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SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC STUDIES ON TAUTOMERISM AND ACIDITY CONSTANTS OF CERTAIN 4-(PHENYLDIAZENYL) BENZENE-1,3-DIOL DERIVATIVES

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Abstract

In this study, monoazo dyes were synthesized through the diazotization of several substituted aminobenzenes and couplings with benzene-1,3-diols. The chemical structures of these compounds were characterized using spectroscopic techniques. The tautomeric properties of the 4-(phenyldiazenyl)benzene-1,3-diol derivative compounds were examined using UV-Vis. spectrophotometry in pure polar or apolar media (dimethyl sulfoxide, ethanol, chloroform, benzene and cyclohexane) under acidic and basic conditions at 25±1 °C, 35±1 °C and 45±1 °C. The percentage of the azo-hydrazone tautomers was calculated for all of the compounds. The UV-Vis. analysis reveals that the azo form is dominant in the presence of azo-hydrazone tautomerism for all azo dyes. Concurrently, the acidity constants for these derivatives were determined using a UV-Vis. spectroscopic technique at 25 °C (±0.1 °C).

Keywords: Azo dyes, Azo-hydrazone tautomerism, Ionization constants, Acidity constants.

BAZI 4- (FENİLDİAZENİL)BENZEN-1,3-DİOL TÜREVLERİNİN SENTEZİ, KARAKTERİZASYONU, TAUTOMER VE ASİTLİK SABİTLERİNİN SPEKTROSKOPİK YÖNTEM İLE HESAPLANMASI

Özet

Bu çalışmada, benzen-1,3-triol ve bazı sübstitüe amino benzen ile monoazo boyar maddeleri sentezlendi. Kimyasal yapıları spektroskopik teknikler ile aydınlatıldı. 4-(fenildiazenil)benzen-1,3-diol türevi bileşiklerinin tautomerik özellikleri saf polar ve apolar çözücülerde (dimetil sülfoksit, etanol, kloroform, benzen ve siklohekzan) asidik ve bazik ortamlarda 25±1 °C, 35±1 °C ve 45±1 °C UV-Vis. Spektrometresinde ölçüldü. Sentezlenen bileşiklerin azo-hidrazon tautomerleri hesaplandı. Bütün azo boyar madde bileşiklerinde azo tautomer formunun baskın olduğu belirlendi. Aynı bileşiklerin asitlik sabitleri 25 °C (±0,1 °C) UV-Vis. Spektroskopik teknik ile belirlendi.

Anahtar Kelimeler: Azo boyarmadde, Azo-hidrazon tautomerizmi, İyonlaşma sabitleri, Asitlik sabitleri.

1. INTRODUCTION

Azo groups (-N=N-) are some of the most investigated functionalities because of their contribution to the chemical industry. Most importantly, azobenzene is stable, and the azo bond exhibits tautomerism. Consequently, new photochemical research has been developed [1-4]. Azo groups exhibit thermal and photochemical switching through their conformers; this principle has been applied when building sensory systems [5-9]. Azobenzene chromophores undergo reversible cis-trans photoisomerization, showing nonlinear optical properties, as well as light-induced dichroism and

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birefringence [7]. Therefore, these groups can be incorporated into thin-layer, photoactive supramolecular polymer materials and into molecular architectures, dendrimers and molecular glasses [10-12].

Strategies based on acidity were implemented for azobenzene for use in many areas of research: the directions of nucleophilic and electrophilic attack, the size of activation energies in organic reactions and others [13-20].

Azo-hydrazone tautomerism has been found for monoazodyes prepared from enol-type coupling components. Many different technical properties and dyeing performances are exhibited by azo-hydrazone tautomers. Therefore, experimentally and theoretically determining azo-hydrazone tautomerism in both solid and solution states may be quite interesting [21-25]. The tautomerism exhibited by the azo groups allows them to display different optical and physical properties. Azo-hydrazones show different colors through tautomerism [26,27]. In *o*-hydroxy or *o*-amino azobenzene compounds, this proton shift includes a proton stretching vibration in the intramolecular, asymmetrical double-well potential of a hydrogen bonding system, although the transfer along the potential surface is not linear [28,29]. Furthermore, substituted azobenzene dyes in acidic and basic media, anionic and cationic tautomeric compounds behavior have been investigated considering that knowledge of the acid dissociation constants (pK_a) becomes essential for the development of compounds with tautomerism [17,30]. However, few studies have dealt with the tautomerism and the acid–base properties of this compound in solution [18,30].

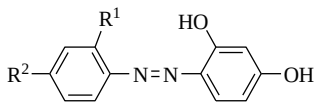
In this paper, we report the synthesis of a series of monoazo dyes using several substituted aminobenzenes and benzene-1,3-diols as coupling components; the structures of these compounds were elucidated using elemental analysis, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. Next, we determine the azo-hydrazone tautomerism and the pK_a values of azo dyes in different buffer solutions applying the UV-Vis. spectroscopic technique.

2. EXPERIMENTAL

2.1. General

The studied compounds were synthesized using the procedure reported by Vogel and Peters [27,31]. The nomenclature and formulae of the studied compounds are shown in Table 1.

Table 1. IUPAC nomenclature of the studied compounds *I* to *V*.



Compound No	IUPAC Names	Substituents	
		R^1	R^2
I	4-[(2-methoxyphenyl)diazenyl]benzene-1,3-diol	$-OCH_3$	-H
II	4-[(2-ethylphenyl)diazenyl]benzene-1,3-diol	$-CH_2CH_3$	-H
III	4-[(2-iodophenyl)diazenyl]benzene-1,3-diol	-I	-H
IV	4-[(4-chlorophenyl)diazenyl]benzene-1,3-diol	-H	-Cl
V	4-[(4-hydroxyphenyl)diazenyl]benzene-1,3-diol	-H	-OH

The chemicals used were analytical grade, and the solvents were purified before use. The elemental analyses were carried out using a Vario El III CHNS (Hanau, Germany) instrument, and the melting points were determined using a Stuart Scientific Melting Point SMP1 apparatus. The absorbance and vibrational measurements were collected using Schimadzu UV2101 Spectrophotometer (Kyoto, Japan) and Perkin Elmer Spectrum 100 FTIR spectrometers (Massachusetts, USA). The ^{1}H- and ^{13}C-NMR spectra were taken using a Bruker DPX FT-NMR (500 MHz. 5 mm PABBO BB-inverse prob) instrument (Billerica, Massachusetts, USA).

2.2. Synthesis

The studied compounds (Table 1) were synthesized according to a method described in the literature [27,31]. To synthesize 4-(phenyldiazonyl) benzene-1,3-diol derivatives ***I-V***, substituted anilines were diazotized using sodium nitrite in the presence of hydrochloric acid. The diazotized compounds were combined with benzene-1,3-diol (resorcinol) to achieve substituted 4-(phenyldiazonyl)benzene-1,3-diol dyes in good yields. The crude product was recrystallized in ethanol. The yields, melting points (m.p.) and elemental analysis data for these compounds were calculated, as shown in supporting data. The structures of the azobenzenes were characterized by elemental analysis, using ^{1}H-NMR, ^{13}C-NMR and FT-IR spectroscopy. The spectroscopic and analytical data are given in Table 2-5.

