Russian Journal of Organic Chemistry, Vol. 38, No. 3, 2002, pp. 385–389. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 3, 2002, pp. 407–410.
Original Russian Text Copyright © 2002 by Skorik, Neudachina, Osintsev, Yatluk, Vshivkov, Osintseva.

Protolytic Equilibria of Some *N,N*-Bis(2-carboxyethyl)aminoazobenzenesulfonic Acids in Aqueous Solution

Yu. A. Skorik[1], L. K. Neudachina[1], A. V. Osintsev[2], Yu. G. Yatluk[2], A. A. Vshivkov[1], and E. V. Osintseva[3]

[1] *Gor'kii Ural State University, pr. Lenina 51, Yekaterinburg, 620083 Russia*

[2] *Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 20, Yekaterinburg, 620219 Russia*

[3] *Institute of Metallurgy, Ural Division, Russian Academy of Sciences, Yekaterinburg, Russia*

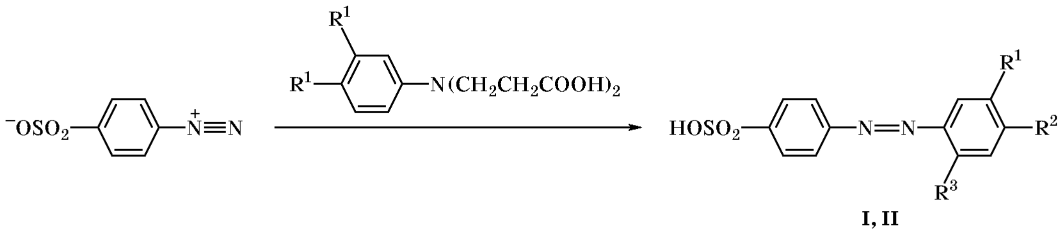
Received June 21, 2000

Abstract—4-[4-Bis(2-carboxyethyl)aminophenylazo]benzenesulfonic acid and 4-[2-bis(2-carboxyethyl)amino-4,5-dimethylphenylazo]benzenesulfonic acid were synthesized for the first time by azo coupling of diazosulfanilic acid with *N*,*N*-bis(2-carboxyethyl)aniline and *N*,*N*-bis(2-carboxyethyl)-3,4-xylidine, respectively. The acid ionization constants of the products were determined, their electron absorption spectra were measured, and schemes of acid–base equilibria in aqueous solution were proposed.

Only a few complexones derived from azobenzene and containing an iminodiacetate group conjugated with the aromatic system have been reported [1, 2]. The presence of conjugated bond system and chelating moiety gives rise to a considerable shift of the absorption maximum in the visible region of electron spectra on complex formation with metals. Therefore, such compounds can be used as metallochromic indicators and photometric reagents. Promising model compounds for synthesis of complexones having an azobenzene moiety are *N*,*N*-bis(2-carboxyethyl)anilines which have been prepared by us previously [3–5]. These compounds exhibit a high selectivity for copper(II) ions but absorb only in the ultraviolet region of the spectrum. Therefore, the goal of the present study was to synthesize and characterize some *N*,*N*-bis(2-carboxyethyl)aminoazobenzenesulfonic acids on the basis of *N*,*N*-bis(2-carboxyethyl)anilines and to examine their protolytic equilibria in aqueous solution.

4-[4-Bis(2-carboxyethyl)aminophenylazo]benzenesulfonic acid (**I**) and 4-[2-bis(2-carboxyethyl)amino-4,5-dimethylphenylazo]benzenesulfonic acid (**II**) were

Scheme 1.



I, II

I, $R^1 = R^3 = H$, $R^2 = N(CH_2CH_2COOH)_2$; **II**, $R^1 = R^2 = Me$, $R^3 = N(CH_2CH_2COOH)_2$.

---

* This study was performed under financial support of the Ministry of Education of the Russian Federation (project no. 015.05.01.004) and CRDF (grant no. REC-005).

