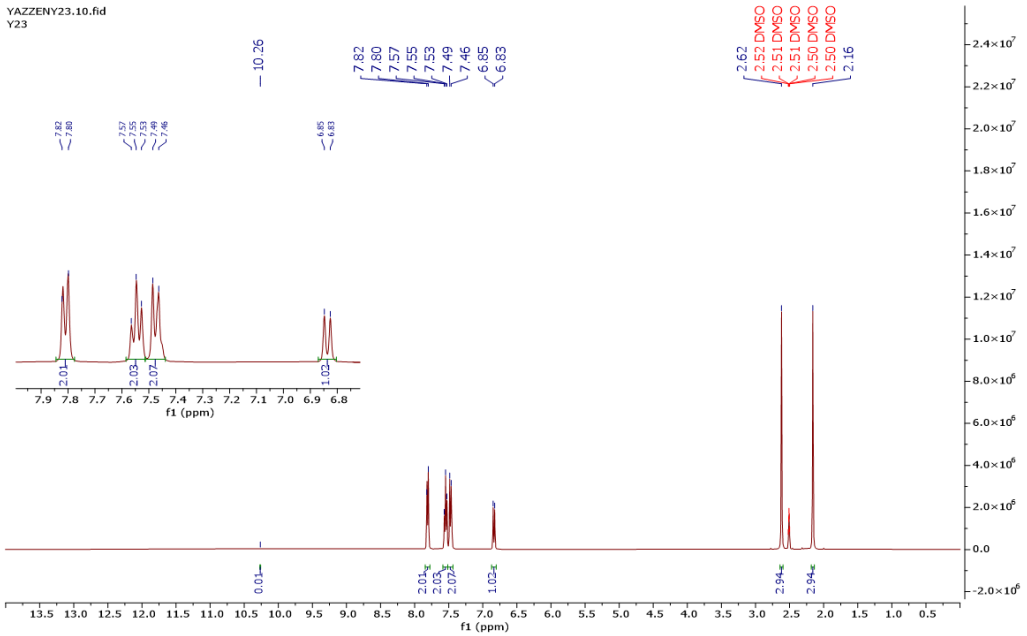


Figure 4. ^{1}H-NMR spectrum of compound Y Standard

