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Synthesis and Chromogenic Properties of Some Water-Soluble 5-Nitro-2-pyridylhydrazones

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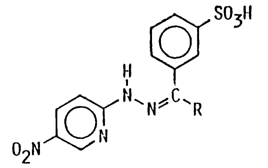
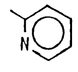
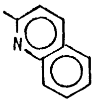
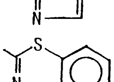
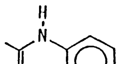
Four new water-soluble hydrazones, α-(5-nitro-2-pyridyl)hydrazono-α-(2-quinolyl)-3-toluenesulfonic acid, α-(5-nitro-2-pyridyl)hydrazono-α-(2-thiazolyl)-3-toluenesulfonic acid, α-(2-benzothiazolyl)-α-(5-nitro-2-pyridyl)-hydrazono-3-toluenesulfonic acid, and α-(2-benzimidazolyl)-α-(5-nitro-2-pyridyl)hydrazono-3-toluenesulfonic acid, were synthesized. Their proton dissociation constants were determined spectrophotometrically. The chromogenic properties of the synthesized hydrazones and their reactions with metal ions were investigated spectrophotometrically in detail. The results revealed that the synthesized hydrazones react with various metal ions including transition metal ions, especially with cadmium(II), nickel(II), and zinc(II) to form stable colored complexes with very large apparent molar absorptivities, so that they were found to be all very useful as highly sensitive spectrophotometric reagents.

Because of the ever increasing interest in the determination of trace elements in industrial, biological, and environmental materials at lower concentrations, there is need for the development of more sensitive analytical methods. The spectrophotometric method involving the use of organic reagents is one of inexpensive and reliable methods to the more complicated and expensive methods such as atomic absorption spectrometry with graphite furnace atomisation and inductively coupled plasma atomic emission spectrometry and compete favorably in sensitivity. On the other hand, hydrazones have attracted much attention as analytical reagents and their applications have been reviewed by Katyal et al.[1] and later by Singh et al.[2] Especially, attention has recently been given to nitrogen containing heterocyclic hydrazones and their metal complexes,[3–6] because of their high molar absorptivities. We have also investigated, over the period of more than 10 years, the development of highly sensitive and selective hydrazone reagents, synthesized recently a series of water-soluble hydrazones derived from 3-(2-pyridylcarbonyl)benzenesulfonic

Table 1. Structures of Synthesized Hydrazones



Hydrazone	Abbreviation	R
α-(5-Nitro-2-pyridyl)hydrazono-α-(2-pyridyl)-3-toluenesulfonic acid[a)]	NPHPTS	
α-(5-Nitro-2-pyridyl)hydrazono-α-(2-quinolyl)-3-toluenesulfonic acid	NPHQTS	
α-(5-Nitro-2-pyridyl)hydrazono-α-(2-thiazolyl)-3-toluenesulfonic acid	NPHTTS	
α-(2-Benzothiazolyl)-α-(5-nitro-2-pyridyl)-hydrazono-3-toluenesulfonic acid	BTNPHTS	
α-(2-Benzimidazolyl)-α-(5-nitro-2-pyridyl)-hydrazono-3-toluenesulfonic acid	BINPHTS	

a) Synthesized in an earlier work.[9)]

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acid,[7–9] studied their chromogenic properties, and found that α-(5-nitro-2-pyridyl)hydrazono-α-(2-pyridyl)-3-toluenesulfonic acid (NPHPTS) having an electron-withdrawing nitro group at the 5-position of the pyridine ring in the hydrazine moiety of its mother compound, α-(2-pyridyl)-α-(2-pyridyl)hydrazono-3-toluenesulfonic acid (PPHTS), is a very favorable spectrophotometric reagent in both sensitivity and selectivity for the determination of metals, especially for that of cobalt.[9]