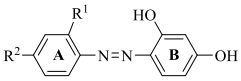
Table 2. Experimental and analytical data for the synthesized compounds.

Comp.	Empiric formula	MW (g / mol)	M.p. (°C)	Yield (%)	Calculated (found) %					
					C	H	N	O	I	Cl
I	$C_{13}H_{12}N_2O_3$	244.25	187	60	63.93 (63.45)	4.95 (3.92)	11.47 (11.49)	19.65 (21.10)	-	-
II	$C_{14}H_{14}N_2O_2$	242.28	143	65	71.10 (69.41)	5.01 (5.82)	11.38 (11.56)	12.50 (13.21)	-	-
II	$C_{12}H_9IN_2O_2$	340.12	182	68	43.17 (42.38)	1.17 (2.67)	8.34 (8.24)	$47.33_{(I+O)}$ (9.41)	- (37.31)	-
IV	$C_{12}H_9ClN_2O_2$	248.67	196	70	56.11 (57.96)	2.13 (3.65)	11.34 (11.27)	$30.42_{(Cl+O)}$ (12.87)	-	- (14.26)
V	$C_{12}H_{10}N_2O_3$	230.22	226	54	58.93 (62.60)	3.78 (4.38)	11.31 (12.17)	25.98 (20.85)	-	-

Table 3. Selected FTIR data for the synthesized compounds (KBr disk, ν (cm^{-1})).

Comp.	ν (O-H)	ν (C-H) aromatic	ν (C=C) aromatic	ν (-N=N-)	ν (C-O-C) aliphatic	ν (C-Cl)	ν (C-I)
I	3156 - 3674	3061	1525 - 1482	1406	1200	-	-
II	3202 - 3672	2972	1594 - 1530	1403	-	-	-
III	3300 - 3672	3026	1600 - 1472	1472	-	-	740
IV	3086 - 3668	2980	1614 - 1489	1450	-	826	-
V	3160 - 3667	2930	1591 - 1472	1383	-	-	-

Table 4. 1H NMR data (in DMSO-d6) for the synthesized molecules.

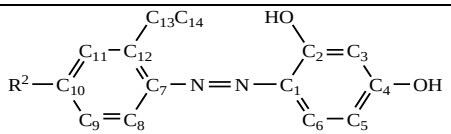


δ (ppm) / *J* (Hz)

I	***II***	***III***	***IV***	***V***
3.75 (s, 3H, -OCH_3, aromatic, ring **A**)	1.25 (t, 3H, -CH_3 of ethylene, ring **A**)	7.86 (d, 1H, aromatic, ring **A**)	7.50 (dd, 2H, aromatic, ring **A**)	6.90 (dd, 2H, aromatic, ring **A**)
6.92 (d, 1H, aromatic, ring **A**)	2.75 (dd, 2H, -CH_2 of ethylene, ring **A**)	7.20 (t, 1H, aromatic, ring **A**)	7.85 (dd, 2H, aromatic, ring **A**)	7.74 (dd, 2H, aromatic, ring **A**)
7.38 (t, 1H, aromatic, ring **A**)	7.35 (m, 1H, aromatic, ring **A**)	7.48 (m, 1H, aromatic, ring **A**)	7.59 (d, 1H, aromatic, ring **B**)	7.55 (d, 1H, aromatic, ring **B**)
7.02 (m, 1H, aromatic, ring **A**)	7.43 (t, 1H, aromatic, ring **A**)	7.62 (d, 1H, aromatic, ring **A**)	6.55 (dd, 1H, aromatic, ring **B**)	6.48 (dd, 1H, aromatic, ring **B**)
7.82 (d, 1H, aromatic, ring **A**)	7.24 (m, 1H, aromatic, ring **A**)	7.54 (d, 1H, aromatic, ring **B**)	6.43 (s, 1H, aromatic, ring **B**)	6.35 (s, 1H, aromatic, ring **B**)
7.65 (d, 1H, aromatic, ring **B**)	7.83 (d, 1H, aromatic, ring **A**)	6.58 (dd, 1H, aromatic, ring **B**)	10.70 (s, 1H, *p*-OH, ring **B**)	12.70 (s, 1H, *p*-OH, ring **B**)
6.47 (dd, 1H, aromatic, ring **B**)	7.60 (d, 1H, aromatic, ring **B**)	6.42 (s, 1H, aromatic, ring **B**)	12.20 (s, 1H, *m*-OH, ring **B**)	10.45 (s, 1H, *m*-OH, ring **B**)
6.41 (s, 1H, aromatic, ring **B**)	6.55 (dd, 1H, aromatic, ring **B**)	10.82 (s, 1H, *p*-OH, ring **B**)	-	10.15 (s, 1H, *p*-OH, ring **A**)
10.75 (s, 1H, *p*-OH, ring **B**)	6.43 (s, 1H, aromatic, ring **B**)	12.70 (s, 1H, *m*-OH, ring **B**)	-	-
14.11 (s, 1H, *m*-OH, ring **B**)	10.50 (s, 1H, *p*-OH, ring **B**)	-	-	-
-	13.00 (s, 1H, *m*-OH, ring **B**)	-	-	-

a s = singlet, d = doublet, dd = doublet of doublet, t = triplet.

Table 5. 13C NMR data (in DMSO-d6) for the synthesized molecules.



C-type	**^{13}C NMR data δ (ppm)**				
	I	***II***	***III***	***IV***	***V***
C1	115.87	115.86	117.74	118.40	117.90
C2	157.76	156.87	150.28	157.40	155.81
C3	103.57	103.39	103.43	104.30	103.44
C4	163.40	163.50	164.29	163.20	162.21
C5	109.95	109.74	110.60	110.10	109.07
C6	134.07	127.41	132.70	126.30	133.28
C7	132.11	148.24	156.16	150.20	143.97
C8	133.19	122.20	132.16	125.20	124.10
C9	121.46	126.60	129.66	130.05	116.42
C10	132.11	130.71	133.30	136.50	160.30
C11	113.43	128.24	140.06	130.05	116.42
C12	155.05	133.14	100.80	125.20	124.10
C13	56.56	23.86	-	-	-
C14	-	14.37	-	-	-

2.3. The Determination of Tautomeric Equilibrium Constants

Absorbance measurements were carried out using a Schimadzu UV2101 spectrophotometer. A thermostated water bath (HAAKE DL30W26) was used to circulate the liquid.

