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Effect of deprotonation on the spectral and luminescent properties of N,N'-bis(2-hydroxy-4-methylbenzylidene)-N-(2-aminoethyl)ethane-1,2-diamine in ethanol

© *L.P. Ardasheva*[1,2], *A.N. Borisov*[1,¶], *T.P. Efimova*[1], *L.D. Popov*[3], *I.A. Estrin*[4]

[1] Herzen State Pedagogical University of Russia, St. Petersburg, Russia
[2] Higher School of Technology and Energy,
St. Petersburg State University of Industrial Technology and Design, St. Petersburg, Russia
[3] Southern Federal University, Rostov-on-Don, Russia
[4] Rostov State University for Railway Transportation, Rostov-on-Don, Russia
¶ e-mail: alexey-borisov@mail.ru

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The absorption and fluorescence spectra of the aromatic azomethine of the N_3O_2-type —N,N'-bis(2-hydroxy-4-methylbenzylidene)-N-(2-aminoethyl)ethane-1,2-diamine were studied in ethanol solutions at 293 K. The adding of potassium hydroxide into alcoholic solutions leads to the deprotonation of azomethine and its transition to the anionic form. The time of establishing equilibrium is determined by the ratio of the concentrations of azomethine and alkali. Deprotonation causes significant changes in the spectral and luminescent properties of azomethine, including an increase in the quantum yield of fluorescence by up to 10 times.

Keywords: luminescence, aromatic azomethines, tautomeric forms, deprotonation.

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Aromatic azomethine bases (Schiff bases) and their complexes are known to luminesce under standard conditions and are regarded as promising materials for the production of electroluminescent devices [1–4]. Specifically, the luminescent properties of aromatic NO and N_2O_2 azomethines are due to the radiative degradation of $^1(\pi^*\pi)$-type singlet excited states in the nanosecond (ns) range. According to literature data, only keto-enamine tautomeric forms of azomethines, which form under photoexcitation, are characterized by emission activity driven by the ultrafast intramolecular transfer of a hydroxyl proton to nitrogen of the imino group [5].

At the same time, experimental data on luminescence of both tautomeric forms of azomethine H_2L (keto-enamine and enol-imine) in solutions are already available. The emission activity of tautomers depends on the energy of excitation radiation and the nature of the solvent that affects the tautomeric equilibrium [6]. It should be noted that the integral intensity of emission bands of tautomers in solutions is low, which translates into low quantum yields of luminescence.

The conversion of azomethines into anionic form as a result of deprotonation of aryl hydroxy groups by alkali presents some features of interest. In the present study, we examine the effect of deprotonation in ethanol solutions on the electronic absorption and emission properties of an N_3O_2-type aromatic azomethine (N,N'-bis(2-hydroxy-4-methylbenzylidene)-N-(2-aminoethyl)ethane-1,2-diamine, H_2L; see Diagram 1). The solvent was chosen for its chemical resistance to alkali, the fine solubility of KOH in ethanol, and the stability of the resulting azomethine solutions.

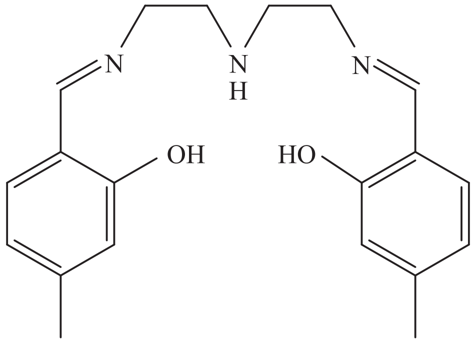

Diagram 1. Graphic formula of azomethine H_2L.

The method of synthesis of azomethine H_2L has been detailed earlier in [6]; the compound has also been identified by NMR and IR spectroscopy, and the parameters of its electronic absorption spectra (EAS) and luminescence spectra in various solvents have been reported.

Experimental

Solutions of H_2L and KOH in absolute ethanol and an aqueous solution of HCl were used in experiments. The solution concentrations were as follows: $C(H_2L) = 5.89 \cdot 10^{-5}$ mol/l, $C(KOH) = 4.72 \cdot 10^{-3}$ mol/l, and $C(HCl) = 0.1$ mol/l. The volumes of solutions and their

