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Articles

Spectroscopic Determination of Acidity Constants of Some Monoazo Resorcinol Derivatives

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The acidity constants, as pK_a values, of six monoazo resorcinol derivatives were determined by the UV–visible spectroscopic technique at 25 °C (± 0.1 °C). The protonation and deprotonation behaviors of the studied molecules were studied from the super basic to the super acid region (i.e., 10 N NaOH to 98 % H_2SO_4) including the pH region. It was observed that deprotonation occurs at the resorcinol ring. The first protonation occurs at the nitrogen atom next to the resorcinol ring, whereas the second protonation occurs at the nitrogen atom next to the phenyl ring.

Introduction

Klotz et al. concluded that the first protonation for 4-aminobenzene dyes takes place exclusively on the amino nitrogen.[1] In a later study, the basicity and absorption spectra of some aminoazobenzenes were correlated with the position of proton addition along with the tautomer concept of proton addition.[2] Further studies on the first conjugated acid of *p*-dimethylaminoazobenzene were reported.[3–6] The basicities of 12 monosubstituted derivatives were determined, and it was concluded that the structure of the conjugate acid of azobenzene involves protons bonded simultaneously to both nitrogen atoms, rather than a localized N—H bond.[7]

In the present work, we report the determination of the basicities, which are expressed as acidity constants, pK_a values, of a series of six multisubstituted 4-(phenyldiazonyl)benzene-1,3-diol derivatives.

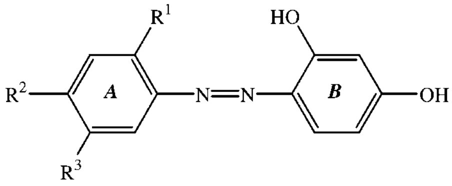
Experimental Section

Materials and Solutions. The studied compounds (Table 1) were of spectroscopic grade, and the method of synthesis is described in refs 8 and 9. Methanol, ethanol, glycine, KOH, H_2SO_4, HC1, CH_3COOH, CH_3COONa, NaOH, KH_2PO_4, Na_2CO_3, $NaHCO_3$, NaCl, methyl orange indicator, phenolphthalein indicator, and standard buffer solutions were from Merck and were not purified further.

Apparatus. pH measurements were performed using a glass electrode. Standard buffer solutions of pH values of 1, 7, and 13 were used in the calibration of the Corning pH/ion analyzer 350 Meter and the Ohaus Advanturer balance, and a Shimadzu UV2101 PC UV–vis scanning spectrometer was used for measurements. Measurements were made at (25 ± 0.1) °C (Badthermostat HAAKE DL 30 W 26).

Procedure. Acid solutions were prepared with H_2SO_4 % (w/w) [(0.0049 to 98) % H_2SO_4] in water.[10] The CO_2-free NaOH solutions were prepared with NaOH pellets [(1 to 16.4) $mol\cdot dm^{-3}$] in water.[11] Buffer solutions were prepared by using Perrin's descriptions.[12] The potentiometric measurements were performed by measuring the hydrogen ion concentration (under nitrogen atmosphere) at (25 ± 0.1) °C, and ionic strengths of the media were maintained at 0.1 using NaCl.

Table 1. IUPAC Nomenclature of the Studied Molecules [1 to 6]



	molecule	substituents		
no.	IUPAC name	R^1	R^2	R^3
1	4-(phenyldiazenyl)benzene-1,3-diol	H	H	H
2	4-[(2,4-dihydroxyphenyl)diazenyl]-benzenesulfonic acid	H	SO_3H	H
3	4-[(2-hydroxyphenyl)diazenyl]-benzene-1,3-diol	OH	H	H
4	4-[(2,4-dihydroxyphenyl)diazenyl]-3-hydroxybenzenesulfonic acid	OH	H	SO_3H
5	4-[(2-chlorophenyl)diazenyl]-benzene-1,3-diol	Cl	H	H
6	4-[(2-nitrophenyl)diazenyl]-benzene-1,3-diol	NO_2	H	H

Spectrometry is an ideal method[13] when a substance is not soluble enough for potentiometry or when its pK_a value is particularly low or high (e.g., less than 2 or more than 11).

This method depends on the direct determination of the ratio of the concentration of molecular species, that is, the neutral molecules corresponding to the ionized species in a series of nonabsorbing buffer solutions for which pH values are either known or measured.[13] For determining the acid dissociation constant of very weak bases, solutions of known H_o (designed for H_2SO_4) take the place of the buffer solutions mentioned

