Spectroscopic Determination of Acid Dissociation Constants of Some Pyridyl Shiff Bases

Cemil Öğretir,*,[†] Hakan Dal,[‡] Halil Berber,[‡] and Fadime Fulya Taktak[§]

Department of Chemistry, Faculty of Arts and Sciences, Osmangazi University, 26040 Eskişehir, Turkey,
Department of Chemistry, Faculty of Sciences, Anadolu University, 26470 Eskişehir, Turkey, and
Department of Chemistry, Faculty of Arts and Sciences, Afyon Kocatepe University, Afyon, Turkey

The acid dissociation constants (pK_a) of eight biologically active pyridyl Shiff bases were determined using a UV−vis spectroscopic technique at 25 ± 0.1 °C. The first acidity constants (pK_{a1}) of the 2-[2-aza-2-(3-methyl-(2-pyridly))vinyl]phenol (**1**), 2-[2-aza-2-(3-methyl-(2-pyridly))vinyl]-6-nitrophenol (**2**), 2-[2-aza-2-(3-methyl-(2-pyridly))vinyl]-4-nitrophenol (**3**), 2-[2-aza-2-(3-methyl-(2-pyridly))vinyl]-4,6-dinitrophenol (**4**), 2-[2-aza-2-(5-methyl-(2-pyridly))vinyl]phenol (**5**), 2-[2-aza-2-(5-methyl-(2-pyridly))vinyl]-6-nitrophenol (**6**), 2-[2-aza-2-(5-methyl-(2-pyridly))vinyl]-4-nitrophenol (**7**), and 2-[2-aza-2-(5-methyl-(2-pyridly))vinyl]-4,6-dinitrophenol (**8**) are found to be associated with the protonation of phenolate oxygen. The second acidity constants (pK_{a2}) are found to correspond to protonation of pyridine nitrogen for compounds **5**, **6**, and **7** and oxoprotonation for molecules **1**, **2**, **3**, **4**, and **8**. The third acidity constants (pK_{a3}) are found to be associated with the protonation of pyridine nitrogen for compounds **1**, **3**, **7**, and **8** and amino protonation for molecules **2** and **5**. For molecules **4** and **6**, it is associated with oxo protonation. The contribution of the ketoamino tautomeric form was found to be considerably important.

Introduction

Shiff bases have been used extensively as ligands in the field of coordination chemistry.[1] One of the most important interest is the use of Schiff bases in the photochromism and thermochromism, which originate from the proton transfer from the hydroxyl O atom to the imine N atom in the solid state.[2−4] Proton transfer reactions in Schiff bases have been studied extensively both experimentally and theoretically in the last three decades.[5−13] The charge transport occurs although overlapping intramoleculer proton transfer may also be a basis for the development of molecular switches.[14] The growing interest in orthohydroxy Schiff bases has been observed lately due to their ability to form intramolecular hydrogen bonds by Π-electron coupling between the acid−base centers.[15−18] Such systems are interesting both from the theoretical and the experimental point of view.[15,16] The intramolecular proton transfer reaction proceeds comparatively easily in these compounds. Intramolecular Π-electron coupling leads to the strengthening of the hydrogen bonds in this systems.[19]

The acid dissociation constants have been used in various areas of research, such as stereochemical and conformational structure determinations,[20,21] the directions of nucleophilic and electrophilic attack, the stabilities of intermediates, the size of activation energies in organic reactions,[22] and the determination of the active centers of enzymes in biochemistry.[23] Following our work on imidazoles and pyridazinones,[24,25] we are now reporting on the acid dissociation constants of some biologically active Schiff bases to elucidate structure−reactivity relationships.

Experimental Section

Materials and Solutions. The studied compounds (Table 1) were of spectroscopic grade, and the procedures of synthesis are described elsewhere.[26] 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 14 were used in the calibration of the Corning pH/ion analyzer 350 m and the Ohaus Advanturer balance; a Shimadzu UV2101 PC UV−vis scanning spectrometer was used for measurements.