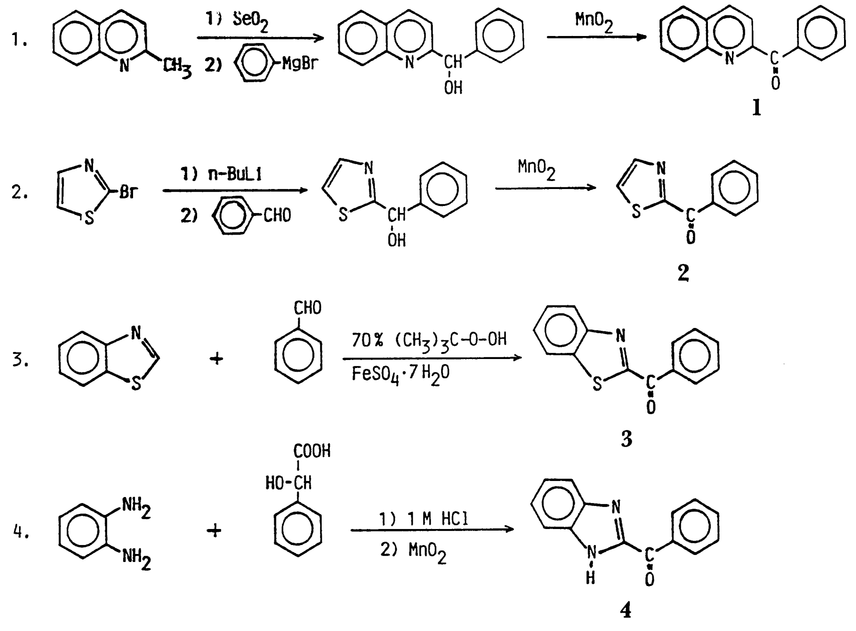
In this work four new water-soluble hydrazones shown in Table 1, in which various substituents were introduced into the ketone moiety of NPHPTS, were synthesized, the effect of the substituents and their chromogenic properties and color reactions with metal ions being investigated and compared.

Experimental

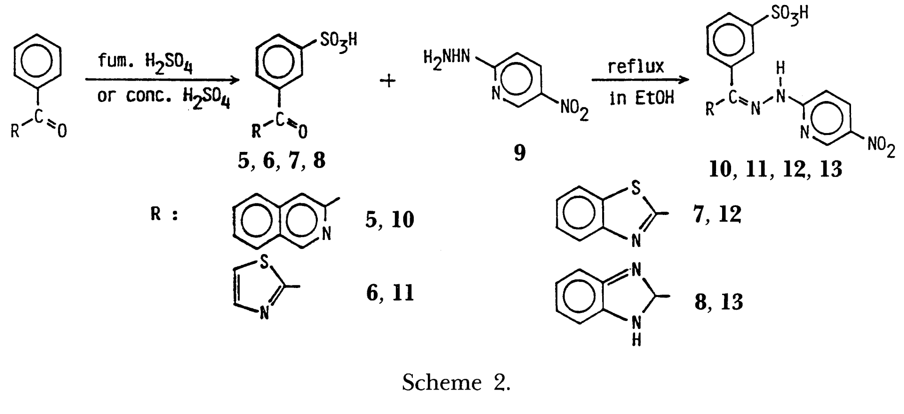
Synthesis of Hydrazones. All the hydrazones were synthesized according to schemes 1 and 2 as follows. The synthesis of NPHPTS has been described previously.[9]

2-Benzoylquinoline (1). Manganese dioxide (activated under vacuum at 110 °C for 2 days, 80 g, 920 mmol) was added to a chloroform solution (300 ml) of phenyl-(2-quinolyl)methanol (4.53 g, 19.3 mmol) which was obtained by the Grignard method[10] using phenylmagnesium bromide [2 M (1 M=1 mol dm^{-3}) in tetrahydrofuran, 35 ml, 70.0 mmol] and 2-quinolinecarbaldehyde (8 g, 50.9 mmol).[11] The reaction mixture was refluxed for 20 h. After cooling the mixture was filtered through a Celite pad and concentrated to yield a pale brown solid, which was recrystallized from ethanol [4.02 g, 89.5%]. Mp: 111 °C. Found C, 82.9; H, 4.85; N, 6.00%. Calcd for $C_{16}H_{11}NO$: C, 82.38; H, 4.95 ; N, 6.00 %. IR(KBr): $\nu_{C=O}$ 1655 cm^{-1}.

2-Benzoylthiazole (2). This substance was prepared referring to the procedure of Kurkjy and Brown.[12] Under nitrogen a solution of butyllithium (25% in hexane, 25.8 ml, 40.0 mmol) and dry diethyl ether (20 ml) were cooled to −30 °C and a solution of 2-bromothiazole (5 g, 30.5 mmol) in dry diethyl ether (20 ml) was added slowly. The reaction mixture was stirred for 15 min and then benzaldehyde (4.18 g, 39.4 mmol) was added dropwise, keeping a temperature under −15 °C. The mixture, after being stirred for 45 min,



Scheme 1.



Scheme 2.

was poured on ice and dilute hydrochloric acid. After removing the precipitate by filtration the acid layer was separated, made alkaline with aqueous ammonia (25 %) and extracted with ethyl acetate (3×150 ml). This extracts were dried over anhydrous sodium sulfate, filtered and reduced to a smaller volume (ca. 200 ml). To this solution was added activated manganese dioxide (40 g, 460 mmol), and the mixture was refluxed for 6 h, filtered through a Celite pad and evaporated to yield a pale brown solid, which was recrystallized from methanol [4.60 g, 79.7%]. Mp: 45 °C. Found: C, 63.4; H, 3.78; N, 7.41; S, 16.5%. Calcd for $C_{10}H_7NOS$: C, 63.47; H, 3.73; N, 7.40; S, 16.49%. IR (KBr): $\nu_{C=O}$ 1635 cm^{-1}.

