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Complexation Behavior of Heterocyclic Hydrazones. I. Structure and Acid-Base Equilibria for Heterocyclic Hydrazones

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The acid-base equilibria of twenty-one hydrazones substituted by phenyl, pyridyl and/or quinolyl groups have been investigated in aqueous solutions over the region of H_- to H_0 acidity function by a spectrophotometric method at 25 °C. For 2-pyridinecarbaldehyde 2-(5-substituted)pyridylhydrazones, although the proton dissociation of the neutral species (HL) satisfied a Hammett correlation, those of H_2L^+ and H_3L^{2+} did not. The thermodynamic parameters for the proton dissociations of H_2L^+ and H_3L^{2+} of seven representative liqands were determined by a temperature-coefficient method at 25 °C and an ionic strength of 0.1 (KCl). The enthalpy and entropy changes for the proton dissociations of H_3L^{2+} and H_2L^+ were influenced by the steric effects of the methyl group and/or the introduced quinolyl ring. An analysis of the pH dependence of the ^1H NMR signals for three hydrazones in an acetone-d_6–D_2O solution gave more profitable information concerning the fine structures of HL, H_2L^+, and H_3L^{2+}. Each ^1H and ^{13}C NMR chemical shift of some ring-substituted methyl derivatives (HL form) in a dioxane–D_2O solution has been briefly assigned. On the other hand, a single-crystal X-ray analysis, ^1H NMR data in chloroform-d and thermodynamic data for di-2-pyridyl ketone 2-pyridylhydrazone (DPPH) suggested that the intramolecular hydrogen bond in the DPPH molecule is broken by the addition of a proton to the H_2L^+ species in an aqueous solution.

2,2′-Bipyridine (bipy), 2,2′:6,2″-terpyridine (terpy) and 1,10-phenanthroline (phen), which are heterocyclic amines containing only nitrogens as coordinating atoms, have often been used as representative ligands, and have played an important role in coordination chemistry as well as in analytical chemistry. The heterocyclic hydrazones belonging to the above-mentioned category and their metal complexes have been investigated in a considerably wide range.[1—3] A large number of *NNN*-tridentate heterocyclic hydrazones have been used as chromogenic reagents in the spectophotometric determination of transition-metal ions.[4—7] However, the information concerning the properties of these hydrazones and their metal complexes so far reported is not sufficient to predict the complexation behaviors as well as to find adequate chemical species which play a major role in chemical analysis. In order to investigate their complexation behaviors in aqueous solutions, we first examined the acid-base behaviors in connection with their structural properties in solution.

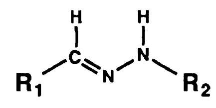
Although a large number of proton dissociation constants of hydrazones have been determined, a mutual evaluation of their values is difficult because of the different experimental conditions used. The thermodynamic parameters of the proton dissociation of hydrazones have been reported for only 2-pyridinecarbaldehyde 2-pyridylhydrazone (PAPH).[8] Although the chemical shifts of the ^1H and ^{13}C NMR spectra of the hydrazone derivatives have been assigned in several organic solvents,[9—11] their NMR behaviors in aqueous or organic aqueous solutions have not yet been investigated. Crystal X-ray analyses of the reagents and their metal complexes have not been reported, except for $Co^{II}(HL)Cl_2$ (HL denotes a neutral form of PAPH).[12] There is also little information concerning the relationship between the acid-base equilibria and the complexation behaviors of these hydrazones.

In the present study we determined the proton dissociation constants of twenty-one *NNN*-tridentate heterocyclic hydrazones in aqueous soltution; the structural formulas of these reagents are shown in Table 1 together with their abbreviated expressions. The thermodynamic parameters for the proton dissociation of representative hydrazones were also determined by the temperature-coefficient method. The proton-dissociation reaction of three hydrazone derivatives (PAPH, PA6MPH, and PA5CPH) in aqueous acetone solutions was investigated by the ^1H NMR method. The chemical shifts of the ^1H and ^{13}C NMR of four hydrazones (PAPH, 6MPAPH, PA6MPH, and 6MPA6MPH) were assigned in aqueous dioxane solutions. The crystal structure of DPPH was determined by single-crystal X-ray diffraction. The acid-base equilibria of hydrazones in aqueous solutions are discussed in conjunction with the spectrometric results.

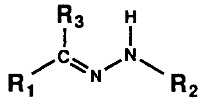
Experimental

Reagents. All of the hydrazones examined were prepared by condensation of the respective aldehydes/ketones and hydrazines in stoichiometric amounts, and were purified by repeated recrystallization from ethanol to a constant melting point. 2-Pyridinecarbaldehyde, 6-methylpyridine-2-carbaldehyde, di-2-pyridyl ketone and 2-hydrazinopyridine were of commercial grade. 2-Quinolinecarbaldehyde was prepared by the oxidation of quinaldine with selenium dioxide. 1-Isoquinolinecarbaldehyde was obtained by the oxidation of 1-methylisoquinoline, which was prepared from glyceraldehyde diethyl acetal by Fischer's method.[13,14] 2-Hydrazinoquinoline and its nitro derivatives were freshly prepared from corresponding 2-chloroquinolines. Other subsituted 2-hydrazinopyridines were prepared by thermal re-

Table 1. Structures and Abbreviations of Hydrazones



Hydrazone (Type I)



R_3 = Py–

Hydrazone (Type II)

	R_1–	R_2–	Abbrevn.
Type I	Py–	Py–	PAPH
	Py–	Qu–	PAQH
	Qu–	Py–	QAPH
	Py–	6-CH_3–Py–	PA6MPH
	6-CH_3–	Py–	6MPAPH
	Qu–	Qu–	QAQH
	6-CH_3–Py–	6-CH_3–Py–	6MPA6MPH
	Py–	5-CH_3–Py–	PA5MPH
	Py–	5-Cl–Py–	PA5CPH
	Py–	5-NO_2–Py–	PA5NPH
	iQu–	Py–	iQAPH
	iQu–	Qu–	iQAQH
	Qu–	5-NO_2–Py–	QA5NPH
	iQu–	5-NO_2–Py–	iQA5NPH
	Phenyl–	Py–	PhAPH
	Py–	Phenyl–	PAPhH
Type II	Py–	Py–	DPPH
	Py–	Qu–	DPQH
	Py–	3-NO_2–Py–	DP3NPH
	Py–	5-NO_2–Py–	DP5NPH
	Py–	Phenyl–	DPPhH

Py-: 2-pyridyl-, Qu-: 2-quinolyl-, iQu-: 1-isoquinolyl-.

flux with hydrazine monohydrate or through diazo compounds which were prepared by diazotization of substituted 2-aminopyridines. The purity of all the reagents was checked by elemental analysis.

The following solutions were used for controlling the acidity in the spectrophotometric measurements: hydrochloric acid, acetic acid, potassium acetate, potassium hydroxide, 2-morpholinoethanesulfonic acid, 3-morpholino-1-propanesulfonic acid, 3-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]amino-1-propanesulfonic acid, 3-cyclohexylamino-1-propanesulfonic acid (Dotite Good's Buffer) and sodium tetraborate. For the NMR measurements, 99.0 atm% D chloroform-*d*, 99.5 atm% D acetone-d_6, 99.75 atm% D deuterium oxide (D_2O) and 99.5 atm% D deuterium chloride (DCl) were used. The other organic and inorganic chemicals were of analytical-reagent grade.