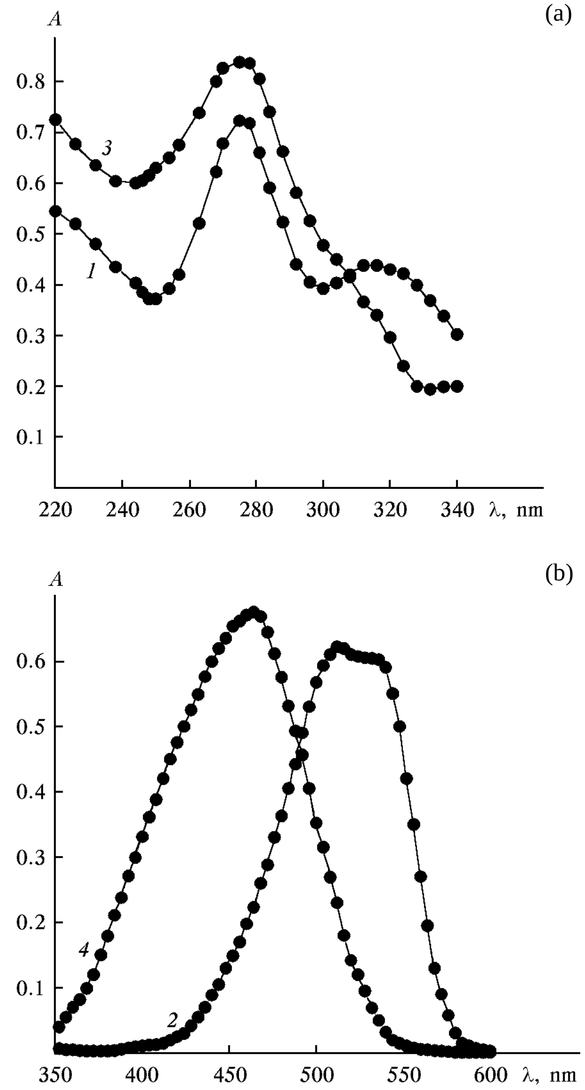


Fig. 1. Electron absorption spectra (a) in the ultraviolet and (b) in the visible region of solutions of 4-[4-bis(2-carboxyethyl)aminophenylazo]benzenesulfonic acid (**I**) (*1, 2*) in 0.1 N hydrochloric acid and (*3, 4*) at pH 10; $c_{\mathrm{I}} \times 10^{-5}$, M: (*1, 3*) 8, (*2, 4*) 1.