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Table 2. UV–Visible Data and Deprotonation Acidity Constants for the Studied Molecules (1 to 6)

		spectral maximum λ/nm			acidity measurements			
		neutral species[a]	monoanion[b]	dianion[c]				
compd	process	(log ϵ_{max})	(log ϵ_{max})	(log ϵ_{max})	λ_{max}[d]	pK_a[e]	pK_a[f]	correlation[g]
1	$n \rightleftharpoons ma$	430.5(3.07)	460.1(3.37)		431.0	6.44 ± 0.032		0.99
	$ma \rightleftharpoons da$		460.1(3.37)	485.5(3.40)	460.0		14.06 ± 0.007	0.98
2	$ma \rightleftharpoons dma$	428.6(3.10)	490.9(3.20)		430.0	7.16 ± 0.023		1.00
	$dma \rightleftharpoons tma$		490.9(3.20)	503.9(3.30)	490.0		13.68 ± 0.073	0.99
3	$n \rightleftharpoons ma$	450.0(3.05)	485.6(3.41)		450.0	10.76 ± 0.079		0.92
	$ma \rightleftharpoons da$		485.6(3.41)	500.0(3.41)	485.0		15.09 ± 0.046	0.99
4	$ma \rightleftharpoons dma$	442.1(3.09)	421.1(3.15)		442.0	6.62 ± 0.075		0.99
	$dma \rightleftharpoons tma$		421.1(3.15)	489.5(3.10)	421.0		13.40 ± 0.110	0.99
5	$n \rightleftharpoons ma$	431.3(3.37)	487.5(3.50)		432.0	6.19 ± 0.035		0.99
	$ma \rightleftharpoons da$		487.5(3.50)	493.8(3.27)	487.0		12.69 ± 0.057	0.99
6	$n \rightleftharpoons ma$	403.0(3.11)	401.0(3.45)		–	–	–	–
	$ma \rightleftharpoons da$		401.0(3.45)	400.0(3.35)	–	–	–	–

[a] Measured in pH = 7 buffer solution. [b] Measured in 0.1 N NaOH. [c] Measured in 10 N NaOH. [d] The wavelength for pK_a determination. [e] First deprotonation acidity constant values ± uncertainties refer to the standard error. [f] Second deprotonation acidity constant values ± uncertainties refer to the standard error. [g] Correlations for log I as a function of pH (or $H\_$) graph.

Table 3. UV–Visible Data and Protonation Acidity Constants for the Studied Molecules (1–6)

		spectral maximum λ/nm			acidity measurements			
		neutral species[a]	monocation[b]	dication[c]				
compd	process	(log ϵ_{max})	(log ϵ_{max})	(log ϵ_{max})	λ_{max}[d]	pK_a[e]	pK_a[f]	correlation[g]
1	$n \rightleftharpoons mc$	430.0(3.07)	384.2(3.37)		431.0	1.69 ± 0.044		0.99
	$mc \rightleftharpoons dc$		384.2(3.37)	460.6(3.38)	431.0		−4.29 ± 0.021	0.99
2	$n \rightleftharpoons mc$	428.6(3.10)	384.4(3.20)		430.0	1.61 ± 0.049		1.00
	$mc \rightleftharpoons dc$		384.4(3.20)	462.3(3.10)	430.0		−6.31 ± 0.034	0.98
3	$n \rightleftharpoons mc$	450.0(3.05)	425.0 to 485.0(3.41)		326.5	6.08 ± 0.029		0.99
	$mc \rightleftharpoons dc$		425.0 to 485.0(3.41)	483.3(3.41)	326.5		−1.19 ± 0.058	0.96
4	$n \rightleftharpoons mc$	442.1(3.09)	434.1 to 490.0(3.10)		442.0	0.17 ± 0.012		0.99
	$mc \rightleftharpoons dc$		434.1 to 490.0(3.10)	471.1(3.09)	442.0		−0.33 ± 0.012	0.99
5	$n \rightleftharpoons mc$	431.30(3.37)	387.5(3.16)		432.5	2.23 ± 0.085		1.00
	$mc \rightleftharpoons dc$		387.5(3.16)	462.8(3.33)	432.5		−1.11 ± 0.020	1.00
6	$n \rightleftharpoons mc$	403.0(3.10)	418.0(3.37)		403.0	2.77 ± 0.037		1.00
	$mc \rightleftharpoons dc$		418.0(3.37)	376.3 to 457.9(3.40)	403.0		−5.53 ± 0.025	0.97

[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] First protonation acidity constant values ± uncertainties refer to the standard error. [f] Second protonation acidity constant values ± uncertainties refer to the standard error. [g] Correlations for log I as a function of pH (or H_o) graph.

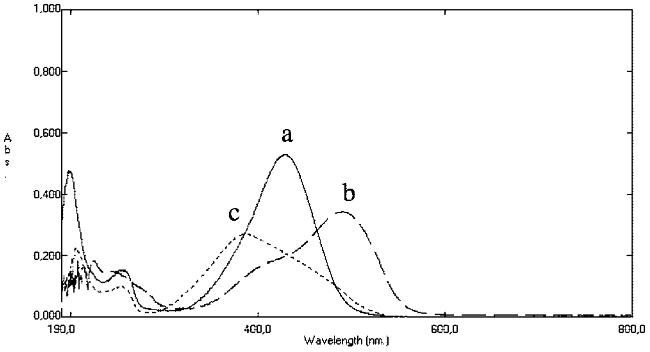


Figure 1. UV–visible spectrum of compound **2**. (a) Neutral molecule, pH = 7. (b) Monoanion, 0.1 N NaOH. (c) Monocation, pH = 1.