Spectrophotometric Measurements. Hitachi U-3400 and U-3210 programmable spectrophotometers were used for measuring the absorbance in quartz cells with a thermostated 1-cm path length (±0.1 °C) or variable path lengths (0.2, 5.0, and 10.0 cm; 25.0±0.2°C). In the determination of the proton dissociation constants in the 1—12 pH region, the ionic strength of the solution was adjusted to 0.1 with potassium chloride. A Toa Dempa HM-30S pH meter with a combined glass-calomel electrode, standardized against JIS buffer solutions (oxalate, phthalate, phosphate, borate, and carbonate), was used for the pH measurements. The hydrogen ion activity term (the so-called mixed constant15)) determined was converted to the concentration term by using the hydrogen ion activity coefficient determined in a 0.1 M (1 M=1 mol dm^{-3}) KCl solution.16) The acidity function of H_- was applied to sodium hydroxide solutions (described elsewhere17)) in the determination of K_{a3}, except for PA5NPH, QA5NPH, iQA5NPH, and DP5NPH, the K_{a3} values of which were determined by the usual pH measurement. In the determination of the proton dissociation constants (K_{aH4L} and K_{aH5L}), the acidity fuction (H_0 function)18) was used for strongly acid solutions (pH<0.2). The H_0 value corresponding to the concentration of hydrochloric acid was obtained from tables compiled by Arnett and Mach.19) The thermodynamic parameters were determined by a temperature-coefficient method. Each constant was estimated from four data points in the temperature range 8—40 °C. Plots of pK_a against $1/T$ gave good straight lines, so that the values of ΔH and ΔS could be obtained from the slope and intercept, respectively, of the equation $pK_a=\Delta H/2.303RT-\Delta S/2.303R$, where R is the gas constant (R=8.3144 J K^{-1} mol^{-1}). In the cases of PAPH and PA5CPH, measurements were carried out in aqueous 28% (v/v) dioxane solutions having an ionic strength of 0.2 M KCl, due to the low solubility of the reagents in water and a mutual comparison of the results. Dioxane was freshly distilled before use.

Nuclear Magnetic Resonance Measurements. The ^{1}H and ^{13}C NMR spectra of the neutral species (HL) of hydrazones in aqueous dioxane solutions (dioxane : D_2O=7 : 3) were measured on a JEOL JNM-GX 400 FT-NMR spectrometer at the Instrumental Center of the Institute for Molecular Science (Okazaki). The C–H two-dimensional NMR spectra for the assignment of ^{13}C atom were measured on a Varian XL-200 FT-NMR spectrometer. The chemical shifts of the imino proton of hydrazones in chloroform-*d*, together with those of the other proton of PAPH, PA6MPH, and PA5CPH in aqueous acetone solutions (acetone-d_6 : D_2O=6 : 4, 8 : 2, and 8 : 2), were measured on a Hitachi R-90 FT-NMR spectrometer. In all cases, the values of the chemical shifts were estimated with respect to tetramethylsilane. The pH of acetone-d_6–D_2O solutions was adjusted by the addition DCl. A Toa Dempa HM-30S pH meter was used for the pH measurement. The electrode system of the pH meter was calibrated with acetone-d_6–D_2O solutions of known DCl concentrations (3.5×10^{-3}—1.0×10^{-2} M).

Analysis of X-Ray Crystal Structure of DPPH. A single crystal of DPPH with approximate dimensions ($0.60\times0.30\times0.10$ mm^3), which was grown from ethanol, was mounted on a MAC MXC^3 automated four-circle diffractometer. The cell dimensions and diffraction intensities were measured using graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) at room temperature. Crystal data: orthorhombic, $P2_12_12_1$, a=10.637(2), b=16.527(2), c=7.917(3) Å, V=1391.8(6) Å^3 and Z=4. The structure was solved by the direct method with MULTAN 78. The hydrogen atoms were located in a difference Fourier map. The structural refinements were made by a full-matrix least-squares method on a Sun SPARK 2 work station (Crystan program system provided by MAC Science). The final R factors were 0.049 and R_w=0.049 for 21 non-hydrogen atoms with anisotropic temperature factors and 13 hydrogen atoms with isotropic temperature factors based on 1127 independent reflections ($3°\leq2\theta\leq50°$ and $|F_o|>3\sigma(|F_o|)$), which were collected by the 2θ–ω scan method. The anisotropic thermal parameters and the F_o-F_c tables are depicted as Document No. 66054 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Protolytic Equilibria of Hydrazones. A neutral species, HL, of almost all of the twenty-one hydrazones display proton dissociation as well as protonation, where H designate the imino hydrogen of hydrazone. The azomethine and imino nitrogens as well as the heterocyclic nitrogens of hydrazone exhibit acid-base behavior. The overall acid-base equilibria of a hydrazone are defined as:

$$\mathrm{HL} \rightleftharpoons \mathrm{L}^- + \mathrm{H}^+ \qquad K_{a3} \qquad (1)$$

$$\mathrm{H_2L^+} \rightleftharpoons \mathrm{HL} + \mathrm{H}^+ \qquad K_{a2} \qquad (2)$$

$$\mathrm{H_3L^{2+}} \rightleftharpoons \mathrm{H_2L^+} + \mathrm{H}^+ \qquad K_{a1} \qquad (3)$$

$$\mathrm{H_4L^{3+}} \rightleftharpoons \mathrm{H_3L^{2+}} + \mathrm{H}^+ \qquad K_{aH4L} \qquad (4)$$

$$\mathrm{H_5L^{4+}} \rightleftharpoons \mathrm{H_4L^{3+}} + \mathrm{H}^+ \qquad K_{aH5L} \qquad (5)$$

where each proton dissociation constant is designated by the symbol K_a. Figure 1 shows the absorption spectra of PAPH at various acid concentrations. The absorbances at the wavelength of maximum absorption for L^- are measured in the determination of K_{a3}, while the wavelength of maximun absorption of $\mathrm{H_3L^{2+}}$ is selected for the determination of the other dissociation constants. In a similar manner as described previously,[17] all of the proton dissociation constants for each hydrazone were determined spectrophotometrically with attention to the isosbestic points resulting from their spectral changes. The obtained acid dissociation constants are listed in Table 2. The pK_a values of the imino and two pyridinium nitrogens have often been found in analytical literature since those for PAPH were first reported by Green et al.[20] However, a mutual comparison of the constants reported is practically difficult, since most of them were determined in various mixed solvents. Different pK_a values for PAPH in aqueous solution have been reported by Green et al.[20] (pK_{a3}=14.5, pK_{a2}=5.71, and pK_{a1}=2.87 at 25 °C, where K_{a3} was a concentration constant and K_{a2} and K_{a1} were mixed constants at $I\approx0$), Green and Goodwin[8] (pK_{a2}=5.62 and pK_{a1}=2.91 at 25 °C and $I\to0$), Anderegg[21] (pK_{a2}=5.83 and pK_{a1}=3.21 at 20 °C and I=0.1 ($\mathrm{KNO_3}$)) and Ishii et al.[22] (pK_{a2}=5.75 and pK_{a1}=3.01, which were obtained by extrapolation of the values in 10—40% aqueous ethanol at I=0.2 ($\mathrm{NaClO_4}$) to null ethanol). Our results for PAPH are in good agreement with those reported by Anderegg. The values of K_{aH4L} and K_{aH5L} have not yet been reported. The absorbance vs. H_0 plots obtained in this work are well interpreted by assuming only two successive protolytic equilibria corresponding to Eqs. 4 and 5.