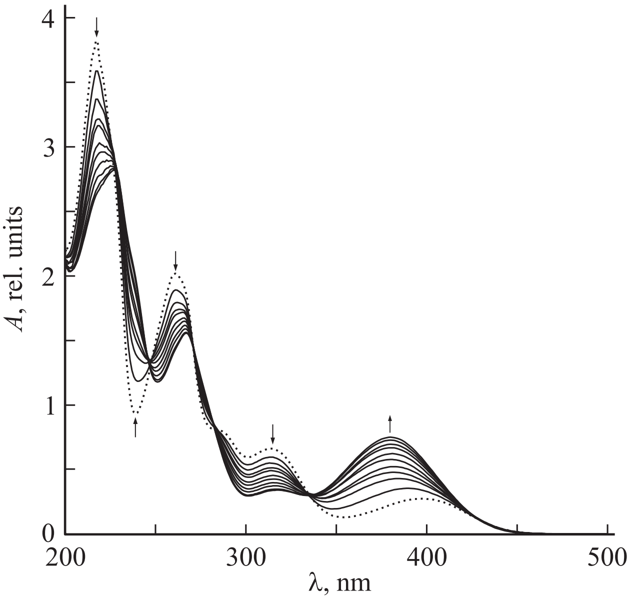

Figure 1. Dynamics of changes in the EAS H_2L of an ethanol solution upon the addition of 1 ml of the KOH solution in 0.1 ml (0.472 μmol) portions. Initial solution: 10 ml, 0.59 μmol H_2L. $l = 1$ cm. The spectrum of the neutral form of H_2L is represented by the dotted curve.

concentrations were chosen in such a way as to reduce the dilution effect to a minimum while maximizing the change in spectral and luminescent parameters. To convert azomethine into anionic form, 1 ml of the KOH solution was added (in a single step or in 0.1 ml portions) to 10 ml of the H_2L solution.

Electronic absorption spectra of azomethine solutions were recorded at 293 K within the range of 200−600 nm with a Shimadzu UV 2550 spectrophotometer.

Luminescence spectra of alcohol solutions of H_2L at 293 K were obtained using a „Fluorat-02-Panorama“ spectrofluorimeter. Relative quantum yields of luminescence (Φrel) were calculated by the Parker method [7]. An aqueous solution of fluorescein in 0.1 mol/l NaOH ($\lambda_{\max} = 520$ nm, $\Phi_{\text{st}} = 0.85$ at 293 K [8]) was used as a standart. The accuracy of determination of Φ_{rel} was 10%.

Results and discussion

The electronic absorption spectrum of azomethine H_2L in ethanol solutions is shaped by spin-allowed transitions of various orbital nature and is shown in Fig. 1 (dotted curve). According to literature data [9], high-intensity absorption bands in the $\lambda < 300$ nm region correspond to $\pi\pi^*$ transitions in aryl groups of azomethine. The absorption in the range 310−360 nm interval is of a mixed nature and caused by $n\pi$ and $\pi\pi^*$ transitions in imino groups [10]. A medium-intensity $n\pi^*$ absorption band is seen in alcohol solutions of H_2L at ~ 400 nm. It is caused by the formation of a keto-enamine tautomer as a result of intramolecular transfer of a hydroxyl proton to a nitrogen atom of the imino group [11].

It should be noted that ethanol solutions of azomethine H_2L exhibit exceptional physicochemical stability. Specifically, the electronic absorption spectra of these solutions retained their parameters for at least eight weeks.

An alcohol solution of KOH acts as an accessible and efficient reagent for deprotonation of aryl hydroxy groups of azomethine. It is evident that the conversion of azomethine into anionic form excludes the possibility of formation of a luminescent keto-enamine tautomer as a result of photoinduced proton transfer. The dynamics of changes in the EAS of the solution of H_2L in ethanol upon the addition of alkali is illustrated in Fig. 1. The addition of the first portion of KOH immediately leads to the emergence of four isosbestic points common to the spectral curves, which were retained throughout the experiment. This indicates that only two compounds (the initial and deprotonated forms of azomethine) are present in the solution and that equilibrium has been established between them.

Spectral changes take the form of an increase in intensity of the absorption band at 400 nm and its hypsochromic shift. Since this band is attributable to the $n\pi^*$ transition in the quinoid form of the anion, this is indicative of accumulation of the anionic form of H_2L in the solution. Deprotonation leads to an increase in contribution of quinoid (II)−(V) structures (Diagram 2) to the distribution of electron density in the anion and results in a corresponding decrease of intensity of the bands with maxima at 218 and 260 nm. In addition, the decrease of the mixed band intensity caused by transitions in the imino groups ($\lambda_{\max} = 315$ nm) is indicative of their involvement in stabilization of the resulting anions. The changes in EAS of azomethine occurring during its deprotonation are in close agreement with the scheme of stabilization of the formed anions by resonance (I)−(V) structures:

Since the changes in EAS are associated with the conversion of azomethine H_2L into anionic form, an equimolar amount of a strong acid (0.05 ml of 0.1 mol/l HCl solution) was added to it in order to shift the equilibrium toward the formation of the initial neutral form (Fig. 2). Note that the addition of acid leads to an almost complete restoration of parameters of the original spectrum in terms of both positioning of the band maxima and their intensity (Fig. 2, curves *1* and *3*).