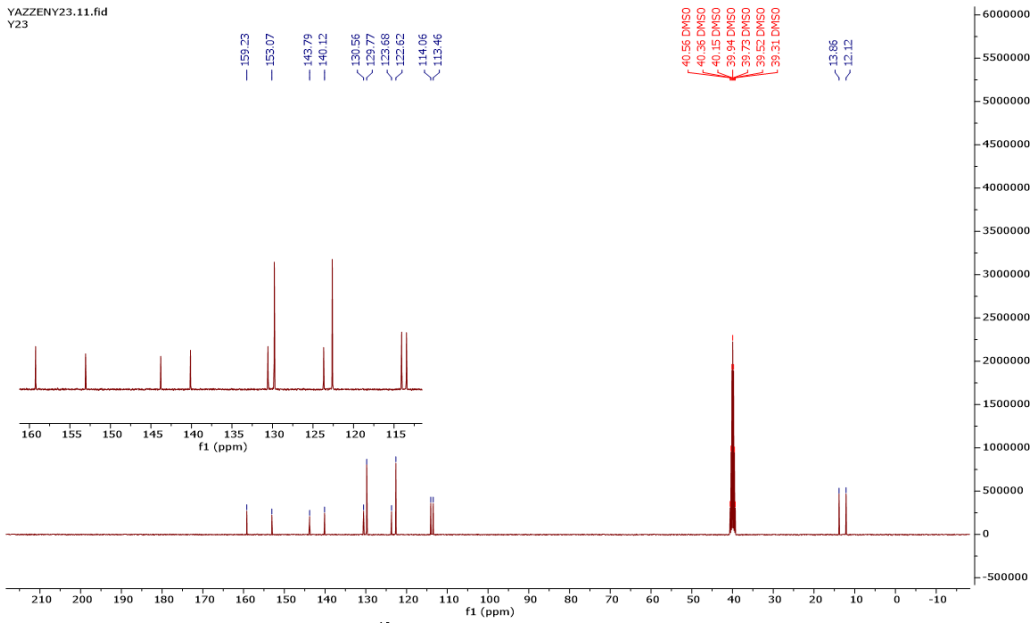
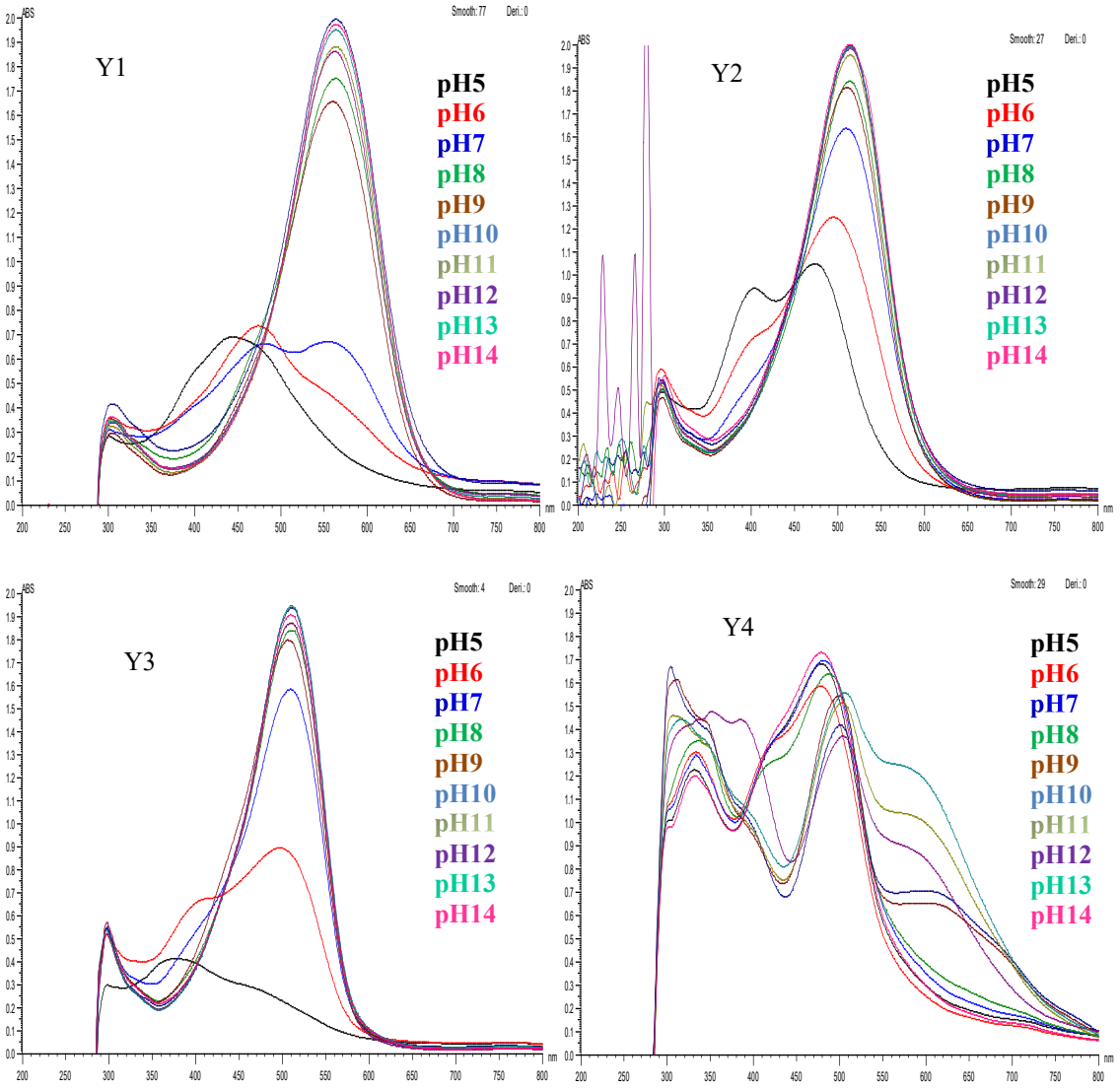