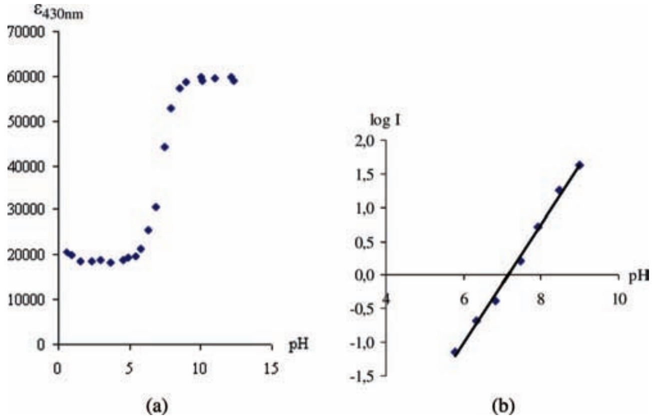


Figure 2. (a) pH−ϵ_{430nm} plot. (b) pH−log I plot for molecule **2** for the first protonation (R^2 = 0.997).

above. For the protonation of the anion of a weak acid, which yields the neutral molecule, the function $H\_$ (designed for NaOH) was used.[14] This scale was constructed by the use of optically absorbing acids just as bases were used for the H_o scale. As a measure of the acidity degree to which a weak organic base is protonated, Hammett and Deyrup established the H_o acidity scale.[15] This scale was improved by Jorgenson and Hartter[16] and then by Johnson et al.[17] For a weak base B which ionizes by simple proton addition, the H_o, $H\_$, or pH values at half-protonations were measured for several compounds during the course of the present work, using the UV–vis spectrophotometric method of Johnson et al.[18] This method takes into account any effect of the medium on the wavelength of the maximum UV absorption and the corresponding extinction coefficient. This effect is particularly significant at high acidities. The protonation of a weak base can be defined as follows

$$\mathrm{HX} + \mathrm{SH} \rightleftharpoons \mathrm{X}^- + \mathrm{SH}^+ \qquad (1)$$

where SH is the solvent. Then, the equilibrium constant might be expressed in terms of activity (eq 2)

$$K_a = \frac{a_{X^-} \cdot a_{SH_2^+}}{a_{HX}} \qquad (2)$$

By inserting the equivalence of a in eq 2 (where $a = c\gamma$; a = activity; γ = activity coefficient; c = concentration), we can derive eq 3

$$K_a = \frac{[X^-]}{[HX]} \cdot \frac{\gamma_{X^-}}{\gamma_{HX}} \cdot a_{SH_2^+} = h_x \frac{[X^-]}{[HX]} \qquad (3)$$

and bearing in mind that

$$h_x = \frac{\gamma_{X^-}}{\gamma_{HX}} \cdot a_{SH_2^+} \qquad (4)$$

when we insert the h_x value in eq 3, we obtain eq 5.

$$H_x = -\log h_x = pK_a - \log \frac{[HX]}{[X^-]} \qquad (5)$$

where H_x is an acidity function. The H_o scale is defined such that for the uncharged primary aniline indicators used a plot of log I (i.e., log([HX]/[X])) against H_o has unit slope. It was observed from work on bases other than the Hammett-type that the slopes of the plots of log I against H, shown by m, were not always unity. Thus, a series of structurally similar bases, like triarylmethanols,[19] primary amides,[20,21] and tertiary aromatic amines,[22] defined individual acidity functions, H_R, H_A, and H''', which have a linear relationship to H_o with m values of 2.0, 0.6, and 1.3, respectively. The various acidity functions do not exhibit linearity but only over limited ranges. Cox and Yates developed the excess acidity function X based on the linearity between the activity coefficients involved in the various acidity functions HX − log C.[21]

Therefore, an experimental plot of log I against H_o does not yield the pK_a at log I = 0, unless it is a Hammett base, but rather the H_o at half-protonation ($H^{1/2}$). The general eq 3 may therefore be applied. By rearranging eq 5, we can get eq 6

$$pK_a = H^{1/2} + \log I \qquad (6)$$

and mathematically it can be expressed as a straight line ($y = mx + n$) with a slope of m so it becomes as follows (eq 7)

$$pK_a = m \cdot H^{1/2} + \log I \qquad (7)$$

Since at the half-protonation point log I will be equal to zero, we will end up with eq 8.