25 mL (approximately 10^{-5} mol L^{-1}) solutions of the studied compounds in dimethyl sulfoxide (DMSO), ethanol (C_2H_5OH), chloroform ($CHCl_3$), benzene (C_6H_6) and cyclohexane (C_6H_{12}) were prepared. The UV-Vis. spectra of these solutions were measured. Afterward, approximately 40 drops of trifluoroacetic acid (CF_3COOH) solution were added to the reference and sample cuvettes to acidify the solution; the UV-Vis. spectra were recorded again. Similarly after adding triethylamine ($(CH_3CH_2)_3N$) to each solution, the UV-Vis. spectra were recorded. The λ_{max} values and absorbances measured at these wavelengths are given in supporting data. The absorbance of the azo (i.e., over 400 nm) and hydrazone forms (i.e., within the range of 270-350 nm, strong absorption) were used in Eq. (1).

$$A_2 / A_1 = \times / (100 - \times) \quad (1)$$

Where A_1 represents the absorption of the hydrazone forms (n - π*), A_2 represents the absorption of the azo forms (n - π*), and × represents the percentage of the azo form (Table 7) [32-34]. The spectroscopic and analytical data are given in Table 6.

Table 6. The acid and base effects on tautomerism in different solvents (25 ± 1 °C, 35 ± 1 °C and 45 ± 1 °C).

Comp.	Media	Solvent				
		DMSO	Ethanol	Chloroform	Benzene	Cyclohexane
		λ_{max} (nm) (Absorbance)				
25 ± 1°C						
I	**Solvent**	402 (1.070) 250 (0.405)	398 (1.262) 266 (0.379) 265 (0.332)	399 (1.953) 258 (0.773)	397 (2.595) 314 (0.370)	400 (0.667) 259 (0.289)
	Acidic	480 (0.969) 261 (0.343)	480 (1.161) 260 (0.384)	488 (1.786) 308 (0.125) 254 (0.330)	491 (0.766)	Unmeasurable
	Basic	Unmeasurable	438 (1.755) 271 (0.511)	401 (1.092)	402 (1.606)	401 (0.313)
II	**Solvent**	390 (1.362) 260 (0.535)	388 (1.771) 252 (0.686)	385 (1.502) 254 (0.673)	386 (1.948	384 (1.668) 251 (0.781)
	Acidic	384 (1.598) 262 (0.592)	462 (1.526) 260 (0.294)	472 (1.714) 309 (0.091) 258 (0.270)	472 (1.943) 321 (0.140)	Unmeasurable
	Basic	Unmeasurable	402 (0.825) 270 (1.057)	393 (1.400)	393 (1.202)	391 (1.599)
III	**Solvent**	400 (1.650) 262 (0.824)	398 (1.821) 264 (0.697)	398 (1.529) 261 (0.799)	397 (1.301)	399 (2.093) 259 (1.086)
	Acidic	399 (1.936) 262 (0.997)	462 (1.567) 260 (0547)	471 (1.393) 315 (0.103) 255 (0.317)	475 (1.167) 318 (0.102)	475 (1.167) 318 (0.102)
	Basic	Unmeasurable	418 (1.762) 270 (0.819)	398 (1.765) 276 (0.330)	407 (0.911)	406 (1.332) 272 (0.694)
IV	**Solvent**	392 (1.807) 260 (0.684)	388 (1.854) 253 (0.698)	389 (1.534)	387 (1.866)	393 (1.114) 256 (0.428)
	Acidic	387 (1.071) 261 (0.499)	459 (1.310) 259 (0.424)	470 (1.382) 322 (0.074) 254 (0.329)	470 (1.713) 324 (0.121)	Unmeasurable
	Basic	Unmeasurable	427 (1.072) 270 (1.419)	395 (0.994)	392 (1.131)	393 (0.664) 271 (0.460)
V	**Neutral**	389 (1.386) 260 (0.610)	386 (1.524) 260 (0.642)	382 (1.095) 260 (0.521)	385 (0.756)	378 (0.028) 261 (0.018)
	Acidic	385 (0.794) 261 (0.368)	489 (1.348) 332 (0.131) 262 (0.258)	481 (1.245) 328 (0.093) 254 (0.257)	483 (0.678) 326 (0.050)	Unmeasurable
	Basic	Unmeasurable	421 (0.727) 270 (0.697)	412 (0.775) 391 (0.852)	393 (0.519)	384 (0.074) 271 (0.567)
35 ± 1°C						
I	**Neutral**	403 (1.095) 260 (0.458)	397 (1.237)	395 (2.025) 268 (0.485)	398 (2.229)	395 (0.701) 260 (0.287)

