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Protolytic and Complexing Properties of Hetarylhydrazones Derived from *o*-Tosylaminobenzaldehyde

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Abstract—New ligand systems were synthesized by condensation of *o*-tosylaminobenzaldehyde with quinolin-2-ylhydrazine and 1-methyl-1*H*-benzimidazol-2-ylhydrazine. Acid–base properties of the resulting hetarylhydrazones and their complexing power toward bivalent copper, nickel, and cobalt ions were studied. The stability constants of the complexes were determined.

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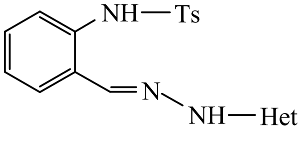
Hetarylhydrazones, i.e., condensation products of heterocyclic hydrazines and carbonyl compounds, having an acyclic moiety, have long attracted researchers' attention, primarily due to their strong complexing power [1–7]. In addition, hetarylhydrazones exhibit diverse biological activity [8–12], possess photochemical properties [13–15] and electriv conductivity [16], and are efficient analytical reagents for metal ions [17–21].

Schiff bases and hydrazones derived from *o*-tosylaminobenzaldehyde, as well as their metal complexes, were the subject of numerous studies [22–28]; however, hetarylhydrazones derived from *o*-tosylaminobenzaldehyde were not reported. Therefore, the goal of the present work was to synthesize new hetarylhydrazones **Ia** and **Ib** by condensation of *o*-tosylaminobenzaldehyde with quinolin-2-ylhydrazine and 1-methyl-1*H*-benzimidazol-2-ylhydrazine and examine their physicochemical properties.



Ia, Ib

Het = 1-methyl-1*H*-benzimidazol-2-yl (**a**), quinolin-2-yl (**b**), Ts = 4-methylphenylsulfonyl.

The structure of hydrazones **Ia** and **Ib** was determined on the basis of their elemental compositions (Table 1), IR, ^{1}H NMR, and electronic absorption spectra, and potentiometric titration data.

The IR spectra of **Ia** and **Ib** (Table 2) contained a broad absorption band in the region 3100–3200 cm^{-1} due to stretching vibrations of NH groups in the hydrazone and tosylamino fragments; stretching vibrations of the azomethine C=N bond appeared at 1615 cm^{-1}; and symmetric and antisymmetric stretching vibrations of the sulfonyl group were observed at 1170–1160 and 1345–1325 cm^{-1}, respectively

Compound **Ia** displayed the following signals in the ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.5 a and 11.1 s (1H each, NH, exchangeable with D_2O), 2.2 s and 3.3 s (3H each, CH_3), 8.3 s (1H, N=CH), 7.0–7.9 m (12H, H_{arom}). The ^{1}H NMR spectrum of **Ib** is similar, δ, ppm: 11.57 11.05 (1H each, NH), 2.2 s (3H, CH_3), 8.25 s (1H, CH=N), 7.1–7.8 m (14H, H_{arom}); addition of D_2O leads to complete disappearance of the NH proton signals, indicating their acidic character.

In the electronic spectra of solutions of **Ia** and **Ib** in ethanol and aqueous ethanol we observed long-wave

Table 1. Colors, melting points, and elemental analyses of compounds **Ia**, **Ib**, and **IIIa**–**IIIf**

Comp. no.	Color	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Ia	Yellow	197	60.5	5.3	16.5	$C_{22}H_{21}N_5O_2S$	60.1	5.0	16.7
Ib	Yellow	196	66.3	4.5	13.3	$C_{23}H_{20}N_4O_2S$	66.4	4.8	13.5
IIIa	Green	>250	57.0	4.1	15.6	$C_{44}H_{40}N_{10}O_4S_2Cu$	57.5	4.6	16.0
IIIb	Green	>250	57.3	4.3	15.9	$C_{44}H_{40}N_{10}O_4S_2Co$	57.9	4.6	16.1
IIIc	Brown	>250	57.1	4.1	16.5	$C_{44}H_{40}N_{10}O_4S_2Ni$	57.9	4.6	16.1
IIId	Green	>250	61.0	4.0	12.3	$C_{46}H_{38}N_8O_4S_2Cu$	61.8	4.3	12.5
IIIe	Brown	>250	61.9	4.1	12.4	$C_{46}H_{38}N_8O_4S_2Co$	62.1	4.3	12.6
IIIf	Brown	>250	62.0	3.9	12.2	$C_{46}H_{38}N_8O_4S_2Ni$	62.1	4.3	12.6