2-Benzoylbenzothiazole (3). A modification of the procedure of Caronna et al. Gaili, and Malatesta[13] was used. To a stirred cooled solution of benzothiazole (2.70 g, 20.0 mmol) were added benzaldehyde (6.33 g, 59.6 mmol) and 25% sulfuric acid (4.3 ml) in acetic acid (10 ml) during 15 min. To this mixture were added dropwise 70% *t*-butyl hydroperoxide (8.2 ml, 60.0 mmol) and iron(II) sulfate heptahydrate (16.7 g) in water (60 ml), keeping a temperature during 5—15 °C. A solution of 1 M sodium carbonate was added until the pH became 5—6. After addition of chloroform (200 ml) the mixture was shaken to extract the target compound and centrifuged. Then the chloroform layer was separated, dried over anhydrous sodium sulfate, treated with activated charcoal and evaporated to give a crystalline solid, which was recrystallized from ethanol [3.35 g, 70%]. Mp: 103 °C. Found: C, 69.6; H, 3.85; N, 5.95; S, 13.1%. Calcd for $C_{14}H_9NOS$: C, 70.27; H, 3.79; N, 5.85; S, 13.40%. IR (KBr): $\nu_{C=O}$ 1630 cm^{-1}.

2-Benzoylbenzimidazole (4). This substance was prepared referring to the procedure of O'Sullivan and Wallis.[14] Mandelic acid (6.09 g, 40.0 mmol) was dissolved in hydrochloric acid (1 M, 80 ml). To this solution was added *o*-phenylenediamine (4.33 g, 40.0 mmol), and the mixture was refluxed for 48 h. After cooling this mixture was made alkaline with aqueous ammonia (25%), and the precipitate formed was collected by filtration, washed thoroughly with water and dried to give a pale brown solid (8.07 g). This solid was dissolved in hot acetone (160 ml), to which was added activated manganese dioxide (36 g, 414 mmol). This suspension was refluxed for 60 h, filtered through a Celite pad and concentrated to yield a pale brown solid, which was recrystallized from methanol [6.79 g, 76.5%]. Mp: 214 °C. Found: C, 75.3; H, 4.49; N, 12.4%. Calcd for $C_{19}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.60%. IR (KBr): $\nu_{C=O}$ 1650 cm^{-1}.

3-(2-Quinolylcarbonyl)benzenesulfonic Acid (5). Under cooling fuming sulfuric acid (25%, 20 ml) was added slowly to 2-benzoylquinoline (**1** 3.88 g, 16.6 mmol), and the mixture was stirred at room temperature for 1 h and cautiously poured into ethanol (20 ml) under cooling. Addition of ethyl acetate (1 liter) caused the precipitate as a dark brown solid. This mixture was filtered, washed thoroughly with acetone and dried overnight at 120 °C under reduced pressure to yield a red-brown solid [4.0 g], which was used in the next step without purification, although it still contained water and sulfuric acid.

3-(2-Thiazolylcarbonyl)benzenesulfonic Acid (6). This compound was prepared under the same conditions as compound (**5**) was synthesized, and obtained as a crude black solid [4.15 g].

3-(2-Benzothiazolylcarbonyl)benzenesulfonic Acid (7). This compound was prepared under the same conditions as compound (**5**) was synthesized, and obtained as a crude black solid [3.76 g].

3-(2-Benzimidazolylcarbonyl)benzenesulfonic Acid (8). 2-Benzoylbenzimidazole (**4**, 6.67 g,30.0 mmol) was dissolved in concentrated sulfuric acid (10 ml) under mild heating, and fuming sulfuric acid (25% SO_3, 30 ml) was added slowly under cooling. This mixture was stirred for 10 min under cooling and then for 20 min at room temperature, and cautiously poured into acetone (30 ml). Addition of ethyl acetate and benzene caused the precipitate. The mixture was filtered, washed thoroughly with acetone, and purified in a column of silica gel by elution with 2-propanol-ethyl acetate-water (2+6+1, v/v). Appropriate fractions were collected and concentrated to afford a pale yellow solid [4.54 g]. The unreacted starting ketone (**4**) was recovered (2.0 g). The shortening of the reaction time for sulfonation lead to a more recovery of the starting ketone. On the other hand, elongation produced disulfonated 2-benzoylbenzimidazole, which had one sulfo group on the benzimidazole ring and the other one on the benzene ring. Much attention should be paied to the sulfonation of 2-benzoylbenzimidazole.