	Acidic	482 (1.101) 261 (0.418)	481 (1.196) 259 (0.431)	488 (1.979) 310 (0.150)	493 (1.955)	Unmeasurable
	Basic	Unmeasurable	438 (1.688) 270 (0.809)	402 (1.067)	401 (1.392)	400 (0.435) 268 (0.632)
II	**Neutral**	390 (1.365) 264 (0.495)	387 (1.749) 251 (0.650)	386 (1.466) 259 (0.578)	385 (1.921)	385 (1.693) 250 (0.806)
	Acidic	386 (1.487) 261 (0.658)	465 (1.555) 259 (0.596)	468 (1.591) 309 (0.164) 256 (0.420)	473 (1.876) 315 (0.112)	Unmeasurable
	Basic	Unmeasurable	426 (0.973) 270 (0.946)	392 (1.403)	392 (1.310)	391 (1.546) 272 (0.466)
III	**Neutral**	403 (1.632) 263 (0.794)	397 (1.779) 260 (0.819)	399 (1.507) 261 (0.791)	401 (1.545)	396 (2.180) 259 (1.160)
	Acidic	401 (2.020) 262 (0.912)	445 (1.227) 259 (0.754)	468 (1.372) 314 (0.089) 254 (0.426)	474 (1.135) 311 (0.081)	Unmeasurable
	Basic	Unmeasurable	419 (1.819) 277 (0.376)	409 (1.033)	406 (0.787)	405 (1.396) 272 (0.735)
IV	**Neutral**	392 (1.774) 263 (0.605)	388 (1.822) 254 (0.672)	385 (1.529) 259 (0.588)	386 (1.750)	389 (1.165) 257 (0.461)
	Acidic	387 (1.027) 262 (0.406)	459 (1.271) 260 (0.394)	468 (1.565) 320 (0.078) 257 (0.242)	466 (1.685) 315 (0.115)	Unmeasurable
	Basic	Unmeasurable	428 (1.136) 271 (0.461)	393 (0.928)	394 (1.096)	391 (0.741)
V	**Neutral**	391 (1.350) 263 (0.528)	384 (1.484) 259 (0.582)	382 (1.105) 260 (0.457)	385 (0.770)	385 (0.040) 312 (0.034)
	Acidic	385 (0.761) 261 (0.389)	492 (1.297 335 (0.142) 258 (0.569)	482 (1.257) 323 (0.113)	483 (0.706) 324 (0.104)	Unmeasurable
	Basic	Unmeasurable	416 (0.743) 270 (1.043)	509 (0.021) 432 (0.674)	391 (0.772)	391 (0.044) 272 (0.576)
45 ± 1 °C						
I	**Neutral**	400 (1.036) 264 (0.358)	399 (1.219) 253 (0.474)	398 (2.029) 257 (0.860)	396 (1.485)	393 (0.733) 260 (0.286)
	Acidic	402 (1.212) 261 (0.495)	481 (1.122) 260 (0.333)	489 (2.057) 323 (0.125) 260 (0.269)	490 (2.167) 268 (0.145)	Unmeasurable
	Basic	Unmeasurable	434 (1.652) 272 (0.841)	404 (1.312)	399 (0.987)	396 (0.424) 273 (0.604)
II	**Solvent**	388 (1.344) 264 (0.448)	387 (1.779) 251 (0.769)	387 (1.462) 254 (0.663)	385 (1.953)	383 (1.775) 251 (0.839)
	Acidic	385 (1.581) 263 (0.688)	463 (1.278) 258 (0.347)	468 (1.769) 315 (0.115)	472 (1.945) 316 (0.174)	Unmeasurable
	Basic	Unmeasurable	425 (1.043) 272 (0.488)	392 (1.596)	390 (1.196)	389 (1.516) 273 (0.772)
III	**Solvent**	403 (1.592) 264 (0.752)	401 (1.748) 260 (0.814)	397 (1.506) 261 (0.799)	398 (1.301) 281 (0.283)	400 (2.097) 259 (1.162)
	Acidic	398 (1.936) 262 (0.903)	462 (1.490) 259 (0.687)	470 (1.447) 313 (0.126) 255 (0.346)	476 (1.161) 318 (0.100)	Unmeasurable
	Basic	Unmeasurable	418 (1.598) 272 (1.260)	407 (0.959)	405 (0.936)	401 (1.411) 274 (0.616)
IV	**Solvent**	391 (1.723) 263 (0.567)	388 (1.819) 254 (0.659)	387 (1.537) 257 (0.614)	385 (1.805)	389 (1.236) 255 (0.520)
	Acidic	387 (1.007) 261 (0.399)	461 (1.272) 261 (0.350)	468 (1.526) 310 (0.101) 257 (0.252)	470 (1.698) 322 (0.128)	Unmeasurable
	Basic	Unmeasurable	429 (1.000) 272 (0.389)	393 (0.923)	395 (1.130)	391 (1.479) 268 (0.602)
V	**Solvent**	396 (1.348) 264 (0.568)	382 (1.485) 259 (0.585)	381 (1.194) 260 (0.541)	385 (0.796)	380 (0.033) 261 (0.035)
	Acidic	387 (0.754) 262 (0.434)	490 (1.311) 333 (0.120) 259 (0.334)	479 (0.847) 315 (0.077) 253 (0.131)	483 (0.783) 334 (0.115)	Unmeasurable
	Basic	Unmeasurable	388 (0.857) 271 (1.057)	388 (0.846)	388 (0.537) 279 (0.430)	388 (0.373)

2.4. The Determination of Acidity Constants

The Albert and Serjant method were used to determine the acidity constant [35]. This method for measuring pK_a values was chosen for its sensitivity. We have conducted several similar studies for previous [30,36-38].

The methanol, ethanol, glycine, KOH, H_2SO_4, HCl, CH_3COOH, CH_3COONa, NaOH, KH_2PO_4, Na_2CO_3, $NaHCO_3$, NaCl, methyl orange, phenolphthalein indicator and standard buffer solutions were of analytical grade and were used without further purification. The pH measurements were performed using a glass electrode. Standard buffer solutions at pH 4, 7 and 9 were used to calibrate the WTW pH/ion analyzer 350 meter, and the WTW 300 balance and a Schimadzu UV2101 UV-Vis. Spectrophotometer scanning spectrometer were used for the measurements.

CO_2-free NaOH solutions were prepared using NaOH pellets (1 to 16.4 mol L^{-1}) in water. The buffered solutions were prepared as described by Perrin [39,40]. The spectrophotometric measurements were performed at 25 ± 0.1 °C [41,42].

The typical UV-Vis. spectra for the neutral and ionic forms of each studied compound (acidic or basic) are given in Fig. 1.

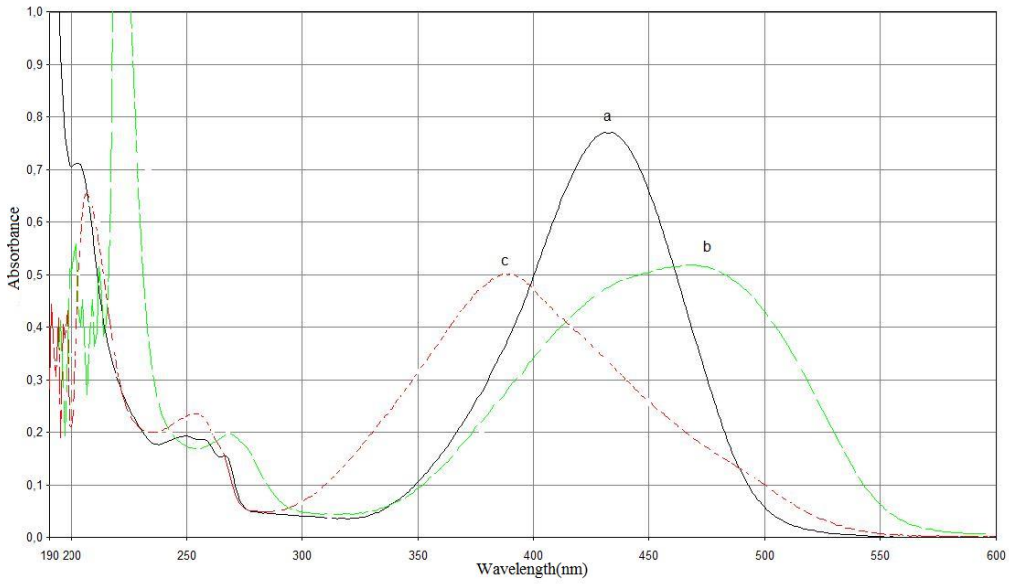


Fig. 1. The UV-visible spectrum of compound *IV*. (a) Neutral compound, pH=7. (b) Mono anion, 0.1 mol L^{-1} NaOH. (c) Mono cation, pH=1.