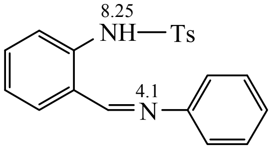
absorption bands at λ 356–358 nm (logε ≈ 4) (Figs. 1, 2). In going to acid medium, the absorption maximum of **Ia** shifts to the blue region (Δλ = 53 nm) (Fig. 1). Protonation of hydrazone **Ib** is accompanied by a red shift (Δλ = 16 nm) and increase in the intensity of the long-wave absorption maximum and appearance of a new band at λ_{max} 284 nm (Fig. 2). Variation of the spectral pattern of **Ib** in going to acid medium is related to *n*→π*-transitions with participation of the nitrogen atom in the heteroring. Less basic hydrazone **Ia** displayed appreciable variation of the spectral pattern in going to alkaline medium.

The acid–base properties of hydrazones **Ia** and **Ib** were studied by potentiometric titration [29] in aqueous ethanol. Their structure suggests existence of protonated, neutral, and deprotonated species, depending on the acidity of the medium. In acid medium, molecules of both hydrazones **Ia** and **Ib** undergo protonation at the endocyclic nitrogen atoms and nitrogen atom of the azomethine group, which possess the highest negative effective charge and electron density. Ionization of **Ia** and **Ib** in alkaline medium involves proton abstraction from the substituted amino group and NH nitrogen atom in the hydrazone fragment. The obtained p*K*a values are given below.

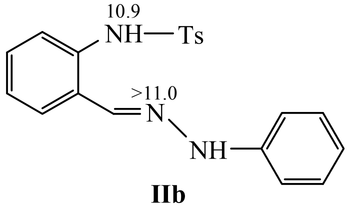
Table 2. Principal absorption bands (ν, cm^{-1}) in the IR spectra of compounds **Ia**, **Ib**, and **IIIa**–**IIIe**

Comp. no.	C=N	SO_{2as}	SO_{2s}	NH
Ia	1615 m	1325 m	1160 m	3200
IIIa	1605 m	1300 s	1150 s	–
IIIc	1605 m	1310 m	1150 s	–
IIIe	1590 s	1280 m	1120 s	
Ib	1615 s	1345 s	1170 s	3100
IIIb	1600 s	1312 w	1100 m	–
IIId	1595 s	1290 w	1105 s	–

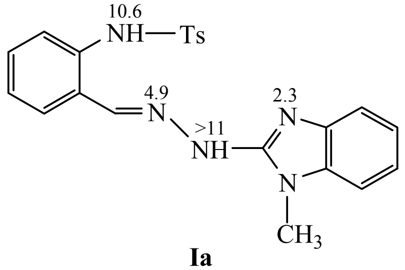
With a view to estimate the basicity of particular nitrogen atoms, we synthesized two model compounds **IIa** and **IIb** and examined their protolytic properties. Taking into account structural similarity of compounds **II** and hydrazones **I**, the obtained p*K*a values were assigned to different nitrogen atoms in molecules **I** as shown below.



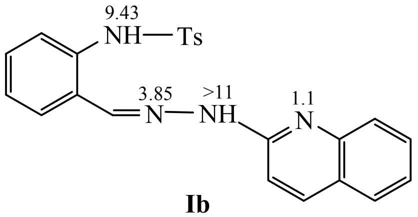
IIa



IIb



Ia



Ib

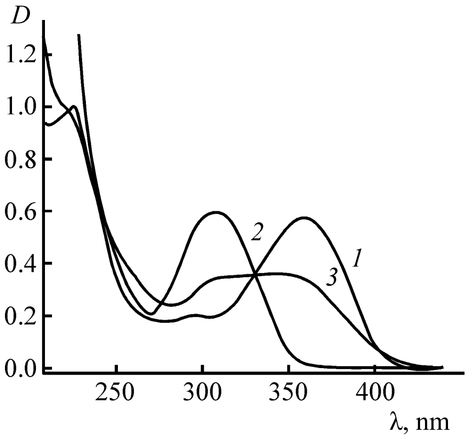


Fig. 1. Electronic absorption spectra of ethanolic solutions of hetarylhydrazone **Ia** ($c_{\mathbf{Ia}}$ = 2.5×10^{-5} M): (*1*) aqueous ethanol, (*2*) acid medium (c_{HCl} = 0.1 M), and (*3*) alkaline medium (c_{NaOH} = 0.1 M).