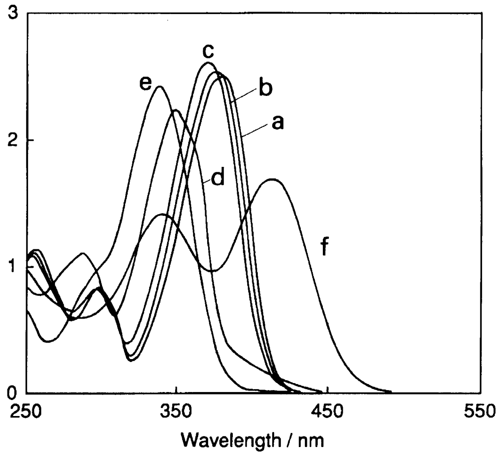


Fig. 1. Absorption spectra of PAPH in aqueous solution. (a) H_0 −3.74, (b) H_0 −1.56, (c) pH 1.08, (d) pH 4.48, (e) pH 8.73, (f) H_- 15.2.

Table 2. Acid Dissociation Constants of Hydrazones at 25 °C and I=0.1

Ligand	pK_{a3}[a]	pK_{a2}	pK_{a1}[b]	pK_{aH4L}[c]	pK_{aH5L}[c]
PAPH	14.82	5.76	3.17	−0.52	−2.49
PAQH	14.12	5.99	2.76	−0.72	−2.45
QAPH	14.1	5.48	2.96	−0.75	−2.30
PA6MPH	15.1	6.20	3.35		
6MPAPH	14.8	6.03	3.84		
QAQH	13.7	5.44	2.50	−0.59	−2.43
6MPA6MPH	15.0	6.44	3.85		
PA5MPH	15.1	5.99	3.28		
PA5CPH	14.1	4.69	2.07		
PA5NPH	11.15	3.99	0.3		
iQAPH	14.6	6.05	3.70	−0.33	−2.00
iQAQH	13.7	5.75	3.64	−0.55	−2.23
QA5NPH	11.05	3.94	0.58	−1.25	
iQA5NPH	11.19	4.91	0.10	−0.5	−2.5
PhAPH	14.9	6.06		−0.65	−2.28
PAPhH	15.5	5.14		−0.83	−2.37
DPPH	15.4	5.41	3.02	0.20	−1.80
DPQH	14.2	5.71	2.80	0.02	−2.12
DP3NPH	13.75	3.76	0.52	−1.78	
DP5NPH	11.18	3.75	0.96	−0.47	−1.3
DPPhH		4.73	1.21	−1.21	−2.9

a) Determined by using H_- function except for PA5NPH, QA5NPH, iQA5NPH, and DP5NPH. b) H_0 function was used for PA5NPH. c) Determined by using H_0 function.

The ^{1}H NMR spectra of PAPH and its monomethyl derivatives in various organic solvents have been assigned by several authors[9,10,23] and a probable confor-

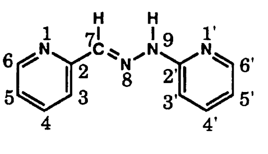


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Chart 1.

mation of HL of PAPH is represented by **1** (Chart 1). The ^{1}H NMR spectra of PAPH (HL form) and its methyl derivatives in aqueous dioxane solution were first examined through a series of NMR studies. The assignment of each spectrum of ^{1}H NMR was carried out by the spin decoupling and the effect of substituent on chemical shifts, in which H_4 and $H_{4'}$ were discriminated by the long-range coupling of H_4 with the formyl proton H_7.9) This H_4 gave an octet showing a fine structure in D_2O24) and acetone-d_6–D_2O solutions (cf. Fig. 4a; $J_{4,7}=0.6$ Hz) as well as in chloroform-*d*9) and CCl_4.10) The results are listed in Table 3. The observed chemical shifts of PAPH, except for the imino proton, are not significantly different from the relevant chemical shifts in dimethyl-d_6 sulfoxide assigned by Bell and Mortimore.10) This implies that the conformation of HL of PAPH in an aqueous solution is also represented by **1**. The protons of the R_2 pyridyl ring of PAPH are more shielded compared with those of the R_1 pyridyl ring. The chemical shift of each ring position in PAPH is subtracted from its counterpart in each of 6MPAPH, PA6MPH, and 6MPA6MPH, the difference being represented as MP, PM, and MM, respectively. Table 4 reveals that the relation, MP+PM≅MM (the additivity of shielding effects), is satisfied for the set. It is obvious from the values of MP and PM that the chemical shifts of another pyridyl ring are little affected by the introduction of a methyl group into the one of pyridyl ring of PAPH.

Although the imino proton signals disappear in a dioxane–D_2O solution, due to a rapid exchange between the imino hydrogen and deuterium, those in chloroform-*d* are obtained as follows (in ppm at a concentration of ca. 8×10^{-2} M): 10.40 for PAPH; 9.10 for PAQH; 8.95 for QAPH; 9.08 for 6MPAPH; 8.5—8.6 for PA5CPH; 13.63 for DPPH; 13.83 for DPQH; 16.05 for DP3NPH; 14.45 for DP5NPH. The imino proton of Type-II hydrozones is relatively more deshielded than that of the relevant Type-I hydrazones, suggesting the presence of an intramolecular hydrogen bond between the imino hydrogen and the nitrogen of the R_3 pyridyl ring for Type-II hydrazones, as mentioned below.

Table 3. ^{1}H NMR Chemical Shifts (in ppm) for Heterocyclic Hydrazones[a)]

Position	Hydrazone			
	PAPH	6MPAPH	PA6MPH	6MPA6MPH
H_3	8.04	7.84	8.01	7.81
H_4	7.84	7.71	7.82	7.70
H_5	7.34	7.19	7.33	7.18
H_6	8.52		8.51	
H_7	8.02	7.97	8.00	7.96
$H_{3'}$	7.37	7.35	7.17	7.14
$H_{4'}$	7.70	7.69	7.57	7.56
$H_{5'}$	6.87	6.86	6.71	6.71
$H_{6'}$	8.13	8.11		
Methyl		2.52	2.38	2.51 2.38

a) Measured in mixed solvent(dioxane : $D_2O=7:3$, total concentration was 4.78×10^{-2}—1.51×10^{-1} M).