Procedure. Acid solutions were prepared with H_2SO_4 (w/w) (0.0049 to 96 % H_2SO_4) in water.[27] The CO_2-free NaOH solutions were prepared with NaOH pellets (1 to 16.4 $mol{\cdot}dm^{-3}$) in water.[28] pH solutions were prepared with various reagents (pH 1 to 3 buffer solutions, 0.1 to 0.3 $mol{\cdot}dm^{-3}$ HC1 + 0.3 $mol{\cdot}dm^{-3}$ glycine; pH 4 to 6 buffer solutions, 0.2 $mol{\cdot}dm^{-3}$ CH_3COOH + 0.2 $mol{\cdot}dm^{-3}$ CH_3COONa; pH 7 to 8 buffer solutions, 0.2 $mol{\cdot}dm^{-3}$ KH_2PO_4 + 0.2 $mol{\cdot}dm^{-3}$ NaOH; pH 12 to 13 buffer solutions, 0.1 $mol{\cdot}dm^{-3}$ NaOH).[29] 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.

Spectrometry is an ideal method[30] 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).

Depending on the direct determination of the ratio of the 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, to provide a series of buffers in highly acid regions, acidity functions H_x were used.[31] Thus, for determining the acid dissociation constant

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* Corresponding author. Tel.: +90 222 239 37 50, ext. 2352. Fax: +90 222 239 35 78. E-mail: cogretir@ogu.edu.tr.
[†] Osmangazi University.
[‡] Anadolu University.
[§] Afyon Kocatepe University.

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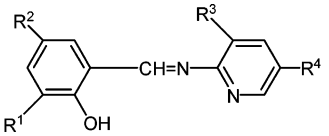
Table 1. Formulas and IUPAC Names for the Studied Compounds 1−8



compd	IUPAC name	R^1	R^2	R^3	R^4
1	2-[2-aza-2-(3-methyl-(2-pyridly))vinyl]phenol	H	H	CH_3	H
2	2-[2-aza-2-(3-methyl-(2-pyridly))vinyl]−6-nitrophenol	NO_2	H	CH_3	H
3	2-[2-aza-2-(3-methyl-(2-pyridly))vinyl]−4-nitrophenol	H	NO_2	CH_3	H
4	2-[2-aza-2-(3-methyl-(2-pyridly))vinyl]−4,6-dinitrophenol	NO_2	NO_2	CH_3	H
5	2-[2-aza-2-(5-methyl-(2-pyridly))vinyl]phenol	H	H	H	CH_3
6	2-[2-aza-2-(5-methyl-(2-pyridly))vinyl]-6-nitrophenol	NO_2	H	H	CH_3
7	2-[2-aza-2-(5-methyl-(2-pyridly))vinyl]−4-nitrophenol	H	NO_2	H	CH_3
8	2-[2-aza-2-(5-methyl-(2-pyridly))vinyl]-4,6-dinitrophenol	NO_2	NO_2	H	CH_3

of very weak bases, solutions of known H_o (designed for H_2SO_4) take the place of the buffer solutions mentioned above. For the protonation of the anion of a strong acid, which yields the neutral molecule, the function $H\_$ (designed for NaOH) was used.[31] 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.[32] This scale was improved by Jorgenson and Hartter[33] and then Johnson et al.[34] 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.[35] 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:[27]

$$HX + SH \rightleftharpoons X + SH_2 \tag{1}$$

where SH is the solvent. Then the equilibrium constant might be expressed in terms of concentration and activity coefficient:

$$K_a = \frac{a_B a_{SH2^+}}{a_{BH^+}}$$

where $a = c\gamma$; $a =$ activity constant; $\gamma =$ activity coefficient; $c =$ concentration:

$$K_a = \frac{[X]}{[HX]} \frac{\gamma_\chi}{\gamma_{H\chi}} a_{SH2^+} = H_x \frac{[X]}{[HX]} \tag{2}$$

Therefore, the pK_a value can be rearranged as follows:

$$H_x = -\log h_x = pK_a - \log \frac{[HX]}{[X]} \tag{3}$$

where H_x is an acidity function. The H_o scale is defined such that, for the uncharged primary aniline indicators used, the plot of log I (i.e., log([BH$^+$]/[B])) 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_o, donated by m, were not always unity. Thus, series of structurally similar bases, like triarylmethanols,[36] primary amides[37,38] and tertiary aromatic amines[39] defined individual acidity functions (H_R, H_A, and H_o), which have a linear relationship to H_o with m values of 2.0, 0.6, and 1.3, respectively. Yates proposed that any acidity function H_x would be proportional to H_o over the entire acidity range, that is, $H_x = mH_o$, with a common point $H_o = 0$.[40]

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 ($H_o^{1/2}$). The general eq 3 may therefore be applied:

$$\log I = m(H_o^{1/2} - H_o) \tag{4}$$

$$\log I = mH_o^{1/2} - mH_o$$

$$\log I = -mH_o^{1/2} + pK_a \text{ and for } \log I = 0$$

It is follows that

$$pK_a = mH_o^{1/2} \tag{5}$$

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 measure m as well as the half-protonation value of $H_o^{1/2}$ for each base studied.