A sigmoid curve of absorbance or extinction coefficients at the analytical wavelength (A, λ) was first obtained in Fig. 2 using the λ_{max} values of the ionic and neutral forms in Figure 1 and the equation $A=\varepsilon \cdot b\ c$, (b = cell width, cm; c = concentration, mol L^{-1}). The absorbance of the fully protonated compound ($A_{ca.}$; absorbance of conjugated acid) and the pure free base ($A_{fb.}$; absorbance of free base) at certain acidity values were calculated by linearly extrapolating the arms of the curve from equation 2, giving the ionization ratio $A_{obs.}$ ($A_{obs.}$; the observed absorbance). This value was converted into molar extinction $\varepsilon_{obs.}$. The observed pK$_a$ values for the mono azobenzene derivatives were determined using Eq. (2).

$$pK_a = pH + \log\left[\frac{A_{obs.} - A_{fb.}}{A_{ca.} - A_{obs.}}\right] \quad (2)$$

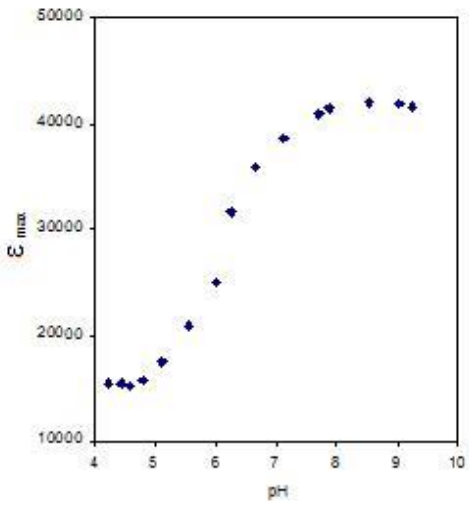


Fig. 2. pH - $\varepsilon_{431\ nm}$ plot for compound *IV*.

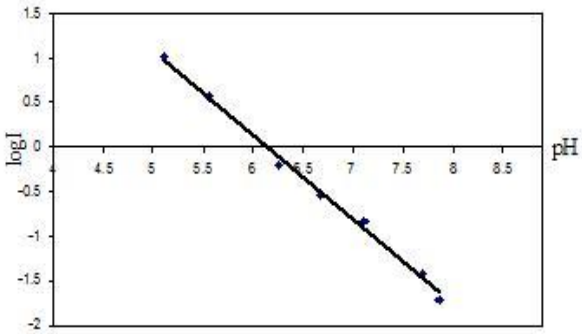


Fig. 3. pH - log *I* plot for compound *IV* for the first protonation.

An experimental plot of log *I* (i.e., log ([$A_{obs.} - A_{fb.}$] / [$A_{ca.} - A_{obs.}$]) against H_x (pH) is equal to pK_a at log *I* = 0; this value describes half of the protonation value ($H_x^{1/2}$) (Fig. 3) [38,39]. The pK_a values were calculated from Eq. (3) and the results are given in Tables 3 and 4.

$$pK_a = m.\ H_x\ ½\ (H_x = H_o,\ H_ \text{ and } pH) \quad (3)$$

In this equation, $H_x^{1/2}$ represents half of the protonation value. This equation can be mathematically expressed as a straight line (y = m. x + n) with a slope of 'm' for log *I* – pH.

3. RESULTS AND DISCUSSION

3.1. Azo-Hydrazone Tautomerism

Eq. (1) was used to calculate the percentage of azo-hydrazone tautomerism and is shown in Table 7.

The investigated compounds seem to show tautomeric equilibria in all solvents at all temperatures (Figs. 4 and 5).

Table 7. The calculated percentage of azo-hydrazone tautomerism for the studied compounds at different temperature in solvents, as well as in acidic and basic media.

Comp.	Solvent	Azo hydrazone tautomer, % [a]								
		25 ± 1 °C			35 ± 1 °C			45 ± 1 °C		
		Solvent	Acidic medium[b]	Basic medium[c]	Solvent	Acidic medium[b]	Basic medium[c]	Solvent	Acidic medium[b]	Basic medium[c]
I	**DMSO**	-	-	-	-	-	-	-	-	-
	Ethanol	-	-	77.45	-	-	67.60	-	-	66.27
	Chloroform	-	93.46	-	-	92.95	-	-	94.27	-
	Benzene	-	-	-	-	-	-	-	-	-
	Cyclohexane	-	-	-	-	-	-	-	-	-
II	**DMSO**	-	-	-	-	-	-	-	-	-
	Ethanol	-	-	43.84	-	-	50.70	-	-	68.13
	Chloroform	-	94.96	-	-	90.66	-	-	94.90	-
	Benzene	-	93.28	-	-	94.37	-	-	91.97	-
	Cyclohexane	-	-	-	-	-	-	-	-	-
III	**DMSO**	-	-	-	-	-	-	-	-	-
	Ethanol	-	-	68.27	-	-	82.87	-	-	55.91
	Chloroform	-	93.11	-	-	93.91	-	-	91.99	-
	Benzene	-	91.96	-	-	93.34	-	-	92.07	-
	Cyclohexane	-	-	65.75	-	-	65.51	-	-	69.61
IV	**DMSO**	-	-	-	-	-	-	-	-	-
	Ethanol	-	-	43.03	-	-	71.13	-	-	71.99
	Chloroform	-	94.92	-	-	95.25	-	-	93.79	-
	Benzene	-	93.40	-	-	93.61	-	-	92.99	-
	Cyclohexane	-	-	-	-	-	-	-	-	-
V	**DMSO**	-	-	-	-	-	-	-	-	-
	Ethanol	-	91.14	51.05	-	90.13	41.60	-	91.61	-
	Chloroform	-	93.05	48.23	-	91.75	-	-	91.67	-
	Benzene	-	93.13	-	-	86.20	-	-	87.19	-
	Cyclohexane	-	-	-	-	-	-	-	-	-

[a] $A_2 / A_1 = x / (100 - x)$, A_1 = Absorbtion of hydrazone tautomerism (π - π^*); A_2 = Absorbtion of azo tautomerism (n - π^*); x = Percent of azo-hydrazone tautomerism, [b] Acidic medium was produced by adding 1 mL CF_3COOH (conc. of compound is 1.6×10^{-5} mol L^{-1}), [c] Basic medium was produced by adding 1 mL $(CH_3CH_2)_3N$ (conc. of compound is 1.6×10^{-5} mol L^{-1}).