Table 4. ^{1}H and ^{13}C NMR Chemical Shifts Relative to PAPH for 6MPAPH, PA6MPH, and 6MPA6MPH

	Hydrazone			
	6MPAPH (MP)	PA6MPH (PM)	6MPA6MPH (MM)	MP+PM
H_3	−0.20	−0.03	−0.23	−0.23
H_4	−0.13	−0.02	−0.14	−0.15
H_5	−0.14	−0.01	−0.16	−0.15
H_7	−0.05	−0.02	−0.06	−0.07
$H_{3'}$	−0.02	−0.20	−0.23	−0.22
$H_{4'}$	−0.01	−0.13	−0.14	−0.14
$H_{5'}$	−0.01	−0.16	−0.16	−0.17
C_2	−0.44	0.11	−0.42	−0.33
C_3	−2.88	0.02	−2.77	−2.86
C_4	0.15	−0.04	0.15	0.11
C_5	−0.49	−0.06	−0.52	−0.55
C_6	9.14	0.05	9.16	9.19
C_7	0.16	−0.16	−0.07	0.00
$C_{2'}$	0.05	−0.30	−0.32	−0.25
$C_{3'}$	−0.02	−3.12	−3.07	−3.14
$C_{4'}$	−0.02	0.23	0.22	0.21
$C_{5'}$	−0.07	−0.70	−0.77	−0.77
$C_{6'}$	0.00	9.23	9.24	9.23

The ^{13}C NMR spectra of the methyl derivatives of PAPH in a D_2O–dioxane solution were assigned by a C–H two-dimensional NMR method. The chemical shifts of the quaternary carbons, C_6 and $C_{6'}$ of 6MPA6MPH, were well assigned by application of the additivity rule. The discrimination between C_2 and $C_{2'}$ was done while by expecting that the chemical shifts of the pyridyl ring would be affected by introducing of the methyl group into the ring. The ^{13}C chemical shifts, thus assigned, are listed in Table 5. Our results, except for the assignments of C_2 and $C_{2'}$, are in agreement with those (in chloroform-*d*) reported by Casey and Traverso,11) who made their assignment without applying the additivity rule. Generally, the chemical shifts of the C_3 and C_5 of 2-substituted pyridine derivatives with an electron-donating group are in a considerably higher field than the relevant chemical shifts of pyridine, whereas those of the 2-substituted pyridine derivatives with an electron-withdrawing group are little changed compared with the relevant chemical shifts of pyridine.25) $C_{3'}$ and $C_{5'}$ of PAPH are markedly shielded compared with the relevant carbon atoms of pyridine, while each chemical shift of C_3 and C_5 of PAPH is almost the same as that of pyridine. Each ^{13}C chemical shift of the R_1 and R_2 pyridyl rings of PAPH are therefore considered as being those of the 2-substituted pyridine derivatives. It is reasonable to conclude that the hydrazine moiety of hydrazones serves as an electron-donating group, and that

Table 5. ^{13}C NMR Chemical Shifts (ppm) for Heterocyclic Hydrazones[a)]

Position	Hydrazone			
	PAPH	6MPAPH	PA6MPH	6MPA-6MPH
C_2	154.66	154.22	154.77	154.24
C_3	120.32	117.44	120.34	117.55
C_4	137.75	137.90	137.71	137.90
C_5	124.00	123.51	123.94	123.48
C_6	149.44	158.58	149.49	158.60
C_7	139.44	139.60	139.28	139.37
$C_{2'}$	156.89	156.94	156.59	156.57
$C_{3'}$	108.03	108.01	104.91	104.96
$C_{4'}$	139.15	139.13	139.38	139.37
$C_{5'}$	116.65	116.58	115.95	115.88
$C_{6'}$	148.06	148.06	157.29	157.30
Methyl		23.62	23.64	23.64 23.64

a) Experimental conditions are the same as described at footnote in Table 3.

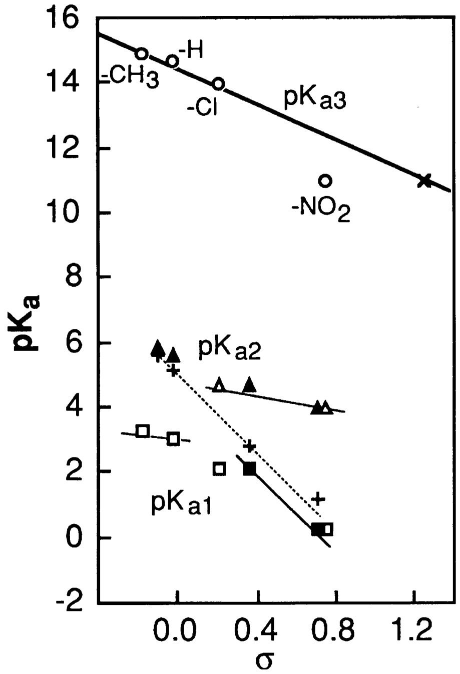


Fig. 2. Plots of Hammett's substituent constant vs. pK_a value. □,■: pK_{a1}, △,▲:pK_{a2}, ○,×:pK_{a3}; open symbols: σ_p value, closed symbols: σ_m value, ×: σ^- value, +: pK_a of 3-substituted pyridine.

the azomethine moiety serves as an electron-withdrawing group. The higher shielding effect of the hydrazine moiety corroborates that the basicity of the R_2 pyridine is higher than that of the R_1 pyridine in aqueous solution.

(a) Dissociation of Imino Proton of Hydrazones. It is well-known that the imino proton of hydrazones can usually dissociate in aqueous solution by a resonance stabilization of the conjugate base. The hydrazones used in this work dissociate their imino proton to conjugate between the aldehyde moiety and the hydrazone moiety: [–C=N–NH–]⟶[–C=N–N=]$^-$. The decreasing order of the pK_{a3} value, PAPhH>PAPH>PAQH>QAQH, may be interpreted by the difference in the electronegativities of carbon and nitrogen and/or a resonance effect of L^-.

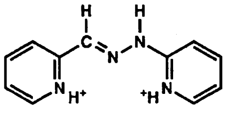
The application of the Hammett rule to the three acid dissociation constants (pK_{a1}—pK_{a3}) of PAPH and PA5XPH (X=M, C and N; cf. Table 1) is depicted in Fig. 2. The imino group is at the *p*-position of each substituent group. The plot of pK_{a3} vs. σ_p gives a straight line, where σ_p is the *para* substituent constant in the Hammett equation. Although the pK_{a3} value of PA5NPH is substantially lower than that expected from a straight line, the discrepancy is well resolved by the adoption of σ^-[26)] for *p*-substituents instead of σ_p. This reveals that the 5-nitro group acts as a strongly resonating electron-withdrawing *para* substituent. Moreover, the resonance structure of the charged quinonoid type of L^- should be effectively stabilized by the 5-nitro group of R_2 pyridyl ring. This leads to an exceedingly high molar absorptivity of ML_2 or ML complex of hydrazones with a nitro group at the 5-position of the R_2 pyridyl ring.[5)]