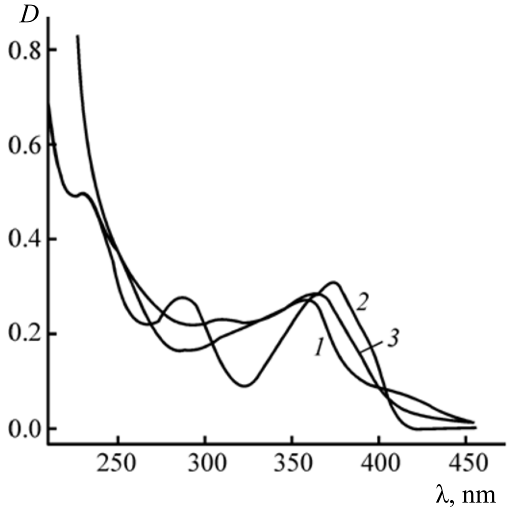
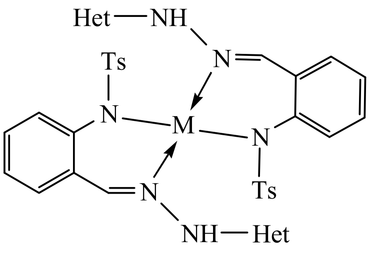


Fig. 2. Electronic absorption spectra of ethanolic solutions of hetarylhydrazone **Ib** ($c_{\mathbf{Ia}}$ = 2.5×10^{-5} M): (*1*) aqueous ethanol, (*2*) acid medium (c_{HCl} = 0.1 M), and (*3*) alkaline medium (c_{NaOH} = 0.1 M).

By reactions of hydrazones **Ia** and **Ib** with Cu(II), Co(II), and Ni(II) salts we obtained the corresponding 1 : 2 (metal–ligand) complexes **IIIa**–**IIIf**. Their structure was determined on the basis of their elemental compositions, IR spectra, and magnetochemical data. Unlike the free ligands, complexes **III** were characterized by reduced frequency of the C=N bond vibrations (Table 2), indicating participation of the azomethine nitrogen atom in the coordination. Deprotonation of the amino group upon complex formation was confirmed by disappearance of NH absorption in the region 3100–3200 cm^{-1}. The low-frequency shift (by 10–20 cm^{-1}) of absorption bands due to symmetric and antisymmetric stretching vibrations of the SO_2 group is likely to reflect its coordination to the metal ion [28]. According to the magnetochemical data, complexes **IIIa**–**IIIf** are mononuclear. Their effective magnetic moments approach the corresponding purely spin values, and they almost do not change as the temperature was reduced down to 77 K.



IIIa–**IIIf**

Het = 1-methyl-1*H*-benzimidazol-2-yl (**a**, **c**, **e**), quinolin-2-yl (**b**, **d**, **f**); M = Cu (**a**, **b**), Co (**c**, **d**), Ni (**e**, **f**).

Complexes **IIIa**–**IIIf** in solutions showed a strong absorption band at λ 415–490 nm in the electronic spectra. The spectral parameters of **IIIa**–**IIIf** are collected in Table 3.

It is known that the yield depends on the acidity of the medium, which is an important factor determining the equilibrium state in complexation process [29]. In the case of hydrolyzable metal ions, rise in pH increases the concentration of anionic ligand, but the concentration of metal ions simultaneously decreases as a result of formation of mono- and dihydroxo complexes. Therefore, to study the complexation reaction for analytical purposes, it was necessary to determine an optimal pH value which ensures the maximal yield of colored product. We examined the dependence of the absorbance of Cu(II), Co(II), and Ni(II) complexes with hydrazones **I** in solution upon pH. The most intense color developed in the pH ranges indicated in Table 4.