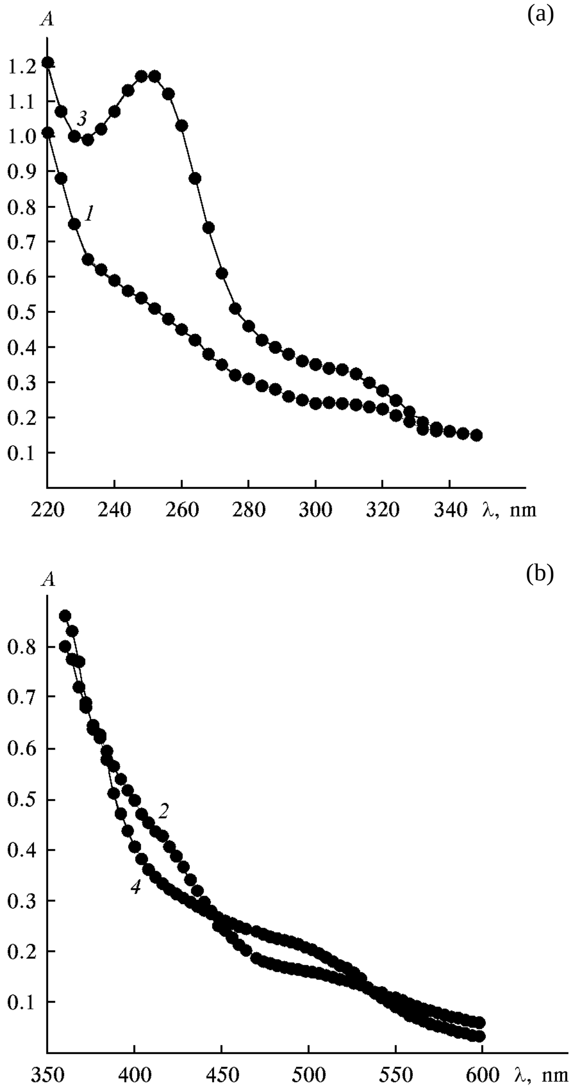
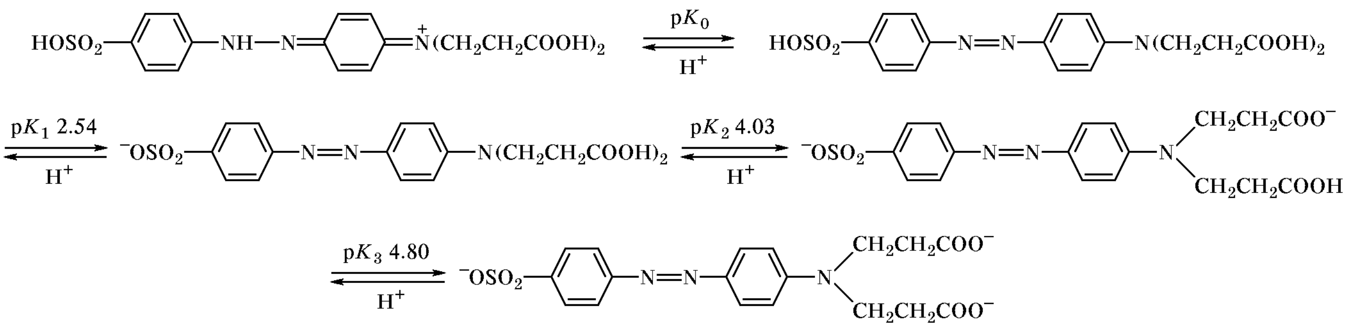


Fig. 2. Electron absorption spectra (a) in the ultraviolet and (b) in the visible region of solutions of 4-[2-bis(2-carboxyethyl)amino-4,5-dimethylphenylazo]benzenesulfonic acid (**I**) in aqueous solution at pH (*1, 2*) 4.0 and (*3, 4*) 10.0; $c_{\mathrm{II}} \times 10^{-5}$, M: (*1, 3*) 0.7, (*2, 4*) 5.