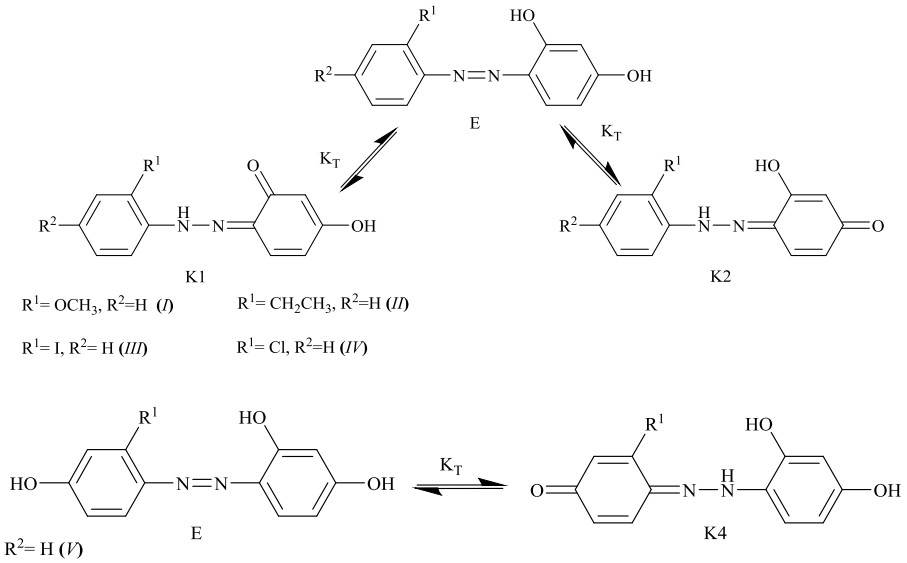
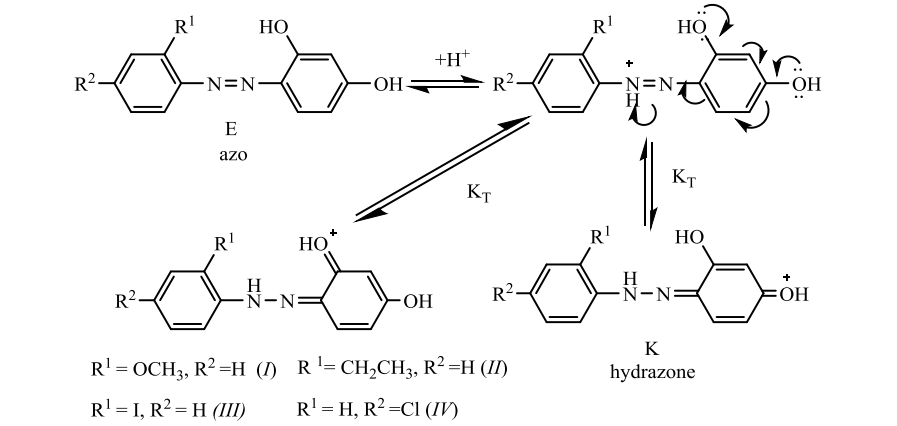


Fig. 4. Possible tautomeric forms of the studied compounds (*I* - *V*).



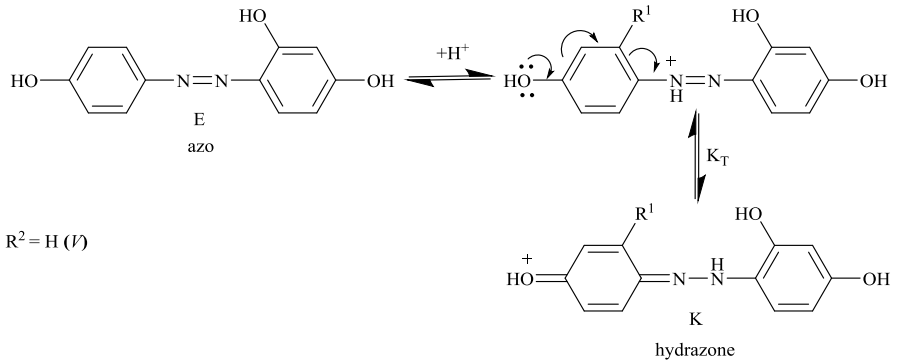


Fig. 5. Possible tautomeric forms of studied compounds (*I* - *V*) in acidic condition.

Compound *I* was in its azo form at all temperatures when chloroform (i.e., polar solvent) was used as a solvent. Compounds *II*, *III* and *IV* were in azo form at all temperatures when chloroform and cyclohexane were used as solvents (Table 7).

As observed from Table 7, the percentage of the azo forms remains the same in chloroform (i.e., polar solvent) and cyclohexane (i.e., nonpolar solvent) at all temperatures (i.e., differences between percentages are so small that they may arise from experimental error). Therefore, we can observe no considerable solvent or temperature effect on the azo-hydrazone equilibrium for compounds *I*-*IV*.

For compound *V***,** the azo form content changes drastically in benzene at 35 ± 1 °C and at 45 ± 1 0°C in an acidic medium. The drastic fall may be related to the polarity of the solvent.

Azo-hydrazone tautomerization also becomes effective in basic media. The possible tautomerization mechanisms are depicted in Fig. 6 [14,29,30]. Proton abstraction from the phenolic hydroxyl group is possible in a basic medium. The subsequent rearrangement of the enolate ion may generate the keto form by transferring the negative charge to the nitrogen atom.

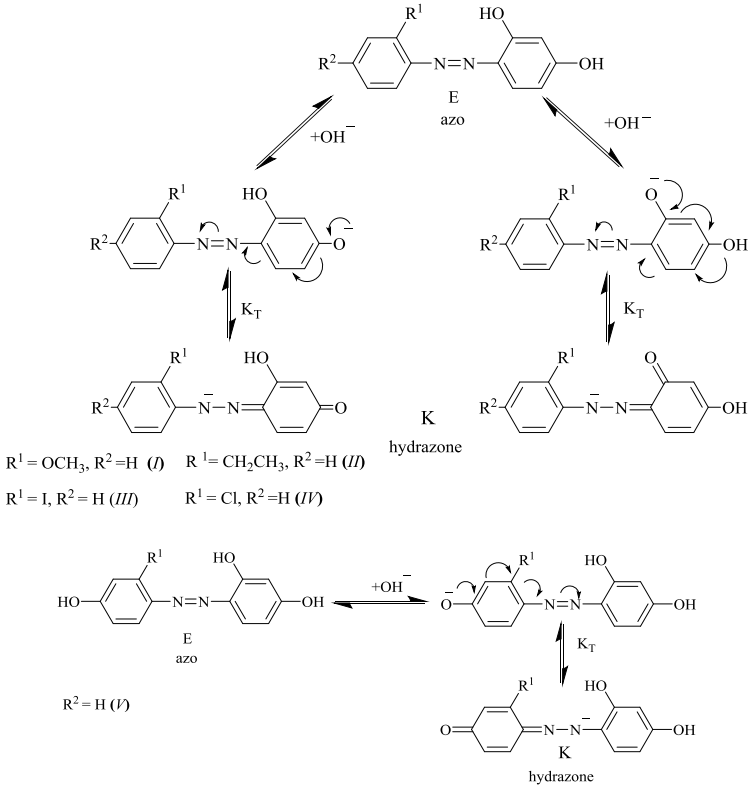


Fig. 6. Possible tautomerism of the studied compounds (*I* - *V*) under basic condition.

Compounds *I*, *II* and *IV* seem to have azo-hydrazone tautomerization at elevated temperatures with only ethanol showing a decreasing percentage trend, respectively (i.e., from 77 → 68 → 66 percent). We can only explain this decrease only with the decreasing polarity of the ethanol solvent.

For compound *II*, we must say the reverse and an increase of the azo form percentage (i.e., 43 → 51 → 68) can be explained by a decrease in the polarity of compound *II*. This is logical because compound *I* is ether substituted but compound *II* is not. A very similar case occurs in compound *IV*. Due to the electron withdrawing chloride atom, the polarity increases more, making the trend similar to compound *II* (i.e. 43 → 71 → 72).