5-Nitro-2-pyridylhydrazine (9). 2-Chloro-5-nitropyridine (6.5 g, 41.2 mmol) was dissolved in ethanol (400 ml) at room temperature. To this solution was added dropwise a solution of hydrazine monohydrate (100%, 20.6 g, 412 mmol) in ethanol (80 ml) during 1 h. The mixture was stirred for 1 h at room temperature, allowed to stand overnight in a refrigerator, filtered and dried to give a yellow-green solid, which was recrystallized from ethanol [5.95 g, 94.1%]. Mp: 200 °C. Found: C, 39.2; H, 4.21; N, 36.2%. Calcd for $C_5H_6N_4O_2$: C, 38.96; H, 3.92; N, 36.35%. IR (KBr): ν_{NHNH_2} 3300, 1650, 1580, 1280 cm^{-1}; ν_{NO_2} 1540, 1320 cm^{-1}.

General Procedure for Synthesis of Hydrazones. 5-Nitro-2-pyridylhydrazine (**9**, 2 g, 13.0 mmol) in hot ethanol (400 ml) was added to a hot ethanol solution (100—200 ml) of the monosulfonated ketone (about 11 mmol), and the mixture was refluxed for 5 h. After cooling overnight, the precipitate formed was collected by filtration and recrystallized from ethanol-water (1+1, v/v) to give pure first crystals. Second and third crops were obtained from the mother liquid. Total yields were about 60—85%.

In case of the preparation of STNPH (**11**) and BISNPH (**13**), 5-nitro-2-pyridylhydrazine (**9**) was dissolved in ethanol-water (4+1, v/v) and ethanol-water (1+1, v/v) respectively instead of ethanol.

Reagents. All reagents were of analytical-reagent grade and all solutions were prepared with distilled, deionized water, unless stated otherwise.

Hydrazone Solutions, 5.0×10^{-4} or 1.0×10^{-3} M. Prepared by dissolving the required amount of each synthesized hydrazone in 0.01 M sodium hydroxide solution. These solutions were further diluted with water if necessary.

Buffer Solutions. Buffers consisting of 1 M chloroacetic acid-1 M sodium chloroacetate, 1 M acetic acid-1 M sodium acetate, 0.2 M 2,4,6-trimethylpyridine-0.2 M perchloric acid, 0.5 M tris(hydroxymethyl)aminomethane-0.5 M perchloric acid, (0.2 M boric acid+0.05 M sodium chloride)-0.05 M sodium borate, 1 M aqueous ammonia-1 M ammonium chloride, or (1 M glycine+1 M sodium chloride)-1 M sodium hydroxide system was used according to the pH values required.

Results and discussion

Identification of the Hydrazones. Identification of the synthesized hydrazones were carried out by elemental analysis and measurements of IR spectra. The results of the former, from which NPHQTS and BINPHTS seem to contain water of crystallization, are shown in Table 2 together with data of melting points, yields and R_f values in thin-layer chromatography, the results of the latter being shown in Table 3. From these results the target hydrazones were confirmed to be obtained.

Properties and Absorption Spectra of the Hydrazones. The synthesized hydrazones are hygroscopic, but remains unchanged for a long period when stored in a desiccator. They are soluble in water and polar solvents such as ethanol and *N*,*N*-dimethylformamide and very soluble in dilute alkaline solutions, but insoluble in less or nonpolar solvents. Their aqueous solutions are stable for at least more than several months when stored in amber bottles.

Absorption spectra of NPHQTS, NPHTTS,

Table 2. Data of Elemental Analysis, Melting Points, Yields, and R_f Values of Synthesized Hydrazones

Hydrazone	Molecular formula	Elemental analysis[a)]/% C	H	N	S	Mp/°C	Yield[c)]/%	R_f value[d)]
NPHQTS	$C_{21}H_{15}N_5O_5S \cdot H_2O$ =467.456	53.64 (53.96)	3.67 (3.67)	14.73 (14.98)	6.88 (6.86)	320[b)]	85.0	0.44
NPHTTS	$C_{15}H_{11}N_5O_5S_2$ =405.403	44.47 (44.44)	2.97 (2.74)	17.02 (17.28)	15.55 (15.82)	320[b)]	71.8	0.47
BTNPHTS	$C_{19}H_{13}N_5O_5S_2$ =455.463	47.13 (47.27)	3.44 (3.11)	15.27 (15.41)	12.83 (12.51)	315[b)]	60.8	0.54
BINPHTS	$C_{19}H_{14}N_6O_5S \cdot 1.5H_2O$ =465.401	48.75 (49.03)	3.37 (3.68)	17.99 (18.06)	7.53 (6.89)	300[b)]	60.3	0.40

a) Figures in parentheses indicate calculated values. b) Decomposed. c) Calculated based on the corresponding hydrazine. d) Used 0.2-mm E. Merck 60F-254 precoated silica-gel plates and 2-propanol-ethyl acetate-water (6+3+2, v/v) as a developing solvent.