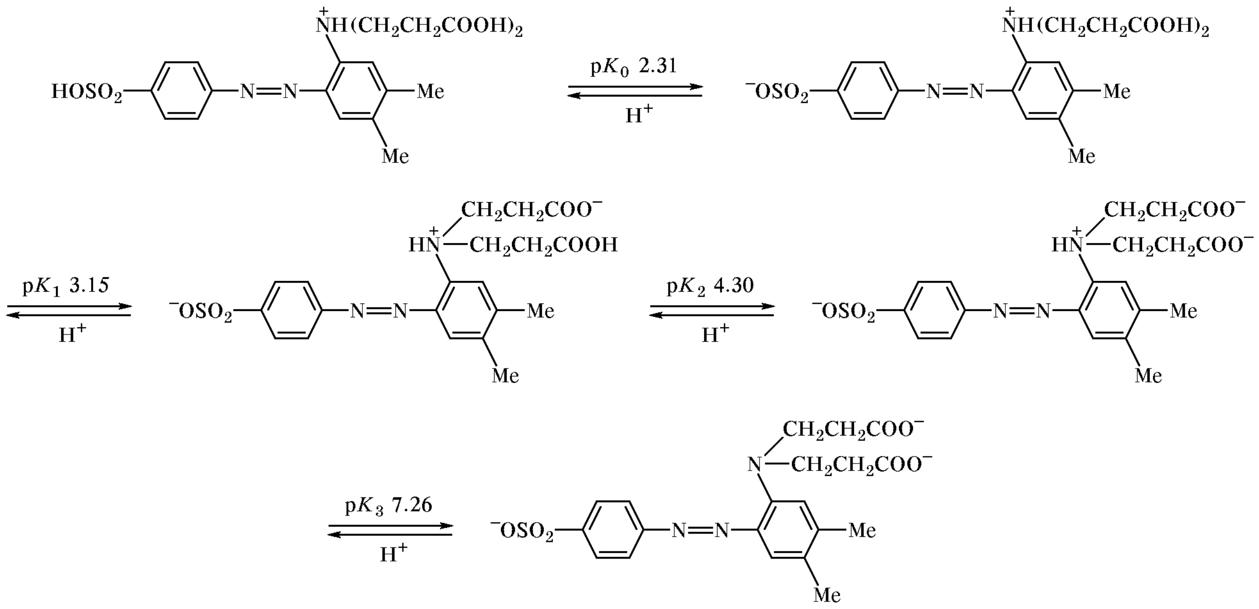
synthesized by us for the first time by azo coupling of diazosulfanilic acid with *N*,*N*-bis(2-carboxyethyl)-aniline and *N*,*N*-bis(2-carboxyethyl)-3,4-xylidine, respectively (Scheme 1). Compounds **I** and **II** are H_3L acids having two additional basic centers, the amino and azo groups, which could give rise to versatile ionization mechanisms. Their acid ionization constants (Schemes 2 and 3) were determined by potentiometry. The ionization constants for cationic forms H_4L^+ (pK_0) were determined by potentiometric titration of solutions containing an equimolar amount of HCl. In order to attain a necessary accuracy in the determination of pK_a the concentration of a weak acid should be no less than the expected ionization constant [6]. Insofar as compound **I** is poorly soluble in acid medium, we failed to determine by potentiometry its pK_0 value with an acceptable accuracy.

Electron absorption spectroscopy is a sufficiently informative tool for studying protolytic equilibria of compounds having a conjugated bond system in aqueous medium. It is known [7–9] that N-substituted aminoazobenzenes can undergo protonation at the amino or azo group. Protonation of both these to form a dication is also possible. Proton addition induces reorganization of the conjugated bond system, so that

Scheme 2.



Scheme 3.



different forms display different spectral parameters. The electron absorption spectra in the ultraviolet and visible regions of aqueous solutions of compounds **I** and **II** at different pH values (0–12) are given in Figs. 1 and 2, and their absorption maxima are listed in table. The acid ionization constants were determined from the pH dependences of optical density at the absorption maximum (Fig. 3): pK_0(**I**) 2.00$\pm$0.03 and pK_3(**II**) 7.40$\pm$0.09. The *S*-like shape of these dependences indicates that only two absorbing species are present in aqueous solution of each compound. Let us arbitrarily call these species protonated and deprotonated. We did not detect completely protonated form, though its existence cannot be ruled out. For example, double protonation of *N*,*N*-dimethylaminoazobenzene is observed only in 14.7 M H_2SO_4 in methanol [10].

The spectral parameters of aqueous solutions of compound **I** are similar to those found for its nearest structural analog, *N*,*N*-dimethylaminoazobenzene-4-sulfonic acid (**III**) (conjugate acid of Methyl Orange), whose ionization mechanism was studied in [11]. With the above in mind and taking into account that sulfo group is more acid than carboxy, we can assert that ionization of acid **I** follows Scheme 2. Compound **I** should possess a weak complexing power because of the very low basicity of the nitrogen atom in the aminodipropionate moiety. Therefore, it may be used as acid–base indicator with visual parameters like those of Methyl Orange, but its indicator range (pH 1.0–3.0) is displaced to the acid region by 1.5 log unit relative to that of Methyl Orange: p*T*(**II**) 2.00, p*T*(**III**) 3.46 [11].