Compound *III* exists in its azo form at all temperatures with an increasing trend in ethanol 68 → 83 → 56 % and in cyclohexane 66 → 66 → 70 %. The percentage in the ethanol solution is 56 at 45 ± 1 °C, and this abnormality may arise due to the change in the polarity of compound *III*. At higher temperatures, iodine may polarize less readily. The same situation can also be observed in cyclohexane (i.e., 70 % at 45 ± 1 °C).

Compound *V* shows the formation of the azo-form in ethanol at a low level (i.e., 51 → 41 %). Almost a 10 unit decrease may arise from the loss of polarity; in chloroform, no azo form formation was observed at 35 ± 1 °C. Therefore, the changes in the polarity of the solvent and the temperature affect the azo-hydrazone tautomerism drastically.

3.2. Acidity Constants

The nomenclature and UV-vis. data, as well as the calculated acidity constants for deprotonation and protonation processes, are shown in Tables 8 and 9, respectively.

Table 8. UV-visible and ionization data for compounds *I* to *V*.

Comp.	Process	Spectral maximum λ / nm			Acidity measurements						
		Neutral species [a] (log ε_{max})	Monoanion [b] (log ε_{max})	Dianion [c] (log ε_{max})	λ_{max} (nm) [d]	Half protonation ($H^{1/2}$) [e]	Half protonation ($H^{1/2}$) [f]	m [i]	pK_{a2} [g]	pK_{a1} [h]	Correlation (R^2) [j]
I	***n*** ⇌ ***ma***	448 (4.52)	468 (4.42)		468	6.50 ± 0.05		1.03	6.69		0.99
	ma ⇌ ***da***		468 (4.42)	484 (4.34)	468		13.15 ± 0.05	0.94		12.36	0.99
II	***n*** ⇌ ***ma***	440 (4.47)	445 (4.41)		445	6.93 ± 0.02		0.92	6.37		0.99
	ma ⇌ ***da***		445 (4.41)	467 (4.27)	445		13.46 ± 0.02	0.90		12.11	0.99
III	***n*** ⇌ ***ma***	434 (4.47)	471 (4.33)		434	6.42 ± 0.01		0.96	6.136		0.99
	ma ⇌ ***da***		471 (4.33)	486 (4.34)	434		13.14 ± 0.09	0.76		9.99	0.99
IV	***n*** ⇌ ***ma***	431 (4.59)	466 (4.41)		431	6.13 ± 0.07		0.95	5.82		0.99
	ma ⇌ ***da***		466 (4.41)	487 (4.40)	431		13.17 ± 0.04	0.74		9.74	0.99
V	***n*** ⇌ ***ma***	432 (4.37)	486 (4.46)		469	11.15 ± 0.07		0.74	8.25		0.99
	ma ⇌ ***da***		486 (4.46)	491 (4.35)	469		14.90 ± 0.04	0.95		14.15	0.99

[a] Measured in pH=7 buffer solution. [b] Measured in 0.1 mol L^{-1} NaOH. [c] Measured in 10 mol L^{-1} NaOH. [d] The wavelength for pK_a determination. [e] Half protonation values ± uncertainties refer to the standard error for the first deprotonation. [f] Half protonation values ± uncertainties refer to the standard error for the second deprotonation. [g] First deprotonation acidity constants values. [h] Second deprotonation acidity constants values. [1] Slopes of log I - pH plot. [j] Correlations for log *I* as a function of pH (or *H_*) graph. *n* neutral, *ma* monoanion and *da* dianion.

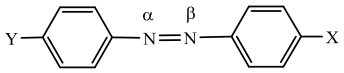
Table 9. UV-visible and ionization data for compounds *I* to *V*.

Comp.	Process	Spectral maximum λ/nm			Acidity measurements						
		Neutral species [a] (log ε_{max})	Monocation [b] (log ε_{max})	Dication [c] (log ε_{max})	λ_{max} (nm) [d]	Half protonation ($H^{1/2}$) [e]	Half protonation ($H^{1/2}$) [f]	m [i]	pK_{a3} [g]	pK_{a4} [h]	Correlation (R^2) [j]
I	***n*** ⇌ ***mc***	448 (4.52)	480 (4.23)		468	2.17 ± 0.07		0.97	2.10		0.99
	mc ⇌ ***dc***		480 (4.23)	478 (4.51)	468		-0.31 ± 0.07	1.40		-0.43	0.97
II	***n*** ⇌ ***mc***	440 (4.47)	386 (4.13)		445	4.67 ± 0.01		0.97	4.53		0.99
	mc ⇌ ***dc***		386 (4.13)	463 (4.52)	445		-0.50 ± 0.05	1.24		-0.62	0.99
III	***n*** ⇌ ***mc***	434 (4.47)	390 (4.28)		434	3.10 ± 0.09		1.23	3.81		0.99
	mc ⇌ ***dc***		390 (4.28)	471 (4.45)	434		-0.95 ± 0.07	1.43		-1.36	0.99
IV	***n*** ⇌ ***mc***	431 (4.59)	387 (4.40)		431	2.72 ± 0.05		1.26	3.42		0.99
	mc ⇌ ***dc***		387 (4.40)	464 (4.58)	431		-0.34 ± 0.04	1.29		-0.44	0.99
V	***n*** ⇌ ***mc***	432 (4.37)	382 (4.33)		469	7.06 ± 0.01		1.02	7.20		0.99
	mc ⇌ ***dc***		382 (4.33)	469 (4.57)	469		0.90 ± 0.04	0.72		0.64	0.99

[a] Measured in pH=7 buffer solution. [b] Measured in pH=1 buffer solution. [c] Measured in 98 % H_2SO_4. [d] The wavelength for pK_a determination. [e] Half protonation values ± uncertainties refer to the standard error for the first protonation. [f] Half protonation values ± uncertainties refer to the second protonation. [g] First protonation acidity constants values. [h] Second protonation acidity constants values. [i] Slopes of log I - *pH* plot. [j] Correlations for log *I* as a function of *pH* (or *H_*) graph. *n* neutral, *mc* monocation and *dc* dication.

The possible ionization patterns are shown in Figs. 6 and 7 at acidic and basic pH values. Eq. (3) was used to calculate the acidity constants.

The acidity constant (pK_a) of azobenzene (X=H and Y=H), N,N-dimethylamino-4-azobenzene (X=NMe_2 and Y=H) and N,N-dimethylamino-4'-hydroxyazobenzene (X=NMe_2 and Y=OH) compounds are reported as -2.50, 3.50 and -0.90, respectively for *βN* azo protonation in the literature [16].

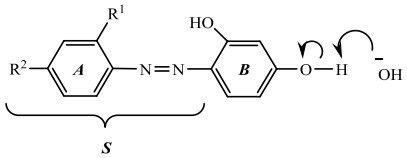


X=H, NMe_2 Y=H, OH

The ionization constants of resorcinol are reported as 9.32 and 11.10, respectively for the first and second deprotonation, respectively [18,43].