It is evident that yet other acidity functions could exist at the extreme alkaline edge of the pH range, namely, above pH 14, for measuring the pK_a values of weak acids and strong bases, the former with an $H\_$ scale and the latter with a H_o scale. This is a more difficult region of pH than the acidic strength dealt with in the foregoing, insofar as the glass electrode becomes increasingly inaccurate and strong OH^- absorption swamps the reading. It is well-established that the basic properties of aqueous alkalies increase in nonlinear fashion with concentration.[39] The use of $H\_$ in highly alkaline solution was described in the literature.[41,42] 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 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 flask 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 than 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 Scimadzu UV2101 PC UV−Vis. A scanning spectrometer was thermostated at 25 °C

Table 2. UV Spectral Data and Acidity Constants (pK_{a1}) of 1−8 for Proton Loss (or Phenolate Protonation) Process

	spectral maximum λ/nm		acidity measurements		
compd	neutral species[a] (log ϵ_{max})	anion[b] (log ϵ_{max})	λ^c/nm	$pK_{a1}{}^d$	corr[e]
1	301.20(3.85)	377.40(3.77)	256.6	7.379 ± 0.0000	0.993
	256.20(4.08)	268.40(3.92)			
2	425.60(4.11)	418.00(3.76)	410.0	5.578 ± 0.0140	0.998
	291.40(4.12)	286.00(3.91)			
3	391.40(4.04)	403.00(4.25)	403.0	7.637 ± 0.0000	0.996
	293.60(3.76)	281.80(3.79)			
4	361.40(4.30)	361.40(4.18)	299.6	7.310 ± 0.0000	0.998
	300.80(4.08)	286.00(3.93)			
5	310.00(3.79)	377.60(3.94)	377.6	9.313 ± 0.0000	0.942
	255.80(4.00)	267.00(4.05)			
6	411.60(4.07)	409.40(4.05)	300.0	6.234 ± 0.0004	0.979
	295.40(3.96)	290.80(3.94)			
7	388.40(4.13)	403.20(4.22)	410.0	7.164 ± 0.0000	0.915
	359.20(4.11)	217.40(3.71)			
8	361.60(4.27)	361.40(4.27)	309.0	6.888 ± 0.0001	0.997
	296.80(3.97)				

[a] Measured in pH = 7 buffer. [b] Measured in pH = 14 buffer. [c] Analytical wavelength for pK_a measurements. [d] pK_{a1} value ± uncertainties refer to the standard error. [e] Correlations for log I as a function of pH graph.

(to within ± 0.1 °C). The wavelengths were chosen such that the fully protonated form of the substrate had a much greater or a much smaller extinction coefficient than the neutral form. The analytical wavelengths, 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 6 gives the ionization ratio where the OD_{obs} (the observed optical density) was in turn converted into molar extinction ϵ_{obs} using Beers law of OD = ϵbc (b = cell width, cm; c = concentration, mol·dm^{-3}):

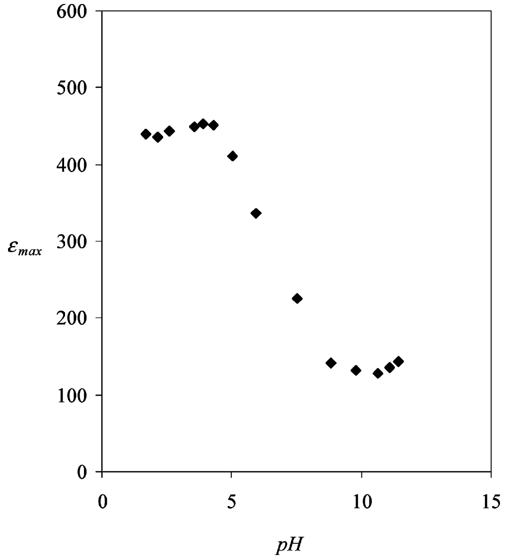


Figure 1. ϵ_{max} as a function of pH (303.60 nm) plot of molecule 1 for the first protonation.