Compound **II** shows considerably different spectral parameters, including the position of absorption bands, their intensity, and pH dependence. The intensities of analogous absorption bands of compounds **I** and **II** change in the opposite directions on variation

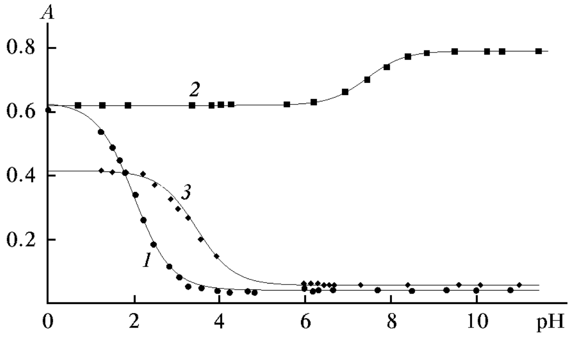


Fig. 3. Dependences of the absorption of aqueous solutions of N-substituted aminoazobenzenesulfonic acids **I**–**III** on pH of the medium: (*1*) **I**, $c = 1 \times 10^{-5}$ M, λ 535 nm; (*2*) **II**, $c = 2 \times 10^{-3}$ M, λ 490 nm; (*3*) **III**, $c = 1 \times 10^{-5}$ M, λ 530 nm.

of pH (Fig. 3). Their ionization constants, determined by spectrophotometry, differ by more than 5 orders of magnitude. These data indicate distortion of conjugation between the amino and azo groups in molecule **II**, which leads to increase of the basicity of the amino group. As a result, the latter undergoes protonation to form zwitterionic structure with reduced basicity of the azo group. The mechanism of ionization of compound **II** can be illustrated by Scheme 3.

The presence in molecule **II** of highly basic nitrogen atom in the aminodipropionate moiety and of azo group (as possible coordination center) in the *ortho* position could give rise to interesting complex formation properties of this compound.

EXPERIMENTAL

Initial *N*,*N*-bis(2-carboxyethyl)anilines were synthesized as described in [3–5]. Sulfanilic acid was diazotized by the procedure reported in [12]. The azo coupling with *N*,*N*-bis(2-carboxyethyl)aniline was performed in strongly acid medium at room temperature, and the reaction with *N*,*N*-bis(2-carboxyethyl)-3,4-xylidine was carried out in neutral medium at a temperature not exceeding 5°C.

Absorption maxima (λ, nm) in the electron spectra of aqueous solutions of N-substituted aminoazobenzenesulfonic acids

Electron transition	Protonated form			Deprotonated form		
	I	**II**	**III**	**I**	**II**	**III**
$\Phi \to \Phi^*$	272	250	274	272	250	274
	315	310	316		310	
$\pi \to \pi^*$	516	425	506	460	430	460
$n \to \pi^*$	535	495	530		490	

4-(4-Dimethylaminophenylazo)benzenesulfonic acid was synthesized by standard procedure [12].

4-[4-Bis(2-carboxyethyl)aminophenylazo]benzenesulfonic acid (I). Yield 80%, mp 225°C. ^{1}H NMR spectrum (Bruker Avance DRX-400, 400 MHz, DMSO-d_6), δ, ppm: 2.53 t (4H, CH_2COOH, J = 7.1 Hz), 3.72 t (4H, NCH_2, J = 7.1 Hz), 6.82 d (2H, 2-H, 6-H, J = 9.3 Hz), 7.73 d.d (4H, 2′-H, 3′-H, 5′-H, 6′-H, J_1 = 8.8, J_2 = 4.0 Hz), 7.78 d (2H, 3-H, 5-H, J = 9.3 Hz). Found, %: C 51.31; H 4.33; N 9.89. $C_{18}H_{19}N_3O_7S$. Calculated, %: C 51.30; H 4.54; N 9.97.

4-[2-Bis(2-carboxyethyl)amino-4,5-dimethylphenylazo]benzenesulfonic acid (II). Yield 60%. mp 170°C. ^{1}H NMR spectrum (Tesla BS-587A, 80 MHz, DMSO-d_6), δ, ppm: 2.10 s (3H, CH_3), 2.16 s (3H, CH_3), 2.41 t (4H, CH_2COOH, J = 7.1 Hz), 3.52 t (4H, NCH_2, J = 7.1 Hz), 6.51–7.74 m (6H, H_{arom}). Found, %: C 53.82; H 4.82; N 8.90. $C_{20}H_{23}N_3O_7S$. Calculated, %: C 53.44; H 5.16; N 9.35.