Table 3. IR Spectral Data of Synthesized Hydrazones ($\mathrm{cm^{-1}}$)[a)]

	ν_{OH}[b)]	$\nu_{C=N}$	$\nu_{C=C}$	ν_{NO_2} ν_{as}	ν_{NO_2} ν_s	ν_{NH}	ν_{SO_2} ν_{as}	ν_{SO_2} ν_s
NPHQTS	3300—3350wb	1650w, 1600m	1575w, 1490m	1530w,	1330s	1290m	1240s,	1030m
NPHTTS		1650m, 1605s		1530m,	1350s	1300w	1215m,	1070m
BTNPHTS		1650m, 1610m	1575m, 1500sh	1530w,	1335s	1280w	1225m,	1030m
BINPHTS	3350mb	1600m	1575m, 1490m	1530sh,	1330s	1280m	1250m,	1020m

a) w: weak, m: middle, s: strong, b: broad, sh: shoulder, b) Water of crystallization

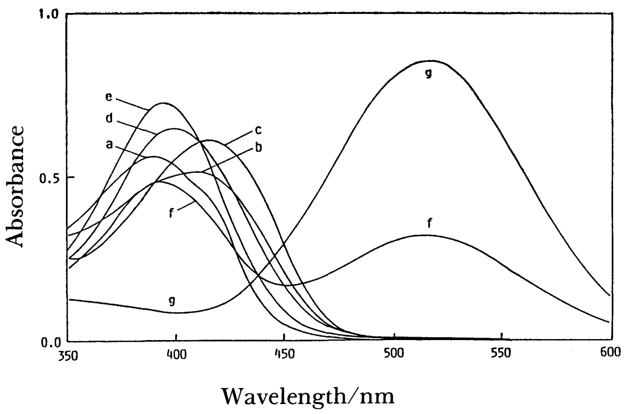


Fig. 1. Absorption spectra of NPHQTS at pH (a), <0; (b), 0.8; (c), 2.6; (d), 4.5; (e), 8:0; (f), 11.2; (g), 13.7. NPHQTS, 2.0×10⁻⁵ M; reference, water.

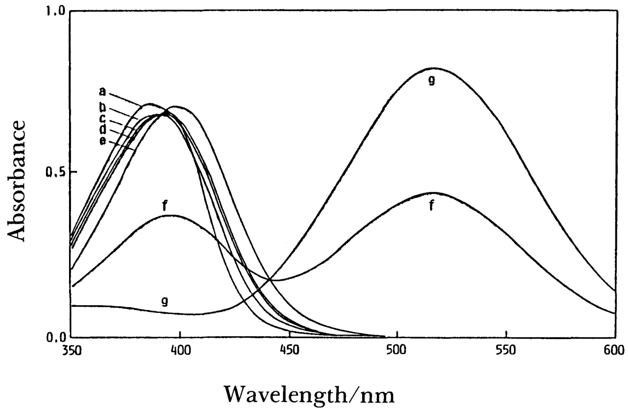


Fig. 2. Absorption spectra of NPHTTS at pH (a), <0; (b), 0.7; (c), 1.2; (d), 1.4; (e), 6.0; (f), 10:8; (g), 13.7. NPHTTS, 2.0×10⁻⁵ M; reference, water.

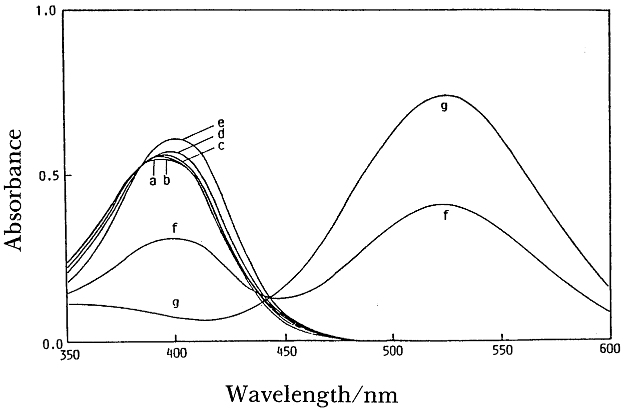


Fig. 3. Absorption spectra of BTNPHTS at pH (a), <0; (b), 0.7; (c), 1.0; (d), 1.4; (e), 6.0; (f), 10.7; (g), 13.6. BTNPHTS, 2.0×10^{-5} M; reference, water.