$$I = \frac{[BH^+]}{[B]} = \frac{(OD_{obs} - OD_{fb})}{(OD_{ca} - OD_{obs})} = \frac{(\epsilon_{obs} - \epsilon_{fb})}{(\epsilon_{ca} - \epsilon_{obs})} \qquad (6)$$

The linear plot of log I against H_x or pH, using the values −1.0

Table 3. UV Spectral Data and Acidity Constants (pK_{a2}, pK_{a3}) of 1−8 for the First and Second Protonations

	spectral maximum λ/nm			acidity measurements					
compd	neutral[a] species (log ϵ_{max})	monocation[b] (log ϵ_{max})	dication[c] (log ϵ_{max})	λ^d/nm	$H^{1/2\,e}$	m^f	$pK_{a2}{}^g$	$pK_{a3}{}^h$	corr[i]
1	377.00(3.85)	303.60(3.94)		303.6	6.59 ± 0.15	0.58	3.82		0.98
	269.00(4.10)	256.20(4.08)							
		303.50(3.79)	382.00(3.20)	290	−6.29 ± 0.05	1.05		−6.60	0.98
		256.50(3.94)	288.00(3.90)						
2	425.60(4.11)	346.80(3.94)		346.8	5.32 ± 0.08	0.50	2.66		0.99
	291.40(4.12)	297.80(4.24)							
		347.00(3.91)	391.20(3.72)	390	−6.97 ± 0.07	1.27		−8.85	0.97
		297.50(4.20)	263.60(4.13)						
3	391.40(4.04)	303.00(4.23)		293.6	5.61 ± 0.08	0.65	3.65		0.97
	293.60(3.76)	233.40(4.33)							
		303.00(4.23)	264.20(4.31)	264.2	−8.46 ± 0.06	0.74		−6.26	0.99
	233.60(4.33)								
4	361.40(4.30)	345.60(4.03)		361.4	1.16 ± 0.05	0.63	0.73		1.00
	292.80(4.08)	299.60(4.25)							
		347.20(3.77)	336.60(3.58)	347	−7.23 ± 0.05	0.41		−2.96	1.00
		299.40(3.93)	331.00(3.59)						
5	302.80(3.79)	311.00(3.59)		311	7.35 ± 0.07	0.95	6.98		0.97
	255.80(4.00)	256.00(3.72)							
		311.80(4.03)	399.00(4.38)	256	−5.71 ± 0.04	1.23		−7.02	0.98
		256.00(4.16)	290.00(3.71)						
6	411.60(4.07)	310.20(4.24)		310.2	6.44 ± 0.05	0.80	5.15		1.00
	295.40(3.96)								
		309.80(4.20)	390.80(4.20)	339.0	−7.68 ± 0.09	0.72		−5.53	0.98
7	388.40(4.13)	308.40(4.43)		387.2	4.57 ± 0.012	0.70	3.20		0.97
	359.20(4.11)								
		308.80(4.26)	266.00(4.39)	266	−9.16 ± 0.09	0.43		−3.94	0.97
		234.60(4.34)							
8	361.60(4.27)	309.00(4.25)		361	0.95 ± 0.09	0.52	0.5		0.98
		308.60(4.02)	340.80(3.62)	308	−6.13 ± 0.08	0.84		−5.15	0.99
		232.80(4.31)	259.20(4.15)						

[a] Measured in pH = 7 buffer solution. [b] Measured in 98 % H_2SO_4. [c] Measured in pH = 1 buffer solution. [d] The wavelength for pK_a determination. [e] Half protonation value ± uncertainties refer to the standard error. [f] Slopes for log I as a function of pH (or acidity function H_o) graph. [g] Acidity constant value for the first protonation. [h] Acidity constant value for the second protonation. [i] Correlations for log I as a function of pH (or H_o) graph.