(b) Protolytic Equilibria for Two Heterocyclic Nitrogens of Hydrazones. The absorption spectra of PAPH in neutral to acid solutions (Fig. 1) indicated that two successive equilibria were present, corresponding to the protonation of two heterocyclic nitrogens. On the other hand, benzaldehyde 2-pyridylhydrazone (PhAPH) and 2-pyridinecarbaldehyde phenylhydrazone (PAPhH) have only one heterocyclic nitrogen in the molecule. The difference in the pK_{a2} values between PhAPH and PAPhH, corresponding to the proton dissociation of pyridinium nitrogen, is ca. +0.9 in logarithmic units. It is therefore reasonable to anticipate that the basicity of R_2 pyridine of PAPH is higer than that of the R_1 pyridine, due to the electron-donating ability of the hydrazine moiety. The apparent difference in the pK_{a2} values, however, suggests the presence of two micro species as H_2L^+ of PAPH; one is protonated at the R_2 pyridine-nitrogen and the other at the R_1 pyridine-nitrogen, although the former is surely predominant, as can be understood by the following ^{1}H NMR data. The dotted line in Fig. 2 represents a plot of pK_a vs. σ_m for 3-substituted pyridine derivatives, showing the introduction of an electron-withdrawing group, such as a chloro or nitro group to the 3-position of pyridine, lowers the values of pK_a of pyridinium nitrogen by 2.4—4.0. For PA5CPH and PA5NPH, however, only a small pK_a-lowering effect of the substituent is observed. That is, the plots of pK_{a2} and pK_{a1} vs. σ do not give straight lines in Fig. 2, although the plot of pK_{a3} vs. σ is linear, as mentioned above. The pK_{a2} values of PAPH and PA5MPH are practically identical with those of pyridine and 3-methylpyridine, respectively, while the pK_{a2} values of PA5CPH and PA5NPH are considerably higher than those expected from the dotted line. On the other hand, a straight line joining the pK_{a1} values of PA5CPH and PA5NPH is parallel, besides being near to the dotted line. The pK_a values of PAPH derivatives located parallel or near to the dotted line firmly suggest that the proton-dissociation site corresponding to the pK_a is the nitrogen of pyridinium bearing a substituent, i.e., an R_2 pyridine-nitrogen. That is to say, PAPH and PA5MPH are first protonated at the R_2 pyridine-nitrogen of HL and subsequently at the R_1 pyridine-nitrogen, while the protonation sites are reversed for PA5CPH and PA5NPH. The slope of the straight line joining the pK_{a2} values of PA5CPH and PA5NPH is much smaller than that of the dotted line. The difference between the pK_{a2} values of PAPH and PA5CPH is almost equal to that for PAPhH and PhAPH mentioned above. These facts clearly indicate that chloro or nitro substituent introduced into the R_2 pyridine of hydrazone does not greatly affect the basicity of the R_1 pyridine-nitrogen.

The pH dependence of the chemical shifts of PAPH, PA6MPH, and PA5CPH in aqueous acetone solutions was examined. The apparent chemical shift (δ') is given by

$$\delta' = \frac{\delta_3[\mathrm{H}^+]^2 + \delta_2 K_{a1}[\mathrm{H}^+] + \delta_1 K_{a1} K_{a2}}{[\mathrm{H}^+]^2 + K_{a1}[\mathrm{H}^+] + K_{a1} K_{a2}},$$

where δ_3, δ_2, and δ_1 denote the chemical shifts of the species H_3L^{2+}, H_2L^+, and HL, respectively. The values of δ_3, δ_2, δ_1 were obtained simultaneously by minimizing $U=\Sigma(\delta'_{i,\mathrm{obs}}-\delta'_{i,\mathrm{cal}})^2$ with the aid of a computer. The values of K_{a1} and K_{a2} in the mixed solvents were predetermined spectrophotometrically:[17] the pK_{a1} values were 2.06, 1.73, and 0.58; the pK_{a2} values were 4.73, 4.81, and 3.20 for PAPH, PA6MPH, and PA5CPH, respectively. The results are depicted in Fig. 3. The properties of terpy in aqueous solution have been discussed based on the maintenance of coplanarity among three pyridyl rings.[27,28] The terminal pyridyl rings of PAPH have also been considered as keeping near coplanarity to the plane of the azomethine double bond.[10] Figure 4 shows the ^{1}H NMR spectra of H_4 and/or $H_{4'}$ for the HL and H_3L^{2+} species of PAPH. As mentioned above, H_4 for HL gives an octet showing a fine structure by a long-range coupling with the formyl proton. In an aqueous acetone solution, H_4 for H_3L^{2+} gives a sextet, which probably results from the near equality between $J_{3,4}$ and $J_{4,5}$, showing no fine structure. Although the reversion of the R_1 pyridine about the C_7–C_2 single bond by the protonation of H_2L^+ (cf. structure **2**) should bring about an interaction between H_3 and formyl proton H_7, i.e., a nuclear Overhauser effect (nOe), the irradiation of H_7 gave no nOe increment at H_3 (Chart 2). These facts suggest that although the pyridinium nitrogen of the R_1 pyridine faces the azomethine nitrogen in the H_3L^{2+} species represented by **2**, the pyridyl ring is inclined slightly to the plane of the azomethine double bond, probably due to an electrostatic repulsion with the positive charge of the R_2 pyridinium nitrogen.



2

Chart 2.

$H_{4'}$ for HL also showed no fine structure of the octet, which causes an sp^3 hybridization of the imino nitrogen; also, the nOe between $H_{3'}$ and the imino proton can't be observed in an aqueous solution. However the change in the chemical shift of each ring proton by protonation gives information concerning the fine structure of the protonated species. It has been reported[10] that the protons of the terminal pyridyl rings of PAPH in trifluoroacetic acid-*d* as a solvent are all more deshielded than in aprotic organic solvents because of the withdrawal of electronic charge by the positive pyridinium nitrogens. A similar NMR behavior was observed in the protonation of bipy.[29] The H_3 of HL of PAPH is deshielded by the magnetic anisotropy of the lone-pair electron of N_8 and the π-electron of the azomethine double bond; $H_{3'}$ is deshielded only by the anisotropy of N_8 (cf. structure **1**).[10,30] The ring and formyl protons of PAPH, PA6MPH, and PA5CPH (except $H_{3'}$) are also more deshielded according to $\mathrm{HL}\longrightarrow H_2L^+\longrightarrow H_3L^{2+}$. The $H_{3'}$ of PAPH and PA6MPH show rather slight upfield shifts with $\mathrm{HL}\rightarrow H_2L^+$. Such upfield shifts would have to result from a release of the anisotropy of $H_{3'}$ by protonation. Thus, the R_2 pyridine-nitrogen of PAPH represented by **1** probably faces the azomethine nitrogen by the protonation of HL. On the other hand, H_3 of PAPH and PA6MPH show no release of the anisotropy of H_3 with $\mathrm{HL}\longrightarrow H_2L^+$ and, thus, the conformation of R_1 pyridine-nitrogen remains unchanged. In the case of PA5CPH, which is first protonated at the R_1 pyridine-nitrogen, the release of anisotropy of H_3 with $\mathrm{HL}\rightarrow H_2L^+$ is shown (cf. Fig. 3c) and moreover, the long-range coupling of H_4 with the formyl proton was not observed for the H_2L^+ species. Thus, the R_1 pyridine-nitrogen of PA5CPH faces the azomethine nitrogen by the protonation of HL. The downfield shift of $H_{3'}$ with $\mathrm{HL}\longrightarrow H_2L^+$, which is about the same extent as that of $H_{4'}$, suggests a maintenance of the conformation of R_2 pyridine-nitrogen by the first protonation. Bell et al. have concluded[30] that the upfield chemical shifts of H_3 and $H_{3'}$ of the Zn(II)–PAPH complex, compared with the relevant chemical shifts of PAPH, can be ascribed to the necessary conformational change of **1**, that is, two pyridine-nitrogens of HL represented by **1** face the azomethine nitrogen by complex formation (cf. structure **2**). On the other hand, $H_{4(4')}$ and $H_{5(5')}$ are situated under no influence of the anisotropy of the sp^2-hybridized azomethine moiety, their changes in chemical shift reflecting only a deshielding effect of the with-