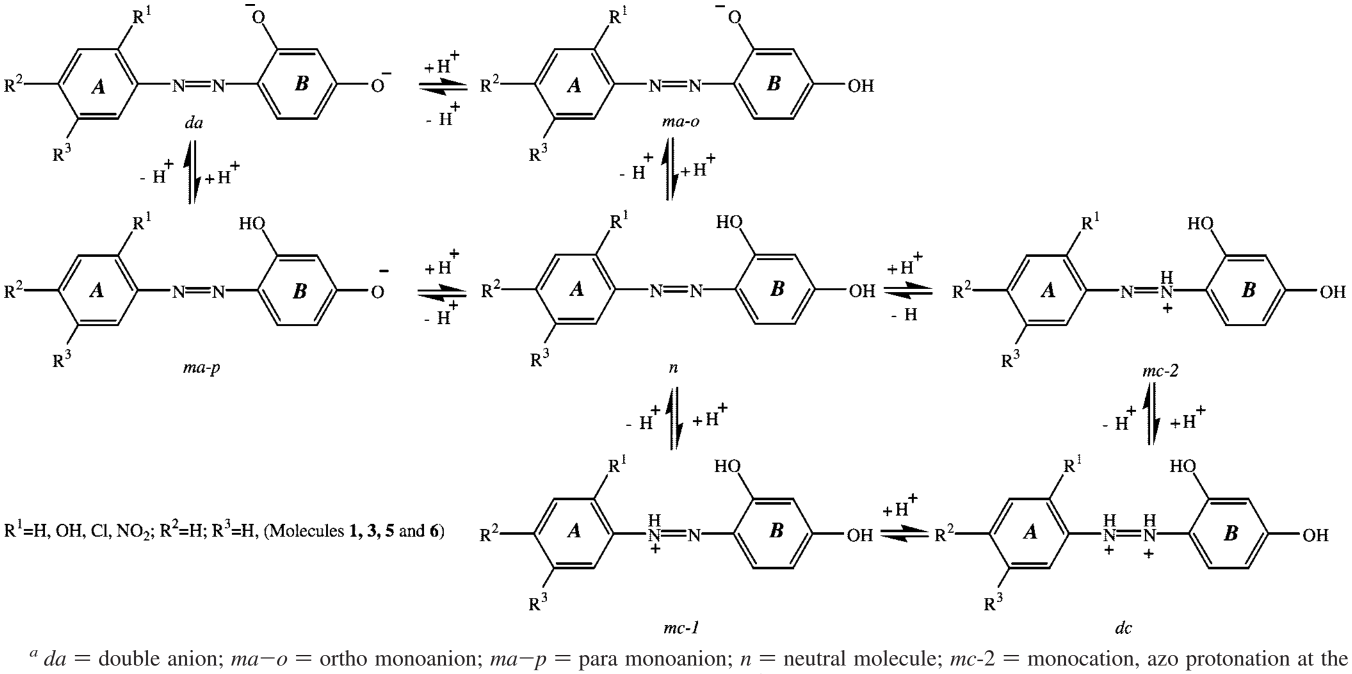
$$pK_a = m \cdot H^{1/2} \qquad (8)$$

Generally, those bases for which m lies roughly between 0.85 and 1.15 are called "Hammett Bases", and m is taken as unity. Therefore, it is important to take into account the size of m as well as the half-protonation value of $H^{1/2}$ in the super acidity region.

It is well established that the basic properties of aqueous alkalies increase with concentration in a nonlinear manner.[21] The use of $H\_$ in highly alkaline solution has been described in the literature.[22,23] The sigmoid curve approach (see below) should be carried out carefully in this region to make sure that the function being used is a relevant one. Any discussion about the acid dissociation constants in this region should be done by taking the half-protonation values rather than the pK_a values.