Figure 5. ^{13}C-NMR spectrum of compound Y Standard

3.3. Acid-Base Properties and Indicator Performance

The acid-base sensing capabilities of the synthesized azo compounds(Y1–Y9) were thoroughly investigated by monitoring their UV-Vis spectral behavior in buffer solutions across a wide pH range (1–14). The compounds exhibited remarkable, reversible color changes and spectral shifts upon protonation and deprotonation, confirming their potential as effective acid-base indicators [17]. The spectral changes are attributed to alterations in the molecular electronic structure induced by pH. In highly acidic media (pH 1–7), the compounds predominantly exist in their cationic form (H_2In^+ or HIn), where protonation occurs at the azo group (–N=N–) or the quinoline nitrogen, disrupting the conjugation between the aromatic rings. This resulted in a hypsochromic shift, with absorption maxima (λ~max~) observed in the range of 391–483 nm. As the pH increased to basic conditions (pH 8–14), deprotonation of the phenolic hydroxyl group (–OH) occurred, generating the anionic form (In^-). This extended the conjugation through the azo bridge, resulting in a bathochromic shift and new absorption bands at longer wavelengths between 448–587 nm [18].

The sharp and distinct color transitions allowed for the precise determination of each compound's effective pH transition range, as summarized in Table 1. Most compounds, including Y1, Y2, Y3, Y4, Y6, Y7, and Y9, exhibited a transition range of pH 7–8. Notably, Y5 and Y8 displayed transitions at pH 8–9 and pH 9–10, respectively. This variance is critically influenced by the position and electronic effect of the nitro substituent. The ortho-nitro group in Y2, Y5, and Y8 introduces steric hindrance and intramolecular hydrogen bonding, subtly altering the pK_a compared to their para- and meta- isomers [19]. The performance of these compounds was compared to standard indicators. For instance, Y8 (pH 9–10) closely mirrors the range of phenolphthalein (pH 8.3–10.0). This demonstrates the ability to fine-tune the indicator properties by selecting the appropriate nitroaniline isomer and coupling component. The dramatic visual color change for each compound is vividly demonstrated in Figure 8. This, combined with the well-defined isosbestic points observed in the absorption spectra (Figure 6), indicates a clean, reversible equilibrium between two predominant species. All findings conclusively demonstrate that the synthesized azo compounds Y1–Y9 are highly suitable for use as novel, effective acid-base indicators with tunable ranges.