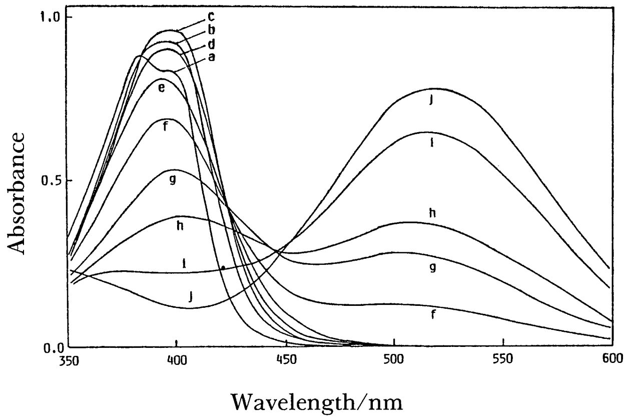


Fig. 4. Absorption spectra of BINPHTS at pH (a), <0; (b), 0.8; (c), 2.1; (d), 3.5; (e), 7.1; (f), 10.5; (g), 11.3; (h), 12.5; (i), 12.9; (j), >14. BINPHTS, 2.0×10^{-5} M; reference, water.

BTNPHTS, and BINPHTS at various pHs are shown in Figs. 1, 2, 3, and 4, respectively. Taking into consideration the species distribution diagrams of these hydrazones shown in Fig. 5, spectra a, c, e, and g in Figs. 1, 2, and 3 correspond to species H_3L^+, H_2L, HL^-, and L^{2-} of NPHQTS, NPHTTS, and BTNPHTS and spectra a, c, e, g, and j in Fig. 4 species H_4L^+, H_3L, H_2L^-, HL^{2-}, and L^{3-} of BINPHTS, respectively, where L denotes the undissociable part of the hydrazones. The absorption maximum and an apparent molar absorptivity of each species of the hydrazones are summarized in Table 4. From these results it is found that more than 100 nm of shifts in wavelength to the longer wavelength side are observed by the deprotonation of species HL^- (HL^{2-} in case of BINPHTS), which corresponds to the deprotonation of the secondary amino group of each hydrazone as stated below. This suggests similar large shifts in wavelength in the complexation of the hydrazones with metal ions, which is a very favorable characteristic when the hydrazones are used for the determination of the metals.

Proton Dissociation Constants of the Hydrazones. As is apparent from their structures and absorption spectra, NPHQTS, NPHTTS, and BTNPHTS are dibasic acids as well as triacidic bases, they having five dissociable hydrogens in strongly acidic solutions above 1 M. However, in less acidic solutions the deprotonations from the sulfo group and C=N nitrogen are complete. Hence these three hydrazones exist in solution in any of the following forms, depending on pH:

$$H_3L^+ \overset{K_{a3}}{\rightleftarrows} H_2L \overset{K_{a4}}{\rightleftarrows} HL^- \overset{K_{a5}}{\rightleftarrows} L^{2-}, \qquad (1)$$

where K_{a3}, K_{a4}, and K_{a5} are the proton dissociation constants. Similarly, BISNPH is a tribasic acid as well as triacidic base. So its acid-base equilibria can be expressed as follows:

$$H_4L^+ \overset{K_{a3}}{\rightleftarrows} H_3L \overset{K_{a4}}{\rightleftarrows} H_2L^- \overset{K_{a5}}{\rightleftarrows} HL^{2-} \overset{K_{a6}}{\rightleftarrows} L^{3-}, \qquad (2)$$

The proton dissociation constants of these hydrazones were determined spectrophotometrically at an ionic strength of 0.2 and 25±0.1 °C. The values obtained are summarized in Table 4. The K_{a3} may be assigned to the deprotonation of the protonated pyridine-nitrogen in the hydrazine moiety. The K_{a4} corresponds to the deprotonation of the protonated heterocyclic ring-nitrogen in the ketone moiety. The K_{a5} corresponds to the deprotonation of the secondary amino group, the K_{a6} corresponding to that of the imino-nitrogen of the benzimidazole group. In Fig.

Table 4. Proton Dissociation Constants, Absorption Maxima (λ_{max}) and Apparent Molar Absorptivities (ε) of Synthesized Hydrazones

Hydrazone	pK_{a3}	pK_{a4}	pK_{a5}	pK_{a6}	HL^- (or H_2L^-)		L^{2-} (or L^{3-})	
					λ_{max}/nm	ε/M^{-1}cm^{-1}	λ_{max}/nm	ε/M^{-1}cm^{-1}
NPHPTS[a]	0.72	4.37	11.49		385	30700	505	37300
NPHQTS	0.70	4.38	11.54		393	33300	513	42600
NPHTTS	<0.80	1.72	10.65		397	38300	515	42600
BTNPHTS	<0.80	1.32	10.74		399	35900	523	43500
BINPHTS	0.70	3.58	10.61	12.61	394	37800	516	38000

a) Determined in an earlier work.[9]