Stability constant is an important physicochemical parameter of coordination compounds. The stability constants of complexes **III** were determined by spectrophotometry using the equilibrium displacement technique, linear dependence (according to Rossoti), and preliminarily calculated equilibrium constant [30, 31]. The resulting stepwise constants were refined by approximating the sum of the partial mole fractions to unity by the following equation:

$$A_i/A_{max} + A_i/A_{max}\beta_1[L] + (A_i/A_{max} - 1)\beta_2[L]^2 = 0.$$

Table 3. Spectral parameters of solutions of complexes **IIIa**–**IIIe** in aqueous acetone ($c = 2\times10^{-5}$ M)

Comp. no.	λ_{max}, nm	ε, l mol^{-1} cm^{-1}
IIIa	430	9.75×10^3
IIIc	425	1.11×10^4
IIIe	430	1.11×10^4
IIIb	490	9.75×10^3
IIId	470	8.13×10^3

Table 4. Optimal pH values for complex formation

Ligand no.	Metal	pH
Ia	Cu(II)	9.45
	Co(II)	10.5
	Ni(II)	10.0
Ib	Cu(II)	8.25
	Co(II)	10.5

Table 5. Stability constants of complexes **IIIa**–**IIIe**

Comp. no.	β_1	β_2
IIIa	1.8×10^9	3.1×10^{17}
IIIc	1.5×10^6	4.5×10^{11}
IIIe	1.6×10^6	1.5×10^{12}
IIIb	6.4×10^9	1.7×10^{19}
IIId	1.0×10^5	2.7×10^{10}

Here, A_i amd A_{max} are, respectively, the intermediate and maximal optical densities obtained from the dependence $A = f(\text{pH})$, and [L] is the ligand concentration. The stability constants of complexes **IIIa–IIIf** are given in Table 5.

EXPERIMENTAL

Hydrazones **Ia** and **Ib** were synthesized accoring to the following procedure. A solution of 0.001 mol of the corresponding hetarylhydrazine in 10 ml of ethanol was added to a hot solution of 0.001 mol of *o*-tosylaminobenzaldehyde [32] in 10 ml of ethanol. The mixture was heated for 4 h under reflux, and the precipitate was filtered off, washed with ethanol, and recrystallized from DMF–ethanol.

Complexes **IIIa–IIIf** were synthesized as follows. A hot solution of 0.01 mol of Cu(II), Ni(II), or Co(II) salt in methanol was added to a solution of 0.01 mol of ligand **Ia** or **Ib** in methanol. The mixture was heated for 4 h under reflux, and the precipitate was filtered off, washed with hot methanol, and dried under reduced pressure.

The IR spectra were recorded on a Varian 1000 FT-IR spectrometer. The ^{1}H NMR spectra were measured on a Varian Unity-300 spectrometer using tetramethylsilane as internal reference and DMSO-d_6 as solvent. The magnetic susceptibilities of the complexes were determined by the relative Faraday method in the temperature range from 78 to 300 K using a setup manufactured at the Physical and Colloidal Chemistry Department, Southern Federal University; Hg[Co(CNS)$_4$] was used as calibration standard. The electronic absorption spectra (λ range 200–800 nm) were determined on a Cary 50 Scan spectrophotometer.

The acidity (pH) of solutions and ionization and protonation constants were determined with the aid of an I-120M ionometer. Potentiometric measurements were performed as follows. Ligand **Ia** or **Ib**, 0.1 mmol, was dissolved in aqueous acetone (1 : 1), 2 ml of 0.1 M hydrochloric acid was added, and the mixture was titrated with a 0.1 M solution of sodium hydroxide. All experiments were run at a constant ionic strength (0.1 M NaCl) under continuous stirring. The titrant was added in 0.02-ml portions using a microburet, and pK_a values were calculated by the formula [29]

$$\mathrm{p}K_a = \mathrm{pH} + \log\frac{(1-a)c_L - [\mathrm{H}^+] + [\mathrm{OH}^-]}{ac_L + [\mathrm{H}^+] - [\mathrm{OH}^-]}.$$

Here, a is the degree of neutralization, and c_L is the ligand molar concentration. The optimal pH values for complex formation and stability constants of the complexes were determined from the dependences $A = f(\text{pH})$ at $c_L = 4\times10^{-4}$ M, $c_M = 2\times10^{-5}$ M, $l = 2$ cm, $A = f(c_L)$ for aqueous acetone (1 : 1) at a constant metal concentration ($c_M = 2\times10^{-5}$ M) and optimal pH value.

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