Potentiometric titration of 2 and 3 mM aqueous solutions of compounds **I** and **II** was performed in an inert atmosphere (nitrogen) at 20±1°C; ionic strength μ 0.1 (KCl). An I-130M ionometer equipped with an ESL-43-07 glass electrode and an EVL-1M3.1 saturated silver chloride electrode was used. At least three titration curves were recorded for each concentration. The titrant was a 0.1 M carbonate-free solution of potassium hydroxide. The ionization constants were calculated by the programs developed by the authors [4], the absolute error in the determination of pK_a values was no more than 0.08 log unit.

Spectrophotometric measurements were performed on an SF-46 spectrophotometer using 1-cm quartz cells. The optical densities were measured relative to a 0.1 N solution of KCl or 0.1 N hydrochloric acid and a 0.1 N solution of KOH for strongly acidic and strongly basic solutions, respectively. The acid ionization constants were calculated [13] by approximation of the experimental dependences of optical density on pH, using the equation $y = a + b/(1 + 10^{c-x})$, where the coefficient c is the sought pK_a.

REFERENCES

1. Dyatlova, N.M., Temkina, V.Ya., and Popov, K.I., *Kompleksony i kompleksonaty metallov* (Complexones and Their Complexes with Metals), Moscow: Khimiya, 1988, pp. 258–265.

2. Lastovskii, R.P., Dyatlova, N.M., Kolpakova, I.D., and Krinitskaya, L.V., *Zh. Obshch. Khim.*, 1967, vol. 37, no. 7, pp. 121–128.
3. Melkozerov, V.P., Neudachina, L.K., and Vshivkov, A.A., *Russ. J. Gen. Chem.*, 1997, vol. 67, no. 1, pp. 92–97.
4. Skorik, Yu.A., Neudachina, L.K., and Vshivkov, A.A., *Russ. J. Gen. Chem.*, 1999, vol. 69, no. 2, pp. 285–290.
5. Skorik, Yu.A., Neudachina, L.K., Vshivkov, A.A., Yatluk, Yu.G., and Gert, N.V., *Zh. Fiz. Khim.*, 1999, vol. 73, no. 12, pp. 2269–2271.
6. Beck, M.T. and Nagypal, I., *Chemistry of Complex Equilibria*, Budapest: Akad. Kiado, 1985. Translated under the title *Issledovanie kompleksoobrazovaniya noveishimi metodami*, Moscow: Mir, 1989, pp. 224–226.
7. Kaminskii, Yu.L., Bershtein, I.Ya., and Ginzburg, O.F., *Dokl. Akad. Nauk SSSR*, 1962, vol. 145, no. 2, pp. 330–331.
8. Bershtein, I.Ya. and Ginzburg, O.F., *Usp. Khim.*, 1972, vol. 41, no. 2, pp. 177–202.
9. Yagupol’skii, L.M. and Gandel’sman, L.Z., *Ukr. Khim. Zh.*, 1979, vol. 45, no. 2, pp. 145–154.
10. Wojciechowski, K. and Szadowski, J., *Polish J. Chem.*, 1986, vol. 60, pp. 797–810.
11. *Indicators*, Bishop, E., Ed., Oxford: Pergamon, 1972. Translated under the title *Indikatory*, Moscow: Mir, 1976, vol. 1, pp. 111–117.
12. *Organikum. Organisch-chemisches Grundpraktikum*, Berlin: Wissenschaften, 1990, 17th ed. Translated under the title *Organikum*, Moscow: Mir, 1992, vol. 2, p. 231.
13. Bulatov, M.I. and Kalinkin, I.P., *Prakticheskoe rukovodstvo po fotometricheskim metodam analiza* (Manual on Photometric Methods of Analysis), Leningrad: Khimiya, 1986, pp. 225–227.