Protonation of the neutral form of azomethine proceeds along nitrogen atoms of the imino groups and causes irreversible changes in composition of the solution. In the experiment, 0.05 ml of the solution of HCl acid (4.72 μmol) were added to the azomethine solution, which was then neutralized with an equimolar amount of KOH. The changes in EAS of the solution are shown in the inset of Fig. 2. Although the isosbestic points remain, the acid eliminates completely the long-wave absorption band. However, the addition of alkali to the acidified solution of H_2L does not restore the original state of the system. This is hardly surprising, since azomethine bases are irreversibly

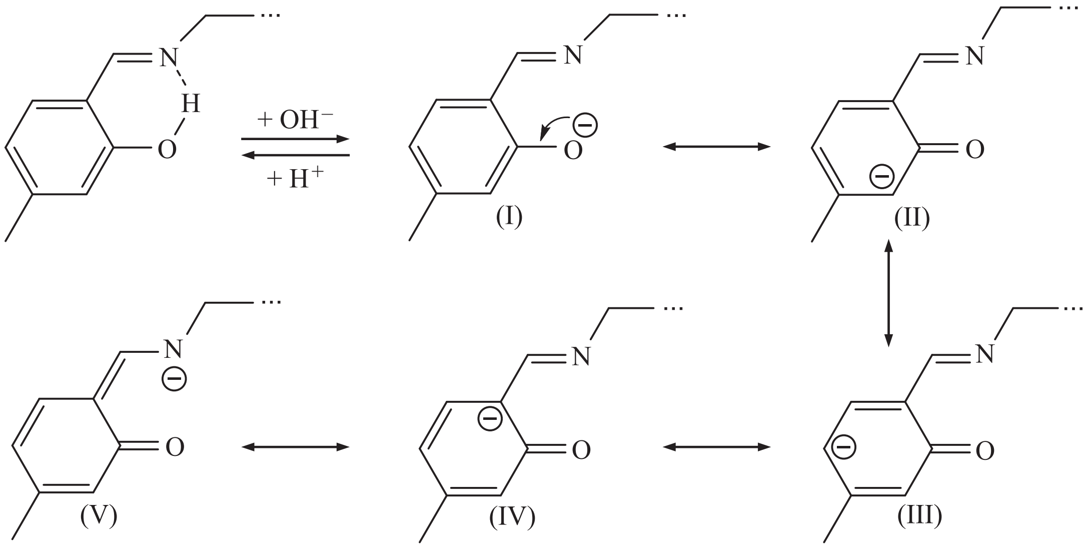

Diagram 2. Structure of conjugated anion L^{2-}.

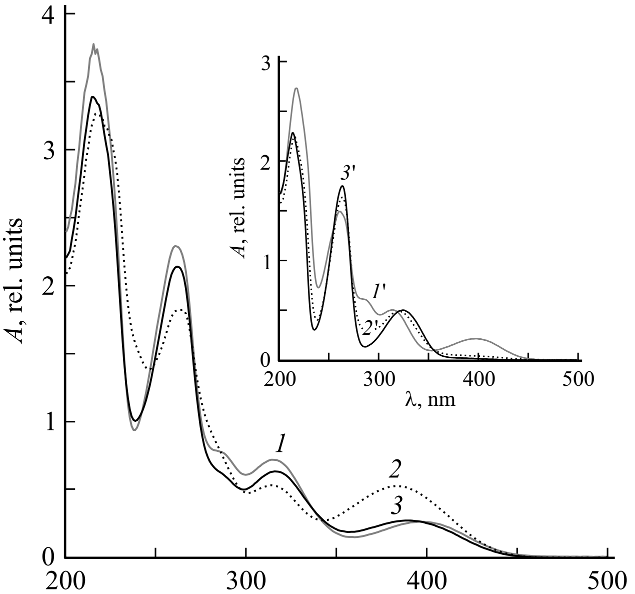

Figure 2. Changes in the EAS of H2L in ethanol upon single-step addition of KOH and HCl in different order: initial solution, 10 ml, 0.59 μmol H_2L (*1*); with the addition of 1 ml of the KOH solution (4.72 μmol) (*2*); with the subsequent addition of 0.05 ml of the HCl solution (4.72 μmol) (*3*). Inset: initial solution, 10 ml, 0.59 μmol H_2L (*1'*); with the addition of 0.05 ml of the HCl solution (4.72 μmol) (*2'*); with the subsequent addition of 1 ml of the KOH solution (4.72 μmol) (*3'*). $l = 1$ cm.

hydrolyzed in acidic solutions [12]. Thus, deprotonation of the neutral H_2L form is, in contrast to its protonation, reversible.