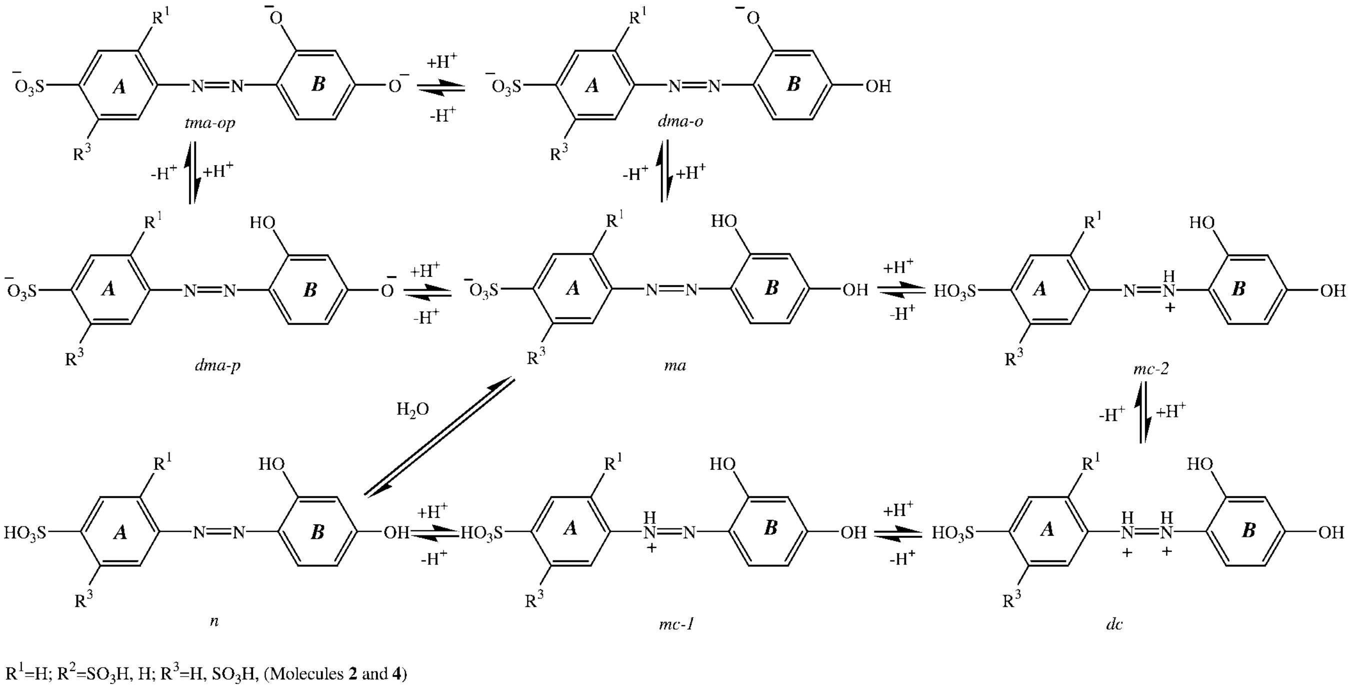
The general procedure applied is as follows: a stock solution of the compound under investigation was prepared by dissolving the compound (about (10 to 20) mg) in water or sulfuric acid of known strength (25 mL) in a volumetric flask. Aliquots (1 mL) of this solution were transferred into 10 mL volumetric flasks and diluted to the mark with sulfuric acid solutions of various strengths or buffers of various pH. The total mass of solution in each flask was measured, and the mass percent of sulfuric acid in each solution was then calculated knowing the mass of sulfuric acid added and the total mass of the final solution. In the case of buffer solutions, the pH was measured before and after addition of the new solution. The optical density of each solution was then measured in 1 cm cells, against solvent blanks, using a constant temperature cell-holder Shimadzu UV2101 PC UV–visible Scanning Spectrometer thermostatted at 25 °C (to within ± 0.1 °C). The wavelengths were chosen such that the fully protonated or deprotonated form of the substrate had a much greater or a much smaller extinction coefficient than the neutral form. The analytical wavelengths,

Scheme 1. Possible Protonation and Deprotonation Pattern for the Studied Molecules 1, 3, 5, and 6[a]



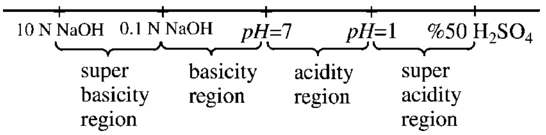
[a] *da* = double anion; *ma−o* = ortho monoanion; *ma−p* = para monoanion; *n* = neutral molecule; *mc*-2 = monocation, azo protonation at the ring (**B**) attached nitrogen atom; *mc*-1 = monocation, azo protonation at the ring (**A**) attached nitrogen atom; *dc* = double cation, diazo protonated.

Scheme 2. Protonation and Deprotonation Pattern for Molecules 2 and 4[a]

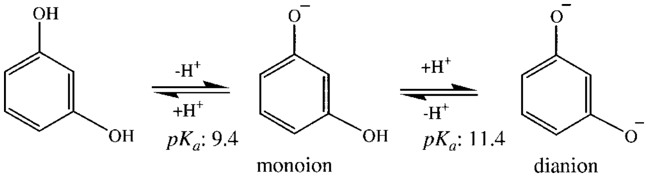


[a] n = neutral molecule; ma = deionization, monoion for SO_3^-; $dma-p$ = double anion for SO_3H and p-OH; $dma-o$ = double anion for SO_3H and o-OH; $tma-op$ = tree anion for SO_3H, o-OH, and p-OH; mc-1 = monocation, azo protonated at the ring (**A**) attached nitrogen atom; mc-2 = monocation, azo protonated at the ring (**B**) attached nitrogen atom; dc = double cation, diazo protonated.

Scheme 3. Acidity and Basicity Scale



Scheme 4. Deprotonation of Resorcinol



the half-protonation values, and the UV absorption maximums for each substrate studied are shown in Tables 2 and 3.