First Deprotonation

The first deprotonation takes places in neutral medium by removal of protonation from the *p*-OH group of ring ***B***. The related mechanism is shown below.



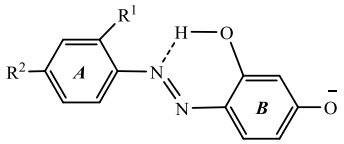
When the compounds were ordered by increasing acidity for the first deprotonation (pK_{a1}), the following trend was obtained:

Compound	:	***V***	***I***	***II***	***III***	***IV***
Half deprotonation (pH$^{1/2}$)	:	7.06	6.50	6.93	6.42	6.13
Slope (*m*)	:	0.74	1.03	0.92	0.96	0.95
pK_{a1}	:	8.25	6.69	6.37	6.14	5.82

increasing acidity ⟶

The pK_a value of resorcinol for the first ionization is reported as 9.32 [18]. Therefore, the attached ***S*** group increased the basicity or decreased the acidity of the resorcinol moiety. If we compare the pK_a values of the studied compounds (*I* to *V*), we can conclude that the electron-withdrawing effects of the iodine and chlorine atoms were reflected by the increase in acidity. If the donor and acceptor groups are conjugated with the aromatic ring, the groups affect the strength of the hydrogen-bond [44,45].

When the process described above occurs, the azo compounds, including the *ortho* substituent, form temporary hydrogen bond. Compounds *III* and *IV* are in the hydrazone form with effective intramolecular N…H—O hydrogen bonding [44,45]. This situation might arise from the formation of stronger hydrogen bonding in the compounds.

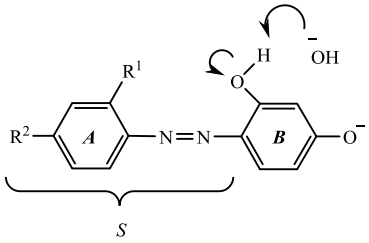


R^1 = I for compound *III*
R^2 = Cl for compound *IV*

The slope of *m*=0.74 for compound *V* is different from that of the other four compounds; those compounds have a slope of approximately unity. This deviation might indicate differences in the deprotonation mechanisms. In compound *V*, the first deprotonation presumably occurs at the *p*-OH group of ring ***A*** unlike the other four compounds; for those compounds, the first deprotonation occurs at the *p*-OH group of ring ***B***.

Second deprotonation

In these compounds, the phenolic hydroxyl group on ring ***B*** located at the *ortho* position to the azo group donates a proton to the medium according to the mechanism outlined below.



Compounds *I* to *V* are more acidic than resorcinol (pK_a value for second deprotonation 11.10) for the second deprotonation. When we take the increasing pK_a values of compounds (*I* to *V*) into account we obtain the following trend:

Compound	***:***	***V***	***I***	***II***	***III***	***IV***
Half protonation ($H_{-}^{1/2}$)	:	14.90	13.15	13.46	13.14	13.17
Slope (*m*)	:	0.95	0.94	0.90	0.76	0.74
pK_{a2}	:	14.15	12.36	12.11	9.99	9.74

increasing acidity ⟶

The effect of the substituents on ring ***B*** can clearly be observed using this trend. The slopes for compounds *I*, *II* and *V* slopes are around unity. However, for compounds *III* and *IV*, the slope (*m*) values are 0.76 and 0.74, respectively. The acidity of compounds *III* and *IV* increased due to the inductive electron-withdrawing effect of the chlorine atom slope about unity. For all compounds, the second deprotonation occurred at the *o*-OH group of ring ***B***.

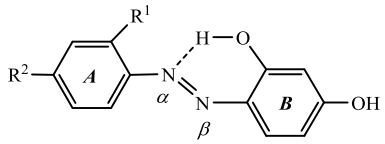
First protonation

When we put the pK_a values in an increasing acidity order for the first protonation we obtained the following trend:

Compound	***:***	***V***	***II***	***III***	***IV***	***I***
Half protonation ($pH^{1/2}$)	:	7.06	4.67	3.10	2.72	2.17
Slope (*m*)	:	1.02	0.97	1.23	1.26	0.97
pK_{a3}	:	7.20	4.53	3.81	3.42	2.10

increasing acidity ⟶

The first protonation seems to occur at the *βN* as suggested in the literature [17]. Obviously the electron donation of the two hydroxyl groups located at the *o*- and *p*-positions of ring ***B*** is more than that of the *p*- located OH group on the ***A***; therefore, *βN* becomes electron rich compared to α*N*. This result correlates well with the Hammett approach. The most acidic compound for the first protonation seems to be compound *I*, while the least acidic (or the most basic) is compound *V*. The slopes of 0.97 and 1.02 reflect the protonation from *βN*. Therefore, the 7.20–2.10=5.10 pK_a unit differences (i.e., 5.10x1.37=6.85 kcal mol^{-1} in energy terms) may arise from the stronger hydrogen bonding formation in compound **1**.



Second protonation

When we put the pK_{a4} values of the studied compounds in increasing acidity order for the second protonation we obtain the following trend:

Compound	:	***V***	***I***	***IV***	***II***	***III***
Half deprotonation ($H_o^{1/2}$)	:	*0.90*	*-0.31*	*-0.34*	*-0.50*	*-0.95*
pK_{a4}	:	*0.64*	*-0.43*	*-0.44*	*-0.62*	*-1.36*
Slope (m)	:	*0.72*	*1.40*	*1.29*	*1.24*	*1.43*

increasing acidity ⟶

All derivatives have the second protonation that occurs at *αN* because *βN* has been protonated. A nitrogen atom next to a quaternary nitrogen atom cannot be protonated easily. Therefore, all pK_a values were lowered (i.e., acidity increased) due to this neighboring group participation. When we consider the slopes of the second protonation measurements for compounds *I* to *V*, all the other compounds seem to protonate with the same mechanism (tertiary amine protonation) apart from compound *V*. However, compound *V* acts differently and exhibits a classic Hammett base protonation mechanism (i.e., m = 0.72). The first protonation might occur due to the electron-donating effect of the *p*-OH group of ring ***A***.

4. CONCLUSIONS

In conclusion, the tautomeric equilibrium of the synthesized monoazo dyes was evaluated in different solvent media. The tautomeric equilibria strongly depended on the solvent medium. In neutral solvent phases, no tautomeric effects were observed. The azo-hydrazones exhibited a tautomeric effect in both basic and acidic media. The tautomerism of both monoazo compounds shows that when changing the solvent polarity, the λ_{max} value is influenced less. Moreover, the acidity constants were investigated in detail. The first deprotonation occurs at the *para* hydroxyl group of ring ***B*** for compounds *I* to *V*. The second deprotonation occurs at the *ortho* hydroxyl group of ring ***B*** for compounds *I* to *V*. The first protonation and the second protonation occur at *βN* and *αN*, respectively, for all compounds.

Acknowledgement(s): This article is dedicated to the memory of our colleague Prof. Dr. Cemil Öğretir who passed away on January 19, 2011.

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