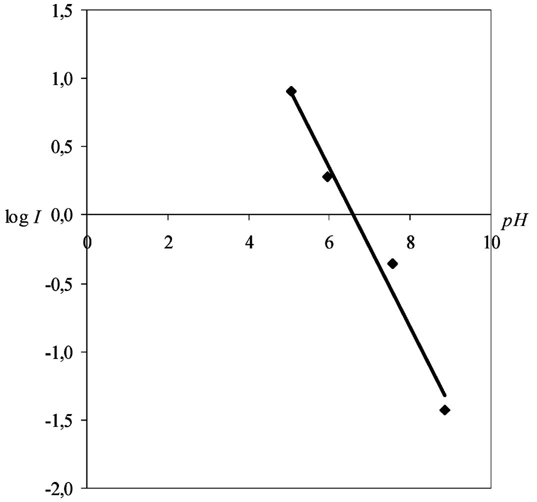


Figure 2. pH as a function of log I (303.60 nm) plot of molecule 1 for the first protonation ($y = -0.5829x + 3.8421$, $R^2 = 0.9799$).

$<$ log $I < 1.0$, had slope m, yielding half-protonation value as $H_x^{1/2}$ or $\mathrm{pH}^{1/2}$ at log $I = 0$ (Figure 2). The pK_a values were calculated by using

$$\mathrm{p}K_a = mH_x^{1/2}\ (\text{or } \mathrm{pH}^{1/2}) \tag{7}$$

Results and Discussion

A major difficulty in obtaining reliable values for the protonation constants of the Schiff bases of salicyl aldehyde with heteroaromatic amines is due to their low solubility and possible hydrolysis in aqueous solutions. Therefore, it is necessary to work at low concentrations, and pH values should be neither extremely low nor extremely high. This poses some limitations on the choice of the method. The spectrophotometric method seems to be the most convenient one. The names and possible protonation patterns of the studied compounds **1**−**8** were depicted in Table 1 and in Scheme 1, respectively.

Depronation. The electronic absorpation spectra and obtained acidity constants for deprotonation (i.e., protonation of phenoxide ion) process are depicted in Table 2. The proton-loss acidity constants ($\mathrm{p}K_{a1}$) have values that range from 5 to 9 and are exposing lower basicities than that of some similar Schiff bases such as salicyl aldehyde, whose $\mathrm{p}K_a$ values were reported to be about 9.[43] The lower basicities (or the higher acidities) of the studied compounds **1**−**8** with the exception of **5** can be attributed to the presence of the strong electron-withdrawing nitro groups. The decrease of the basicity of **3**, **4**, **7**, and **8** is presumably due to the presence of the nitro group in para position of the phenol ring. Taking the first protonation (i.e., phenolate anion) or deprotonation values into account, we can put the studied compounds in a decreasing basicity order as follows:

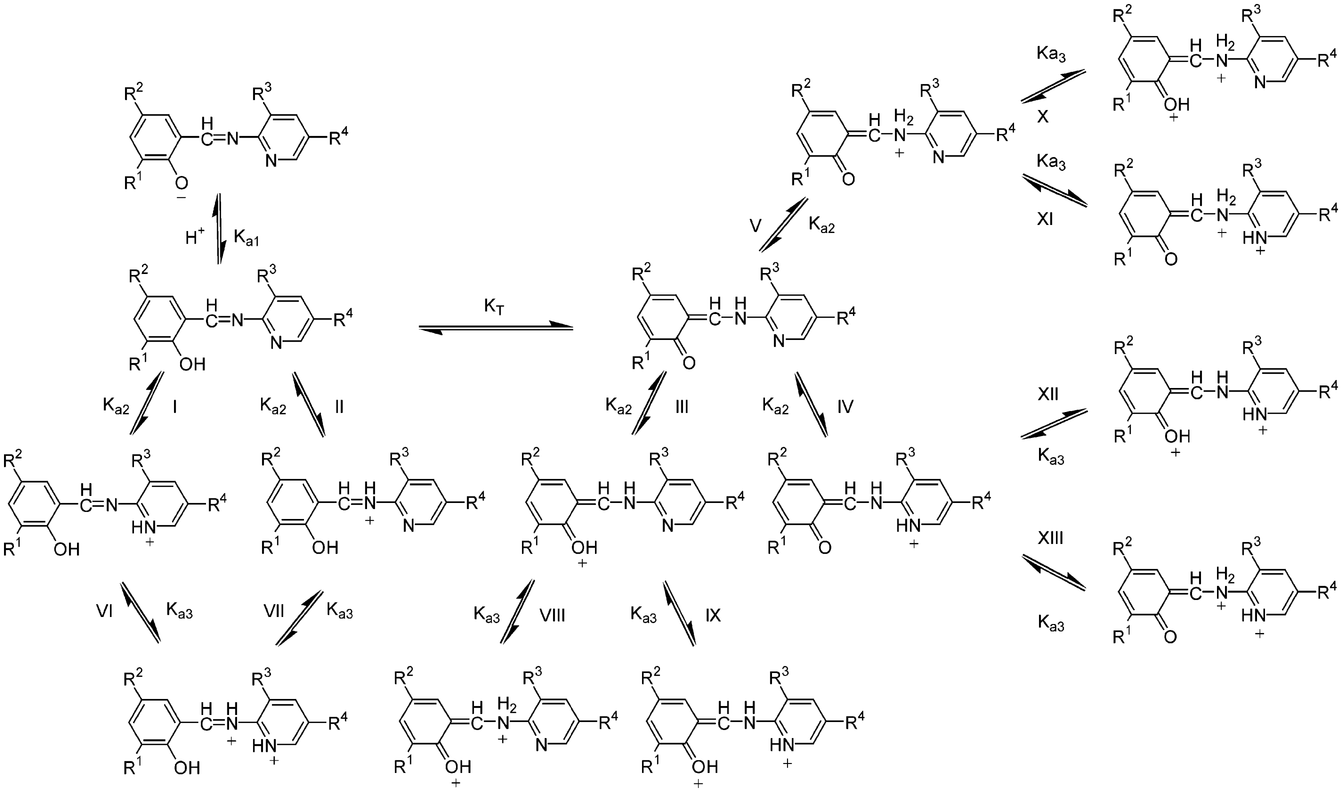
Molecule:	**5**		**3**		**1**		**4**		**7**		**8**		**6**		**2**
pK_{a1}	: 9.31	>	7.64	>	7.38	>	7.31	>	7.16	>	6.89	>	6.23	>	5.58

Decreasing basicity ⟶

This order of decreasing basicity seems logical when one thinks about the inductive electron-donating effect of the methyl group and strong electron-withdrawing effect of the nitro group. The drastic decrease in basicity power for **2** and **6** might well originate from the hydrogen bonding between the hydrogen atom of hydroxyl (−OH) group and minus charged oxygen atom of the nitro ($\mathrm{O{=}N^+{-}O^-}$) groups, which are located next to each other (i.e., ortho substituted) (Figure 3).

Protonation. The UV spectral and protonation data of the studied compounds **1**−**8** are shown in Table 3. Obviously, substitution of the imino nitrogen on the pyridine ring at position 2 leads to a drastic decrease in the basic character of this group due to close proximity of the electron-withdrawing pyridine nitrogen and the basicity of pyridine increases.The sequence of

Scheme 1. Possible Protonation Pattern for Studied Molecules 1−8



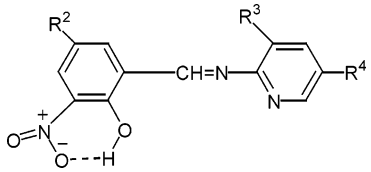


Figure 3. Intramolecular hydrogen bonding.

protonation changes and the first acidity constant (pK_{a1}) of **1**−**8** may be associated with the protonation of the phenolate oxygen, the second acidity constant (pK_{a2}) may be associated with the protonation of the pyridine nitrogen, and the third acidity constant (pK_{a3}) may be associated with the protonation of the imino group of enolimine. Looking at the *m* value, of the log *I* acidity graphs, which are about 0.5, we can predict that the contribution of the ketoamino tautomeric form is important in molecules **1**, **2**, **3**, **4**, and **8** and that these molecules protonate primarily at oxo group (path III). For molecules **5**, **6**, and **7**, the slopes of the log *I* acidity values are about unity and are indicative of pyridine nitrogen atom (path I).

For the third pronation (pK_{a3}), the slopes of log *I* acidity groups (Table 3) are about unity for molecules **1**, **3**, **7**, and **8**, indicating the pyridine nitrogen atom (path IX). They are about 1.30 for molecules 2 and 5, indicating amino protonation (path XIII). For molecules **4** and **6**, however, the slope at about 0.50 is indicative of oxo protonation (path XII).

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