Calculations of half-protonation values were carried out as follows: the sigmoid curve of optical density or extinction coefficients at the analytical wavelength (OD, λ) was first obtained (Figure 1). The optical density of the fully protonated molecule ($OD_{ca.}$; optical density of conjugated acid) and the pure free base ($OD_{fb.}$; optical density of free base) at an acidity were then calculated by linear extrapolation of the arms of the curve. Equation 8 gives the ionization ratio where the OD_{obsd} (OD_{obsd}; the observed optical density) which was converted into a molar extinction ϵ_{obsd} using Beers' Law of OD = $\epsilon \cdot b \cdot c$ (b = cell width, cm; c = concentration, $mol \cdot dm^{-3}$).

$$I = \frac{[HX]}{[X^-]} = \frac{(OD_{obsd} - OD_{fb.})}{(OD_{ca.} - OD_{obsd})} = \frac{(\epsilon_{obsd} - \epsilon_{fb.})}{(\epsilon_{ca.} - \epsilon_{obsd})} \qquad (9)$$

The linear plot of log I against H_o or pH, using the values $-1.0 < \log I < 1.0$, had a slope m and yields the half-protonation value as $H^{1/2}$ at $\log I = 0$ (Figure 2). The pK_a values were calculated by using eq 9.

Since the half-protonation value is equal to pK_a in the pH region, pK_a is going to be equal to the $H^{1/2}$ value of 7.16.

Result and Discussion

Nomenclature and UV–visible spectroscopic data related to deprotonation and protonation processes are depicted in Tables 1 to 3. Possible protonation patterns are shown in Schemes 1 and 2. It seems that the obtained results should be discussed in accord with the scale shown in Scheme 3.

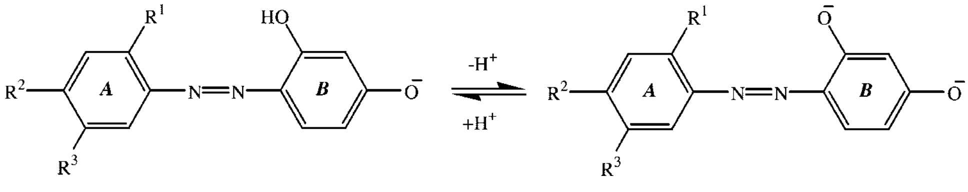
0.1 N to 10 N NaOH Region. The obtained acidity constants for this region can be arranged in the following increasing acidity order (Table 2).

Molecule :	3	1	2	4	5
pK_a :	15.09	14.06	13.68	13.40	12.69

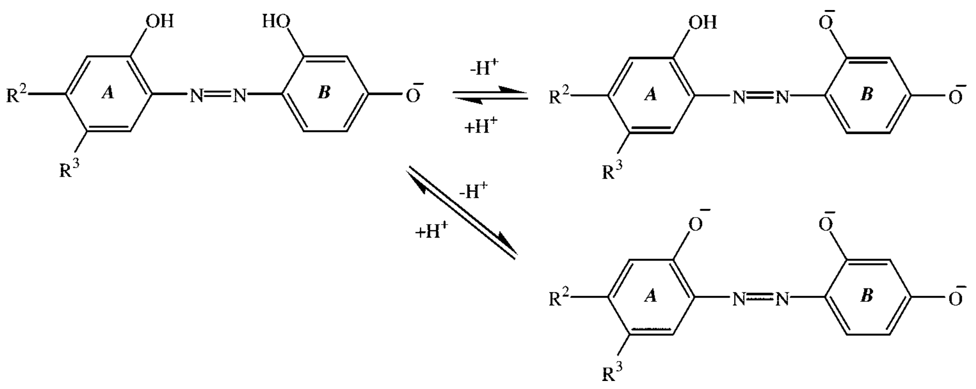
increasing acidity →

The mechanism for the ionization process for compounds **1** to **5** seems to be the same, and they can be considered as the

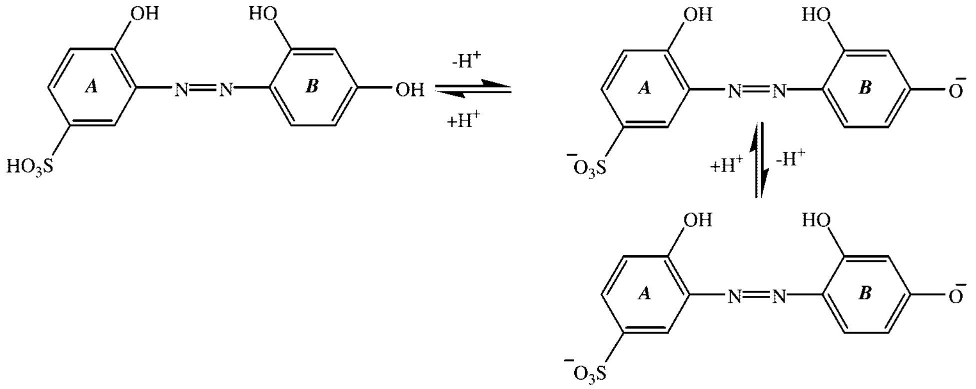
Scheme 5. Second Deprotonation Pattern for Molecules 1, 2, 4, and 5