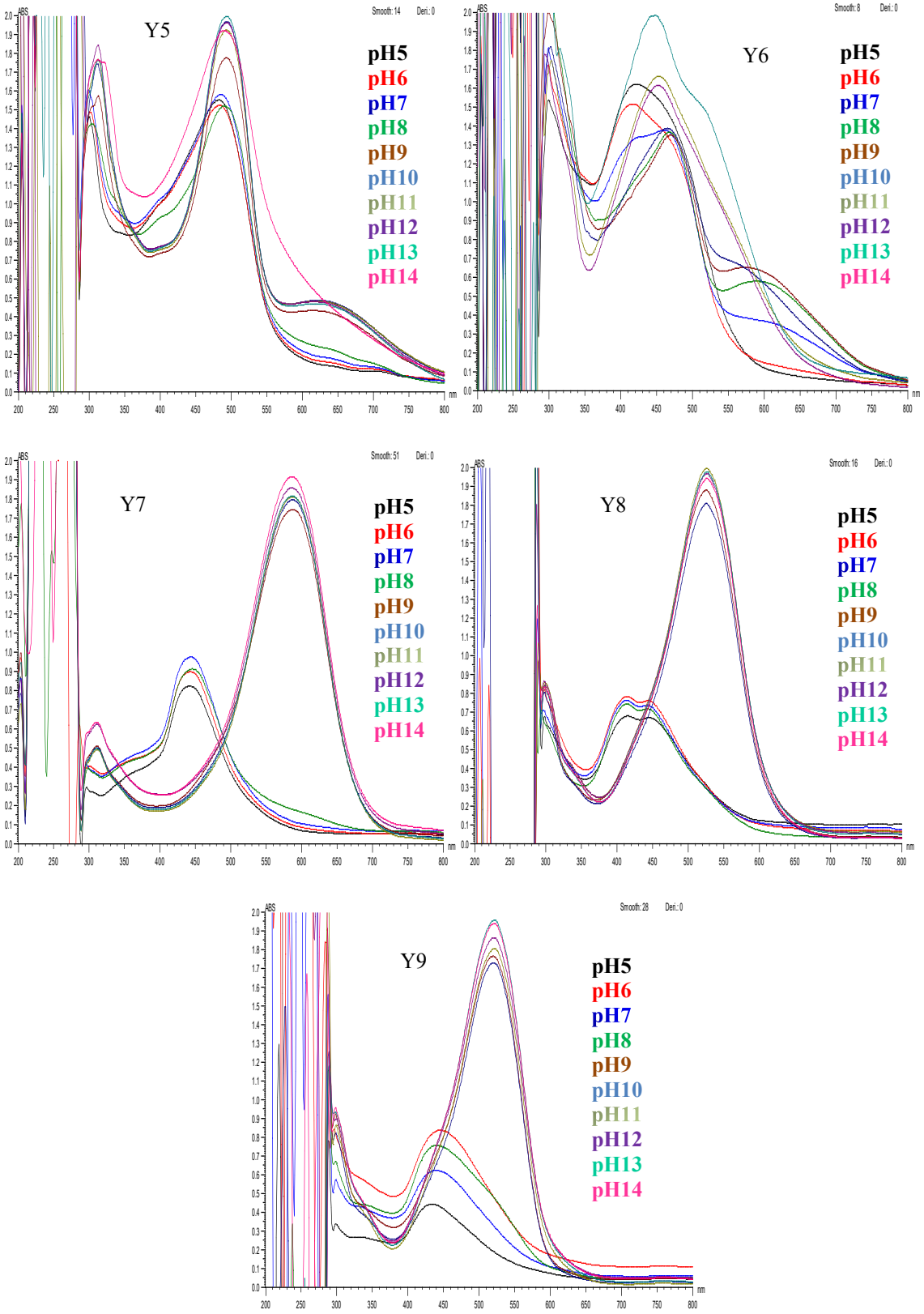


Figure 6. The visible absorption spectra of the compounds Y1-Y9 in different pH solutions

The synthetic compounds spectral responses to various pH levels were used to determine their pH sensing ranges. Each molecule showed a distinct change in absorbance upon protonation or deprotonation, as shown in Figure 7, indicating their potential application as acid-base indicators. Table 1 provides a summary of the exact pH range at which the compounds showed notable color or spectrum variations [19].

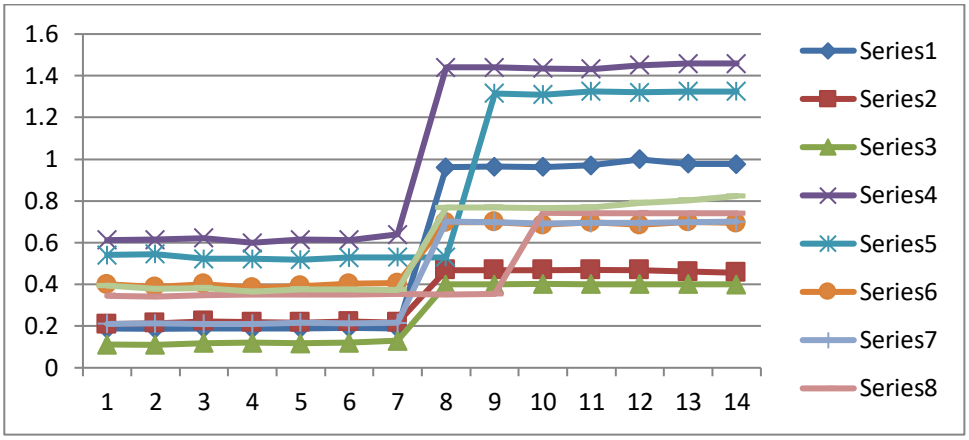
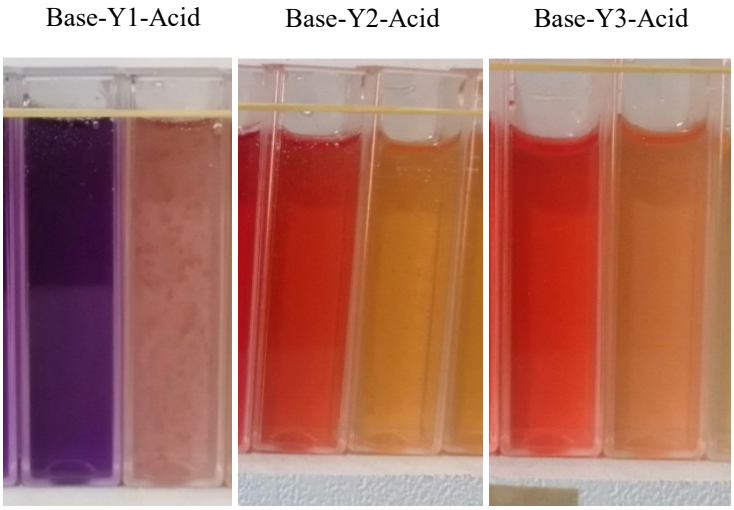


Figure 7. Absorption curve of the compound Y1-Y9

Table 1. The performance of pH range for compounds (Y1-Y9)

Comp.	pH range
Y1	7-8
Y2	7-8
Y3	7-8
Y4	7-8
Y5	8-9
Y6	7-8
Y7	7-8
Y8	9-10
Y9	7-8

The color change of compounds Y1-Y9 was determined using acidic and basic solutions. Figure 8.