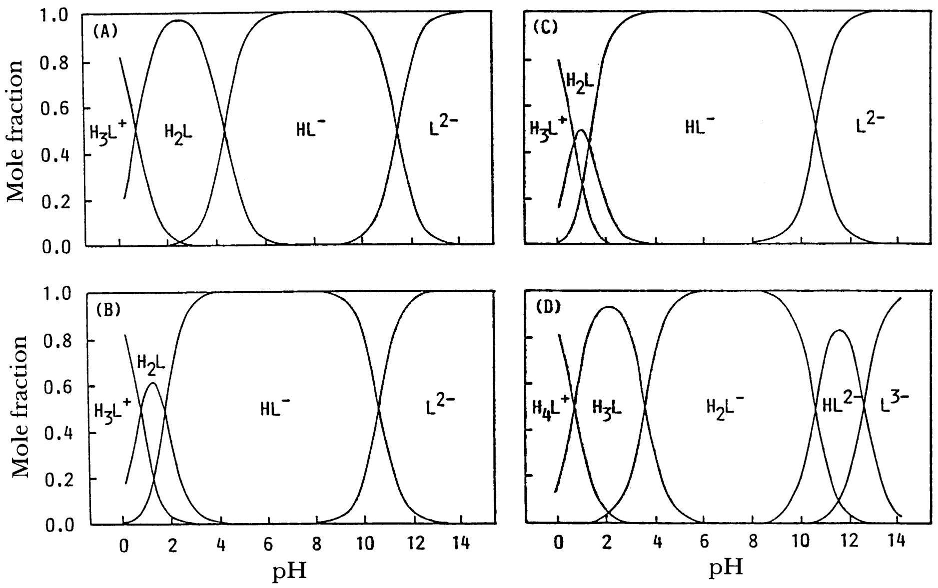


Fig. 5. Species distribution diagrams of (A), NPHQTS; (B), NPHTTS; (C), BTNPHTS; (D), BINPHTS.

5 are shown species distribution diagrams of the synthesized hydrazones prepared on the basis of their proton dissociation constants.

Color Reactions of the Hydrazones. Color reactions of the synthesized hydrazones with metal ions at pH 4, 7, and 10 were investigated. The results are shown in Tables 5, 6, 7, and 8. Every hydrazone reacted well with various metal ions including transition metal ions to form stable complexes. Especially with cadmium(II), cobalt(II), copper(II), iron(II), nickel(II), palladium(II), and zinc(II) reacted these hydrazones to form colored complexes with large molar absorptivities. These results suggest that the synthesized hydrazones are all very useful as highly sensitive spectrophotometric reagents for metal ions, especially for nickel(II), zinc(II), and cadmium(II).

Comparison of the Synthesized Hydrazones with NPHPTS. On comparison of the hydrazones synthesized in this work with NPHPTS synthesized in an earlier work,[9] the following facts are found: By substituting the pyridyl group in the ketone moiety of NPHPTS for a quinolyl, thiazolyl, benzothiazolyl, or

Table 5. Absorption Maxima and Apparent Molar Absorptivities of NPHQTS Complexes

Complex	pH 4		pH 7		pH 9	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
	nm	$M^{-1}cm^{-1}$	nm	$M^{-1}cm^{-1}$	nm	$M^{-1}cm^{-1}$
Ag(I)	—	—	—	—	514	16 500
Al(III)	—	—	—	—	—	—
Bi(III)	—	—	506	5 000	—	—
Cd(II)	—	—	505	42 500	505	86 500
Co(II)	530	47 000	530	47 000	530	47 000
Cr(III)	—	—	—	—	—	—
Cu(II)	518	38 000	507	65 500	507	73 000
Fe(II)	505	48 000	505	48 000	505	48 000
Ga(III)	486	44 000	513	4 000	—	—
Hg(II)	498	4 500	498	61 000	498	69 500
In(III)	510	2 000	496	6 500	—	—
Mn(II)	—	—	509	2 000	509	45 000
Ni(II)	510	40 000	510	81 000	510	81 000
Pb(II)	—	—	518	13 500	518	6 000
Pd(II)	564	15 500	467	20 500	467	34 500
Ti(IV)	521	2 500	516	2 500	516	2 000
V(IV)	537	2 500	537	5 000	—	—
V(V)	538	18 500	—	—	—	—
Zn(II)	506	1 000	506	76 500	506	83 500