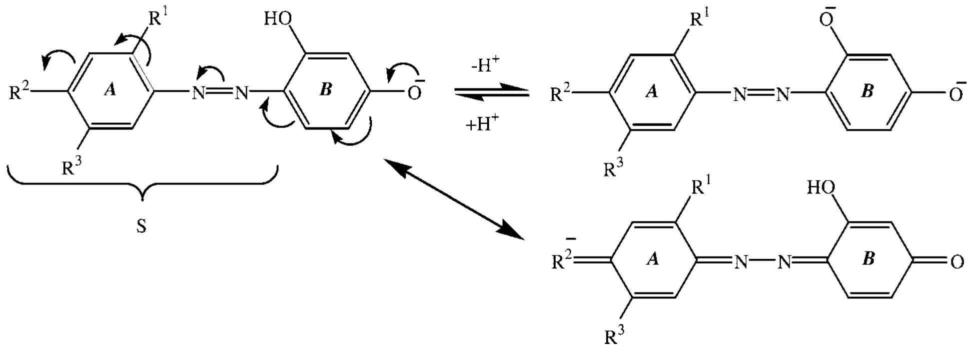
Scheme 6. Possible Second Deprotonation Pattern for Molecule 3



Scheme 7. Deprotonation Pattern for Molecule 4



Scheme 8. Deprotonation Pattern for Molecules 1 to 3 and 5



second deprotonation by taking into account the similarity of resorcinol ionization (Scheme 4).[24]

The most basic or the least acidic molecule seems to be molecule **3**. In fact, molecule **3** has two pK_a values within this region. The second pK_a value was found to be 10.76 (Table 2). This situation arises due to the presence of the third phenolic OH group on the ring **A** which may cause an alternative root for ionization. Since the value of 10.76 is close to the pK_a of phenol (i.e., pK_a = 10.00[25]), we can say that ionization takes place at the phenolic ring **A**, and the deprotonation mechanism therefore is different from the other molecules **1**, **2**, and **5** which are deprotonating with a mechanism similar to resorcinol (Schemes 5 and 6).

In molecule **4**, however, the presence of the sulfonium group causes an entirely different deprotonation mechanism, and the priority of ionization probably goes to that group. So the ionization pattern becomes as shown in Scheme 7.

0.1 N NaOH−pH 7 Region. For molecules **1**, **2**, **4**, and **5**, we can easily see that these molecules are more acidic than the resorcinol molecule for the first deprotonation, and when we rearrange them in an increasing acidity order we get the following trend (Table 2).

Molecule :	**2**	**1**	**5**	**3**
pK_a :	7.16	6.44	6.19	6.08

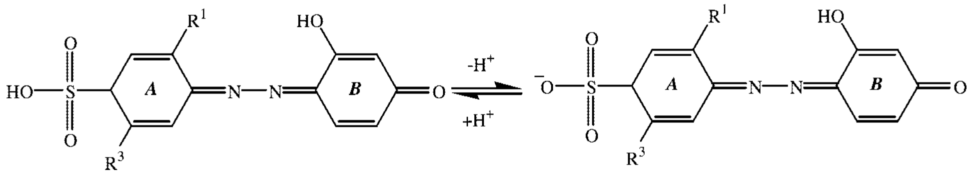
increasing acidity ⟶

It seems that the first deprotonation of molecules **1** to **3** and **5** occurs with a mechanism similar to that shown in Scheme 8.

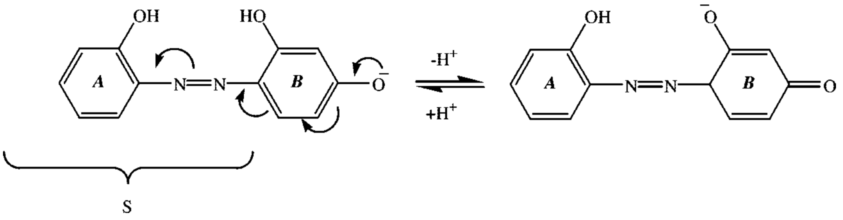
Molecule **2** becomes less aidic due to the electron-withdrawing *p*-sulfonium group. In this way, substituent group **S** withdraws electrons from the ring **B** and makes the deprotonation possible from the sulfonium group as shown in Scheme 9.

Molecule **3** becomes more acidic because it has an electron-donating *meta*-oxygen ion and an electron-withdrawing ortho positioned **S** group which makes the phenolic OH group of the ring **B** slightly more acidic than the others. So the deprotonation may occur as shown in Scheme 10.