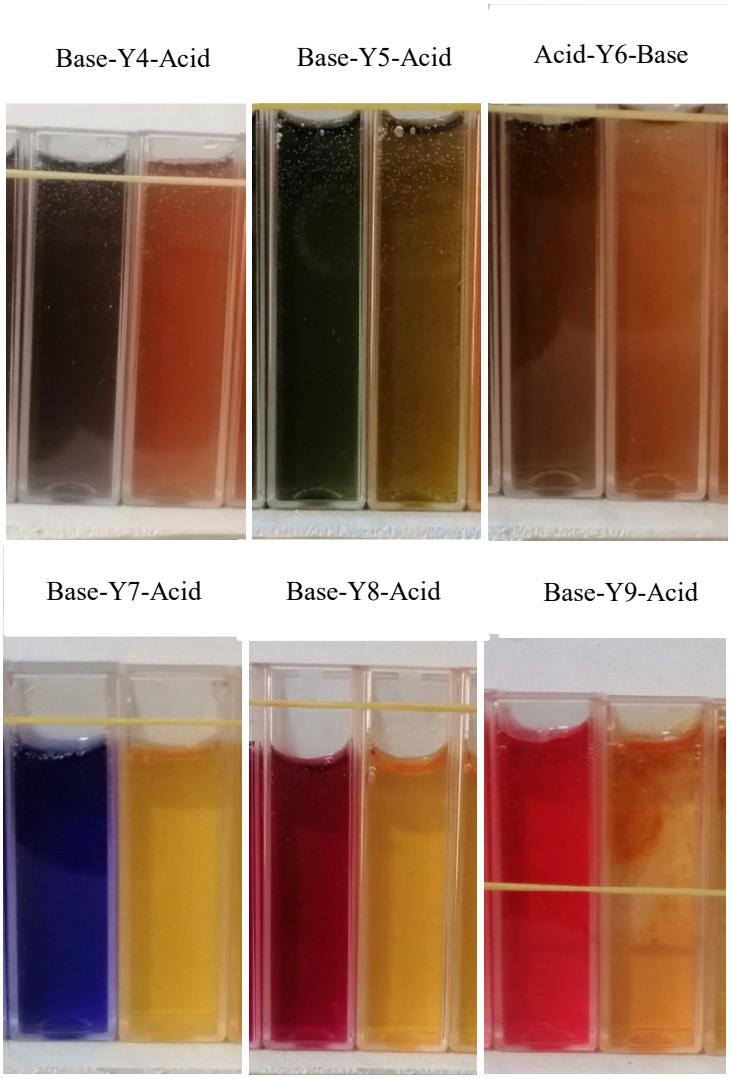


Figure 8. Colors of Y1-Y9 compounds in acidic and basic medium

4. CONCLUSION

In this study, nine novel azo compounds (Y1–Y9) were successfully synthesized via diazotization and coupling reactions, and their structures were unequivocally confirmed through comprehensive spectroscopic characterization (FT-IR, ^{1}H-NMR, and ^{13}C-NMR). The investigation into their acid-base indicator properties revealed that all synthesized compounds exhibit sharp, reversible color changes and distinct UV-Vis spectral shifts in response to pH variations. The cationic forms (pH 1–7) absorbed at 391–483 nm, while the anionic forms (pH 8–14) absorbed at 448–587 nm, with specific transition ranges between pH 7–10 depending on the substituent's position (ortho, meta, or para). These characteristics, particularly the performance of compounds like Y8 (pH 9–10), which is comparable to phenolphthalein, confirm their high potential as effective acid-base indicators. The results confirm that these compounds can serve as reliable acid-base indicators in analytical applications. Future studies will focus on evaluating their long-term stability, toxicity profile, and immobilization on solid supports to develop practical pH sensors or test strips for educational and industrial use.

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