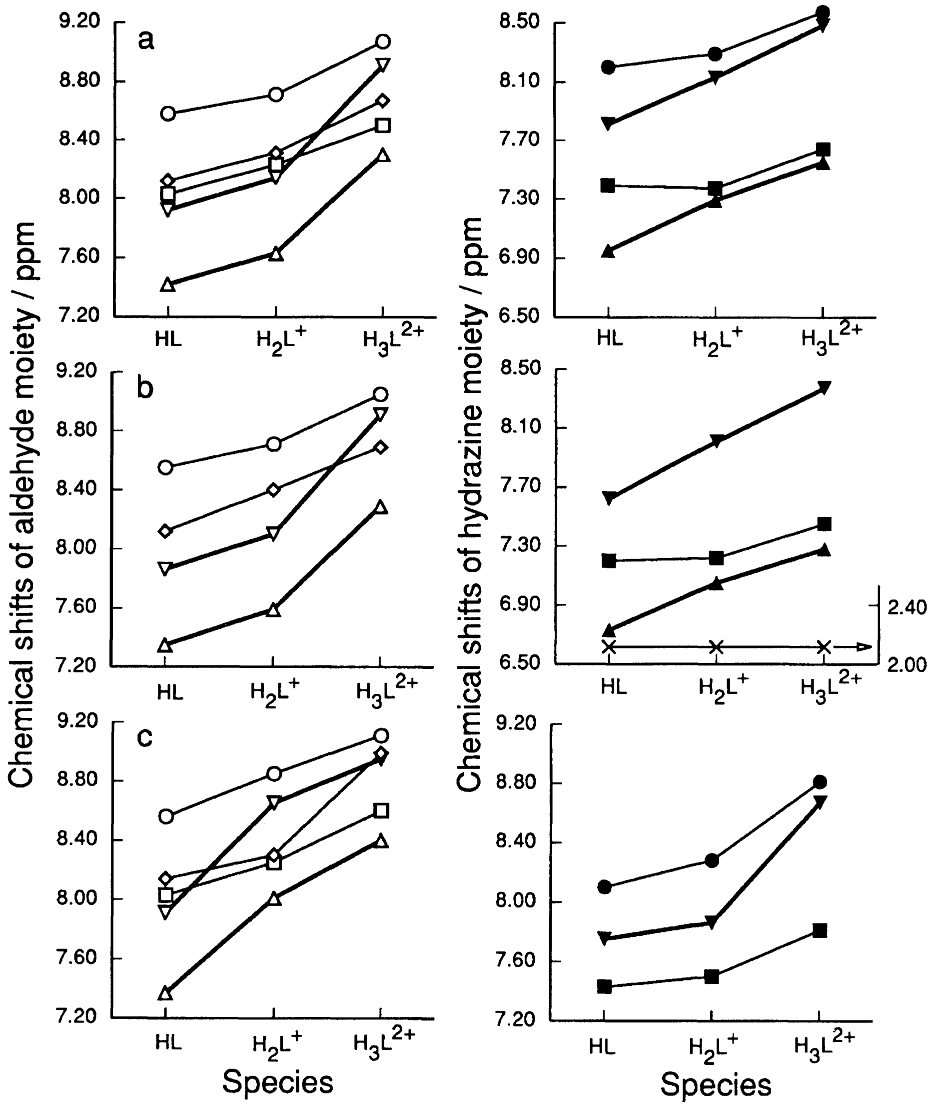


Fig. 3. ^{1}H NMR chemical shift for HL, H_2L^+, and H_3L^{2+} of (a) PAPH, (b) PA6MPH, and (c) PA5CPH. ○: H_6, △:H_5, ▽: H_4, □: H_3, ◇: H_7, ●: $H_{6'}$, ▲: $H_{5'}$, ▼: $H_{4'}$, ■: $H_{3'}$, ×: methyl proton.

drawal of electronic charge by protonation. The plots for H_4 and H_5 shown by thick lines in Fig. 3 are divided into two types: The downfield shifts from H_2L^+ to H_3L^{2+} are larger than those from HL to H_2L^+ for PAPH and PA5MPH, while the situation is reversed for PA5CPH. This coorborates the idea that the first protonation site of HL of PAPH and PA6MPH is the R_2 pyridine-nitrogen, but that PA5CPH is first protonated at the R_1 pyridine-nitrogen. In the case of PAPH and PA6MPH, the downfield shifts from HL to H_2L^+ for H_4 and H_5 are the same as that for H_3, which is located under the influence of the anisotropy. This strongly suggests that the conformation of the R_1 pyridine is maintained by the first protonation to the R_2 pyridine-nitrogen. On the other hand, PAPH shows a small downfield shift from H_2L^+ to H_3L^{2+} for H_3 relative to that for H_4 and H_5, suggesting that the release of the anisotropy of the sp^2-hybridized azomethine moiety arising from the rotation of the R_1 pyridine about the C_2–C_7 single bond considerably counteracts the deshielding effect on H_3 by protonation. The change in each chemical shift of H_6 and $H_{6'}$ by protonation is similar to that of H_3 and $H_{3'}$, respectively, which is partly attributable to the change in the anisotropy of the sp^2-hybridized pyridine-nitrogen. It is interesting that there is no change in the chemical shift of the methyl proton of PA6MPH with $HL \longrightarrow H_2L^+ \longrightarrow H_3L^{2+}$.

The thermodynamic parameters for the acid dissociations of several hydrazones are listed in Table 6 together with those for the other reagents bearing donor nitrogen atoms. The parameters for Eqs. 2 and 3 are identified by subscripts 2 and 1, respectively. The entropy term $T\Delta S_2$ for PAPH is the same as for diethylenetriamine (dien), terpy and phen, which would reflect the same extent of the ordering of water molecules around the charged nitrogen of monoprotonated species. It has often been pointed out[27] that the trans and trans-trans configurations of bipy and terpy were changed to cis

Table 6. Thermodynamic Parameters ($kJ\,mol^{-1}$) for Acid Dissociation of H_3L^{2+} and H_2L^+ in 0.1 M KCl Solution at 298 K[a)]

Ligand	$H_3L^{2+} \rightleftharpoons H_2L^+ + H^+(K_{a1})$			$H_2L^+ \rightleftharpoons HL + H^+(K_{a2})$		
	$-\Delta G_1$	$-\Delta H_1$	$T\Delta S_1$	$-\Delta G_2$	$-\Delta H_2$	$T\Delta S_2$
PAPH	−18.5 (−14.8)	−25.4 (−25.2)	6.9 (10.4)	−34.0 (−31.1)	−22.5 (−27.2)	−11.5 (−3.9)
PA5CPH	(−8.1)	(−15.3)	(7.2)	(−24.3)	(−17.8)	(−6.5)
6MPAPH	−22.6	−24.3	1.7	−35.2	−22.6	−12.5
6MPA6MPH	−22.4	−24.8	2.4	−37.1	−36.0	−1.2
QAPH	−17.4	−17.3	0.1	−31.3	n.d.[b)]	n.d.[b)]
PAQH	−17.5	−14.9	−2.6	−35.3	−31.4	−3.9
DPPH	−17.8	−17.4	−0.4	−31.4	−26.6	−4.8
dien[c)]	−51.4	−50.2	−1.2	−55.6	−46.9	−8.7
terpy[c)]	−20.6	−21.8	1.2	−27.1	−14.6	−12.5
phen[c)]	−8.6			−27.6	−15.1	−12.5
Pyridine[c)]				−29.8	−20.1	−9.7

a) Values in () were determined in 28 (v/v)% aqueous dioxane (I=0.2, KCl). b) n.d.: not determined (because of low solubility). c) Quoted from Ref. 15.