The conversion of azomethine into anionic form exerts a significant influence on its emission activity in alcohol solutions. The most significant change induced by deprotonation is a sharp increase in integral luminescence intensity (ILI). In addition, a bathochromic shift of the long-wavelength band is observed both in the excitation spectra (from 355 to 377 nm; Fig. 3, *a*) and in the luminescence spectra (from 465 to 493 nm; Fig. 3, *b*) relative to the neutral form of H_2L. Curves *2* and *3* in the excitation and luminescence spectra are characterized by isosbestic points, which indicates that the anionic form of azomethine is converted into the neutral one upon acidification of the solution.

Figure 4 presents the temporal changes in the excitation and luminescence spectra of the H_2L solution after single-step addition of alkali. A significant ILI enhancement is evident, while the shape of the bands and the positions of their maxima are preserved. It is important to note that, in contrast to the neutral form, the luminescence parameters of the anionic form of azomethine do not depend on the excitation energy. The slow accumulation of the anionic H_2L form in the solution after the addition of alkali explains the ILI enhancement over a period of 50 min. This is probably attributable to the influence of the concentration factor under the experimental conditions. The addition of 4.72 μmol KOH to the solution of azomethine (0.59 μmol) in a single step immediately raises the ILI by a factor of almost 20 (from 0.73 to 14.56 rel. units; Fig. 5, curve *1*). The quantum yield of luminescence increases by an order of magnitude (from 0.02 to 0.20). A virtually linear ILI growth was observed within the next 50 min (Fig. 5, curve *2*). The overall factor of ILI enhancement after the addition of alkali was close to 80.

Thus, deprotonation of azomethines is an efficient method for accumulating a single luminescent anionic form in a solution, which is accompanied by a significant increase in quantum yield. The high sensitivity of the spectral-