Table 6. Absorption Maxima and Apparent Molar Absorptivities of NPHTTS Complexes

Complex	pH 4		pH 7		pH 9	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
	nm	$M^{-1}cm^{-1}$	nm	$M^{-1}cm^{-1}$	nm	$M^{-1}cm^{-1}$
Ag(I)	—	—	—	—	509	24 500
Al(III)	—	—	—	—	—	—
Bi(III)	—	—	—	—	507	8 000
Cd(II)	—	—	—	—	494	53 500
Co(II)	522	9 000	522	36 000	522	36 000
Cr(III)	—	—	—	—	—	—
Cu(II)	512	38 000	491	54 000	491	66 500
Fe(II)	494	11 000	494	33 500	494	33 500
Ga(III)	501	1 500	—	—	—	—
Hg(II)	481	4 000	481	34 500	481	61 000
In(III)	504	2 000	504	2 000	504	2 000
Mn(II)	—	—	—	—	498	3 500
Ni(II)	496	2 000	496	47 500	496	78 500
Pb(II)	—	—	489	1 500	489	1 500
Pd(II)	502	22 000	522	23 500	512	31 000
Ti(IV)	488	1 500	488	2 000	517	3 000
V(IV)	—	—	500	1 000	500	2 000
V(V)	—	—	—	—	—	—
Zn(II)	—	—	—	—	—	—

benzimidazolyl group, 1) bathochromic shifts of 8—18 nm are observed in absorption spectra of the hydrazones, the magnitude of the shift being in the sequence of quinolyl<thiazolyl≃benzimidazolyl<benzothiazolyl group. This suggests that similar bathochromic shifts occur in absorption spectra of their metal complexes, which has actually been confirmed in this work. 2) The pK_{a5} values of the hydrazones decrease by about 0.8 except for the case of NPHQTS and in addition, the pK_{a4} values of NPHTTS and BTNPHTS decrease by about 2.7 and 3.1, respectively. This suggests that the synthesized hydrazones react with metal ions to form complexes at lower pHs than those at which NPHPTS reacts. 3) Apparent molar absorptivities of metal complexes of the synthesized hydrazones are all very large and nearly the same as those of NPHPTS complexes.

These facts serve as useful informations for the molecular design of the hydrazone compound as the spectrophotometric reagent.

Table 7. Absorption Maxima and Apparent Molar Absorptivities of BTNPHTS Complexes

Complex	pH 4		pH 7		pH 9	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
	nm	$M^{-1}cm^{-1}$	nm	$M^{-1}cm^{-1}$	nm	$M^{-1}cm^{-1}$
Ag(I)	—	—	495	2 000	495	19 000
Al(III)	—	—	—	—	—	—
Bi(III)	—	—	—	—	526	5 000
Cd(II)	—	—	503	4 500	503	75 000
Co(II)	538	57 500	538	57 500	538	51 500
Cr(III)	—	—	516	2 000	516	2 500
Cu(II)	530	43 000	522	45 500	508	61 000
Fe(II)	509	49 000	509	49 000	509	40 500
Ga(III)	515	2 500	501	1 000	—	—
Hg(II)	474	3 000	452	22 000	452	27 500
In(III)	—	—	513	2 000	513	2 000
Mn(II)	—	—	—	—	508	3 500
Ni(II)	517	52 000	517	88 000	517	83 000
Pb(II)	—	—	526	2 400	—	—
Pd(II)	590	15 500	476	26 000	481	33 500
Ti(IV)	500	3 700	500	2 500	530	3 500
V(IV)	544	1 000	513	3 000	513	3 000
V(V)	547	3 000	—	—	—	—
Zn(II)	—	—	509	35 000	509	85 000

Table 8. Absorption Maxima and Apparent Molar Absorptivities of BINPHTS Complexes

Complex	pH 4		pH 7		pH 9	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
	nm	$M^{-1}cm^{-1}$	nm	$M^{-1}cm^{-1}$	nm	$M^{-1}cm^{-1}$
Ag(I)	—	—	504	1 500	499	9 000
Al(III)	—	—	—	—	—	—
Bi(III)	507	2 000	494	2 000	513	1 000
Cd(II)	—	—	493	16 500	493	66 500
Co(II)	517	66 500	513	62 500	513	62 500
Cr(III)	—	—	491	4 000	—	—
Cu(II)	509	41 000	509	41 000	496	50 000
Fe(II)	496	54 000	496	54 000	496	51 500
Ga(III)	472	29 500	489	2 500	492	2 000
Hg(II)	490	3 000	445	5 500	495	7 000
In(III)	493	27 500	493	2 500	487	20 000
Mn(II)	—	—	488	2 000	492	28 000
Ni(II)	498	27 000	498	87 000	498	84 500
Pb(II)	—	—	505	7 500	505	6 000
Pd(II)	562	27 500	521	25 000	517	27 000
Ti(IV)	492	4 000	492	4 000	492	4 000
V(IV)	511	6 000	511	9 000	504	3 500
V(V)	516	25 000	516	5 500	—	—
Zn(II)	—	—	493	48 000	493	77 500

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