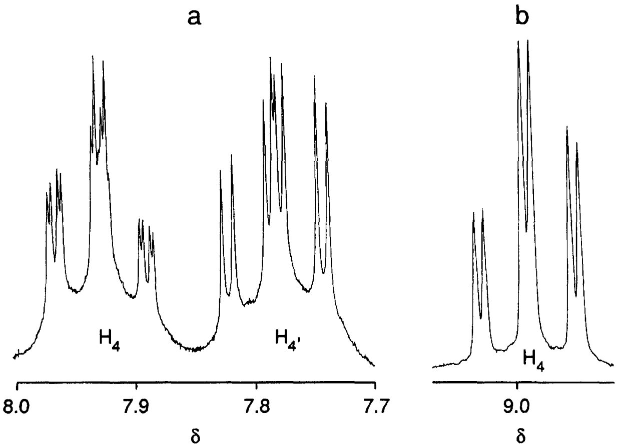


Fig. 4. ^1H NMR spectra of the ring proton of PAPH in aqueous acetone solutions (acetone-d_6 : D_2O=6 : 4). (a) pH 5.83, (b) pH 0.44.

and trans-cis configurations by first protonation, respectively. That is, in the monoprotonated form of bipy or terpy, the protonated pyridyl group rotates about the C–C single bond, its pyridinium nitrogen being spatially directed to the nitrogen of the adjacent pyridyl group. The ΔH_2 for PAPH is more endothermic than ΔH_2 for terpy and phen and rather near to the ΔH of proton dissociation of a single pyridinium nitrogen (Table 6), indicating that the proton dissociation of H_2L^+ of PAPH is characterized as that of the substituted pyridinium nitrogen. This would be attributable to a breaking of the conjugation of PAPH at the imino group, –NH–. In a comparison of PAPH with PA5CPH, the difference in ΔG_2 mainly results from that in ΔH_2. This is ascribed to an inherent low electron density of the R_1 pyridine-nitrogen. The values of ΔG_2 for 6MPA6MPH and PAQH are not much different from that for PAPH. The increment of ΔH_2 for the former hydrazones is almost compensated by the $T\Delta S_2$ term, suggesting a favorable hydration of the charged nitrogen of H_2L^+.

The proton dissociation of H_3L^{2+} is more favorable in ΔS compared with that of H_2L^+. Doubly charged hydrazones cause a higher ordering of water molecules around the protonation sites than do singly charged hydrazones and, thus, the proton dissociaton of H_3L^{2+} accompanies the release of a great deal of water molecules, compared with that of H_2L^+. As pointed out above, the ΔH for the proton dissociation of the R_1 pyridinium nitrogen should be essentially less endothermic than that of the R_2 pyridinium nitrogen, due to the low electron density of the R_1 pyridine. The ΔH_1 for PAPH, corresponding to the proton dissociation of the R_1 pyridinium ion, is nevertheless rather more endothermic than ΔH_2. This suggests the release of a higher ordering of water molecules around H_3L^{2+} of PAPH by proton dissociaton. The entropy changes (ΔS_1) for the PAPH analogs listed in Table 6 are dependent on their molecular structure, the values varying from positive to nearly zero. This evidently indicates that the hydration of H_3L^{2+} of the PAPH analogs is subject to a steric hindrance. The NMR results suggested a reversion of the R_1 pyridyl ring about the C_7–C_2 single bond by protonation of H_2L^+ of PAPH (cf. structure **2**). Similarly to PAPH, the N_1, N_8, and $N_{1'}$ atoms of these analogs surely face one another in their H_3L^{2+} forms, although the R_1 pyridyl ring is slightly inclined to the plane of the azomethine double bond. Thus, hydration of doubly charged hydrazone, H_3L^{2+} in a bowl of N_1, N_8, and $N_{1'}$, is hindered by the 6-methyl group or the methine hydrogen at the 8-position of the quinolyl ring bonded to the carbaldehyde moiety.

Although ΔH_2 for DPPH is not very different from that for PAPH, ΔH_1 for DPPH is much less endothermic than ΔH_1 for PAPH. Considering the ^1H NMR result mentioned above, these observations can be rea-

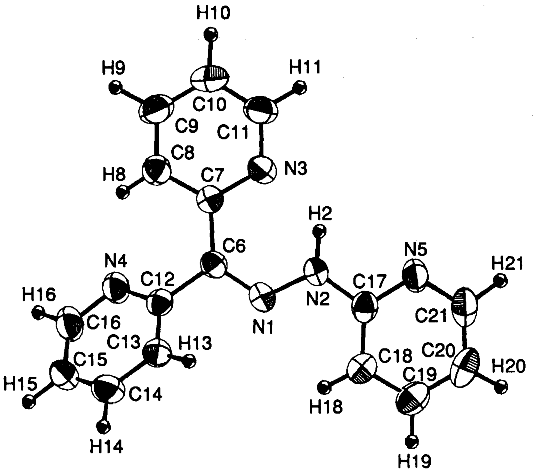


Fig. 5. ORTEP view of DPPH. The atoms are represented by 50% probability thermal ellipsoids.

Table 7. Positional Parameters and Isotropic Thermal Parameters

Atom	x/a	y/b	z/c	B_{eq}/Å^2
N(1)	0.0452(3)	0.0858(2)	0.2284(4)	3.27(9)
N(2)	0.1212(3)	0.1416(2)	0.1570(5)	3.7(1)
N(3)	0.0610(3)	0.2374(2)	0.4066(4)	3.8(1)
N(4)	−0.2091(3)	0.0446(2)	0.4766(4)	3.9(1)
N(5)	0.2293(3)	0.1913(2)	−0.0672(5)	4.2(1)
C(6)	−0.0129(4)	0.1008(2)	0.3696(5)	3.0(1)
C(7)	−0.0090(4)	0.1766(2)	0.4697(5)	2.9(1)
C(8)	−0.0696(4)	0.1842(3)	0.6244(6)	3.9(1)
C(9)	−0.0606(5)	0.2559(3)	0.7138(6)	4.8(1)
C(10)	0.0111(5)	0.3180(3)	0.6481(6)	4.7(1)
C(11)	0.0698(5)	0.3061(3)	0.4961(6)	4.4(1)
C(12)	−0.0910(4)	0.0300(2)	0.4236(5)	3.0(1)
C(13)	−0.0435(4)	−0.0480(2)	0.4084(6)	3.8(1)
C(14)	−0.1208(5)	−0.1127(3)	0.4490(6)	4.6(1)
C(15)	−0.2412(5)	−0.0982(3)	0.5006(6)	4.5(1)
C(16)	−0.2804(4)	−0.0193(3)	0.5149(6)	4.6(1)
C(17)	0.1641(4)	0.1287(3)	−0.0052(6)	3.4(1)
C(18)	0.1429(4)	0.0574(3)	−0.0944(5)	3.7(1)
C(19)	0.1877(4)	0.0522(3)	−0.2557(6)	4.4(1)
C(20)	0.2517(5)	0.1166(4)	−0.3237(7)	4.7(1)
C(21)	0.2711(4)	0.1839(3)	−0.2266(6)	4.7(1)
H(2)	0.130(4)	0.192(3)	0.207(6)	3.8
H(8)	−0.119(4)	0.142(3)	0.661(6)	3.9
H(9)	−0.109(5)	0.262(3)	0.830(7)	4.8
H(10)	0.018(5)	0.370(4)	0.710(7)	4.7
H(11)	0.122(5)	0.352(3)	0.448(6)	4.4
H(13)	0.044(4)	−0.056(3)	0.375(6)	3.8
H(14)	−0.090(5)	−0.172(3)	0.441(6)	4.6
H(15)	−0.300(5)	−0.145(3)	0.526(6)	4.5
H(16)	−0.364(4)	−0.009(3)	0.557(6)	4.6
H(18)	0.097(4)	0.014(3)	−0.040(6)	3.7
H(19)	0.168(4)	0.004(3)	−0.325(7)	4.4
H(20)	0.281(5)	0.116(3)	−0.438(7)	4.7
H(21)	0.313(5)	0.234(3)	−0.268(6)	4.7