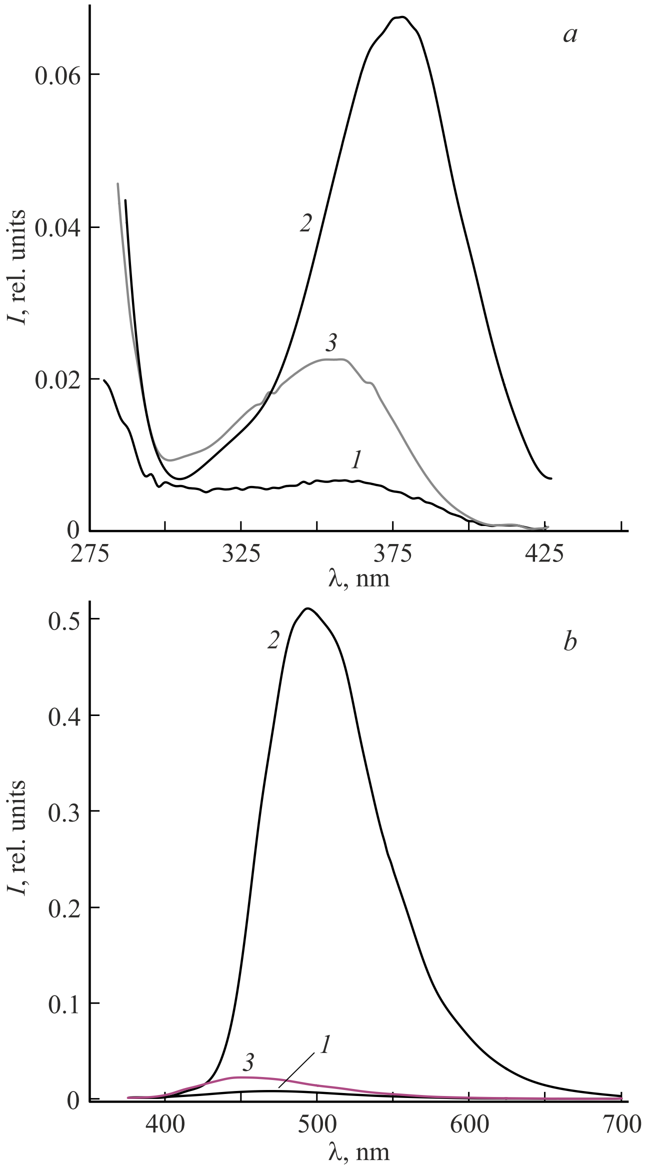

Figure 3. (*a*) Excitation spectra of (recording wavelength $\lambda_{reg} = 440$ nm) H_2L ($C = 5.89 \cdot 10^{-5}$ mol/l): (*1*) initial solution (10 ml), (*2*) 60 min after single-step addition of 1 ml of the KOH solution (4.72 μmol), (*3*) after the addition of 0.05 ml of the HCl solution (4.72 μmol) to solution *2*. (*b*) Emission spectra (excitation wavelength $\lambda_{ex} = 365$ nm) of H_2L ($C = 5.89 \cdot 10^{-5}$ mol/l): (*1*) initial solution (10 ml), (*2*) 60 min after single-step addition of 1 ml of the KOH solution (4.72 μmol), (*3*) after the addition of 0.05 ml of the HCl solution (4.72 μmol) to solution *2*.

luminescent parameters of azomethine to the concentration of alkali in ethanol solutions makes the studied compound a potential sensor.

Conflict of interest

The authors declare that they have no conflict of interest.

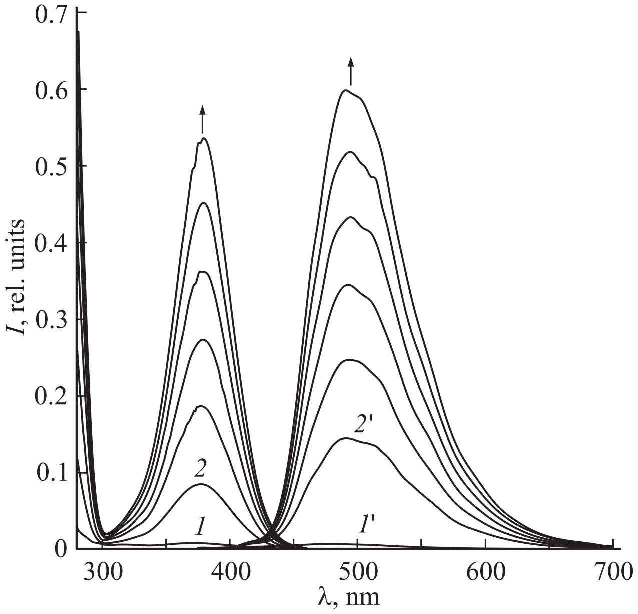

Figure 4. Dynamics of changes in excitation spectra (*1, 2*) of H_2L ($C = 5.89 \cdot 10^{-5}$ mol/l, 0.59 μmol) $\lambda_{reg} = 490$ nm and luminescence spectra (*1′, 2′*) $\lambda_{ex} = 365$ nm: (*1, 1′*) initial solution; (*2, 2′*) immediately after the addition of 1 ml of the KOH solution (4,72 μmol). Further measurements were carried out in 10 min intervals; total time — 50 min.

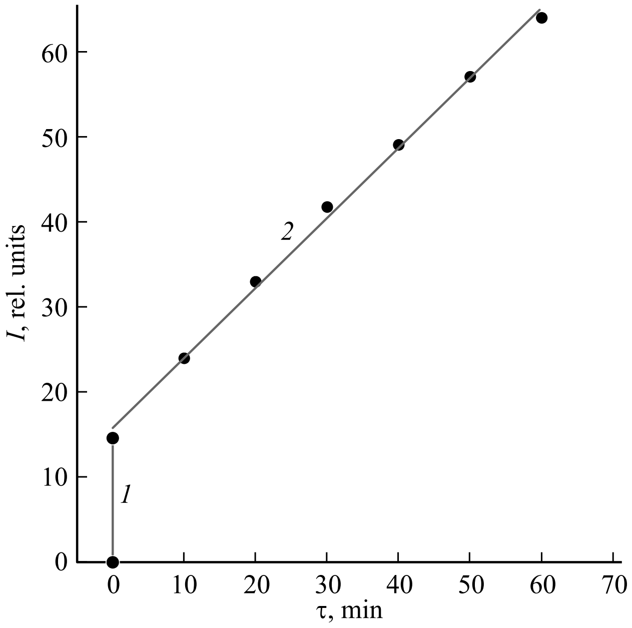

Figure 5. Growth of the integral luminescence intensity of H_2L ($C = 5.89 \cdot 10^{-5}$ mol/l, 0.59 μmol), $\lambda_{ex} = 365$ nm: (*1*) immediately after the addition of 1 ml of the KOH solution (4.72 μmol); (*2*) after the addition of alkali at time intervals.

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