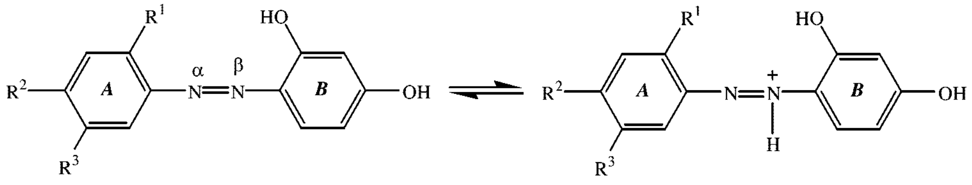
Scheme 9. First Deprotonation Pattern for Molecule 2



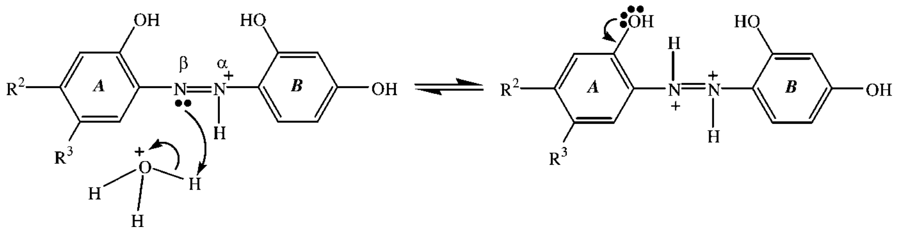
Scheme 10. First Deprotonation Pattern for Molecule 2



Scheme 11. First Protonation Pattern for Molecules 1 to 6



Scheme 12. First Protonation Pattern for Molecules 1 to 6



Molecule **5** is more acidic than molecule **1** because of the electron-withdrawing effect of the chlorine atom on ring **A**. It makes the ionization easier; however, the mechanism of the first deprotonation of molecule **5** and **1** remains the same.

pH 1 to 7 Region. When we put the pK_a values of this region in an increasing acidity order for the first protonation, we obtain the following trend (Table 3).

Molecule :	**6**	**5**	**1**	**2**	**4**
pK$_a$	: 2.77	2.23	1.69	1.61	0.17

increasing acidity ⟶

The first protonation of the studied molecules (Scheme 11) presumably occurs within this slightly acidic region, and with the exception of molecule **3**, the obtained pK_a values are close to each other. For molecule **3**, the first deprotonation occurs in this region of acidity (i.e., pK_a = 6.08) as we have discussed earlier. The protonation in the pH = 1 to 7 range seems to take place at *βN* as suggested in the literature.[2]

The presence of two phenolic hydroxide groups would of course increase the electron density on *βN* through mesomeric electron donation which is located on ring **B** at the ortho and para positions. In molecule **4**, obviously the electron-donating power of the *o*-hydroxyl group has subsided, and the electron-withdrawing power of the sulfonium group comes into effect, making the *βN* more electron-poor. Therefore, molecule **4** becomes the most acidic, whereas molecule **6** becomes the least acidic due to a strong electron-withdrawing effect of the nitro group which is located at the ortho position of ring **A**. It is well-known that the nitro group is a meta directing group. Molecule **5** has a chloride atom which is located at the ortho position of ring **A**. Since the chloride atom withdraws electrons inductively but donates mesomerically, it is ortho para directing and will decrease the electron density of ring **A** making the whole molecule slightly more acidic than that of the nitro group, and as such, it has a smaller pK_a value than that of molecule **6**. In molecule **1**, there is no substituent on ring **A** which means that there exists no effective group on the atom to change the acidity of the molecule. Therefore it is more acidic than molecules **5** and **6**. The pK_a value of 1.61 is very close to the pK_a value of molecule **2** (i.e., pK_a = 1.61), and this is an indication of a very small electron-withdrawing effect of the sulfonium ion in molecule **2**.

−H_o Region. When we put the studied molecules in increasing acidity order for the second protonation, we get the following trend (Scheme 12).

Molecule :	**4**	**3**	**6**	**5**	**1**	**2**
pK$_a$	: -0.12	-0.69	-1.16	-1.23	-2.04	-2.45

increasing acidty ⟶

The second protonation takes place at *βN* for all derivatives because α*N* is already protonated.

As will be appreciated, it is not easy to protonate a nitrogen atom which is next to a quaternary nitrogen atom. For that reason, we can say that all pK_a values were lowered because of this neighboring group participation. The least affected molecule was found to be molecule **4**, followed by molecule **3**. In both molecules, the effect of σ_o(OH) is present on ring **A**. However, in molecule **4** the σ_m(SO_3H) group is effective in decreasing the acidity. The close values of pK_a for the second protonation of molecules **5** and **6** are also expected because they possess the electron-withdrawing Cl atom and NO_2 group on ring **A**, respectively. These electron-withdrawing groups are located ortho to the reaction center. The strongly electron-withdrawing effects of the σ_o(Cl) and σ_o(NO_2) groups caused a lowering of the pK_a values of molecules **1** and **3** for the second protonation as expected. The presence of the SO_3H group at the para position to the reaction center on ring **A** reduces the electron density on the β nitrogen atom by the mezomeric electron-withdrawing effect (i.e., substituent constant for this group is $\sigma_p(SO_3H) = 0.50$) and makes molecule **2** the most acidic for the second protonation.[26]

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