Table 8. Interatomic Distances (Å)

Atom–Atom	Length	Atom–Atom	Length
N(1)–C(6)	1.301(5)	C(10)–C(11)	1.307(7)
N(1)–N(2)	1.350(5)	C(11)–H(11)	1.02(5)
N(2)–H(2)	0.92(5)	C(12)–C(13)	1.390(6)
N(2)–C(17)	1.379(6)	C(13)–H(13)	0.98(5)
N(3)–C(11)	1.341(6)	C(13)–C(14)	1.386(6)
N(3)–C(7)	1.347(5)	C(14)–H(14)	1.03(6)
N(4)–C(16)	1.336(6)	C(14)–C(15)	1.365(8)
N(4)–C(12)	1.347(5)	C(15)–H(15)	1.01(5)
N(5)–C(17)	1.339(5)	C(15)–C(16)	1.375(7)
N(5)–C(21)	1.344(6)	C(16)–H(16)	0.96(5)
C(6)–C(7)	1.482(5)	C(17)–C(18)	1.392(6)
C(6)–C(12)	1.498(5)	C(18)–H(18)	0.96(5)
C(7)–C(8)	1.390(6)	C(18)–C(19)	1.366(6)
C(8)–H(8)	0.92(5)	C(19)–H(19)	0.99(5)
C(8)–C(9)	1.383(7)	C(19)–C(20)	1.374(8)
C(9)–H(9)	1.06(5)	C(20)–H(20)	0.96(5)
C(9)–C(10)	1.380(7)	C(20)–C(21)	1.367(8)
C(10)–H(10)	0.99(6)	C(21)–H(21)	1.00(5)

sonably explained by the presence of an intramolecular hydrogen bond in aqueous solution, as well as in an organic solvent. Breaking such a hydrogen bond might be accompanied by considerable heat absorption. Thus, the enthalpy data obtained suggest that breakage of the hydrogen bond occurs in the process $H_2L^+ \longrightarrow H_3L^{2+}$.

(c) Proton Dissociations in Strongly Acid Solution. Type-I hydrazones exhibited nearly identical values of pK_{aH4L} and pK_{aH5L}, respectively. The variations in the ^{15}N NMR chemical shifts of $>\mathrm{N}\overset{\frown}{=}\mathrm{C}<$ or $>\mathrm{N}\overset{\frown}{=}\mathrm{N}<$ compounds have been accounted for in terms of the characteristic of π-bonding between the nitrogen atom and the neighbor atoms, which brings about a nitrogen lone-pair delocalization effect.$^{31)}$ Equations 4 and 5 should therefore be characterized as a proton dissociation of the protonated nitrogens of azomethine and the imino group. PhAPH and PAPhH, bearing only one pyridyl ring, can be classified as bidentate ligands, such as bipy and phen. The second protonation site of these hydrazones is the nitrogen of azomethine, while that of bipy and phen is another ring nitrogen. The difference in the values of pK_{a2} and pK_{aH4L} for these hydrazones is much larger than the corresponding difference for bipy and phen. This strongly indicates a low basicity of the azomethine nitrogen compared to the basicity of the nitrogen of bipy or phen. The values of pK_{aH4L} for DPPH and DPQH are larger than those for Type-I hydrazones. This suggests that the R_3 pyridine-nitrogen is protonated in preference to the nitrogen of azomethine.

(d) Crystal X-ray analysis of DPPH.# Figure 5 depicts a possible crystal structure of DPPH determined by single-crystal X-ray diffraction. The atomic coordinates, bond lengths, and selected bond angles are

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#In this section, each numbered atom corresponds to that shown in Fig. 5.

Table 9. Selected Bond Angles (°)

Atom–Atom–Atom	Angle	Atom–Atom–Atom	Angle
C(6)–N(1)–N(2)	120.9(3)	N(3)–C(11)–C(10)	123.6(4)
H(2)–N(2)–N(1)	119(3)	N(4)–C(12)–C(13)	122.1(4)
H(2)–N(2)–C(17)	120(3)	N(4)–C(12)–C(6)	117.8(3)
N(1)–N(2)–C(17)	118.9(3)	C(13)–C(12)–C(6)	120.0(4)
C(11)–N(3)–C(7)	118.4(4)	C(14)–C(13)–C(12)	118.7(4)
C(16)–N(4)–C(12)	117.3(4)	C(15)–C(14)–C(13)	119.4(4)
C(17)–N(5)–C(21)	116.5(4)	C(14)–C(15)–C(16)	118.4(4)
N(1)–C(6)–C(7)	127.4(3)	N(4)–C(16)–C(15)	124.0(4)
N(1)–C(6)–C(12)	111.0(3)	N(5)–C(17)–N(2)	113.2(4)
C(7)–C(6)–C(12)	121.6(3)	N(5)–C(17)–C(18)	123.5(4)
N(3)–C(7)–C(8)	121.0(4)	N(2)–C(17)–C(18)	123.3(4)
N(3)–C(7)–C(6)	116.6(3)	C(19)–C(18)–C(17)	118.1(4)
C(8)–C(7)–C(6)	122.4(4)	C(18)–C(19)–C(20)	119.4(5)
C(9)–C(8)–C(7)	119.8(4)	C(21)–C(20)–C(19)	119.0(5)
C(10)–C(9)–C(8)	118.8(4)	N(5)–C(21)–C(20)	123.5(4)
C(11)–C(10)–C(9)	118.4(4)		

listed in Tables 7, 8, and 9. The pyridine nitrogen N(3) is maintained at a distance of a hydrogen bond with imino hydrogen H(2) (N(3)···H(2)=1.90(5) Å). The azomethine double bond (C(6)=N(1)) is almost coplanar to the R_3 pyridyl ring, and is nearly coplanar to the R_2 pyridyl ring, which probably arises from a π-delocalization of the lone-pair electrons of the imino nitrogen.[31] That is, the R_2 and R_3 pyridyl rings are inclined at 10.6° and 2.89°, respectively, to the best plane defined by the C(6), N(1), and N(2) atoms, whereas the R_1 pyridyl ring is inclined at 43.9°. The steric structure of N(4)–N(1)–N(5) is similar to the trans-trans conformation of 4′-phenyl-2,2′ : 6′,2″-terpyridine.[32] The structure of 2-benzoylpyridine phenylhydrazone, in which R_1 is a pyridyl ring and R_2 and R_3 are phenyl rings, has been determined by Butler and Johnston;[33] the ring-keeping coplanarity to the azomethine double bond is not the R_3 phenyl ring, but the R_1 pyridyl ring. The hydrogen bond, suggested for DPPH, between the imino hydrogen H(2) and the pyridine-nitrogen N(3) of the R_3 pyridyl ring is, in our opinion, responsible for the torsion of the R_1 pyridyl ring.

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