N,N′-Bis(9-anthrylmethyl)diamines as Fluorescent Chemosensors for Transition Metal Cations

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Abstract—*N,N′*-Bis(9-anthryl)-substituted diamines, imidazolidines, and hexahydropyrimidines were synthesized, and their luminescence properties and complexing ability were studied. *N,N′*-Bis(9-anthrylmethyl)-ethane-1,2-diamine and *N,N′*-bis(9-anthrylmethyl)butane-1,4-diamine were found to be effective and selective PET chemosensors for Zn^{2+} and H^+, respectively. 2-[1,3-Bis(9-anthrylmethyl)hexahydropyrimidin-2-yl]-6-methoxyphenol can be used as fluorescent chemosensor for mercury(II) cations.

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We previously showed that *N,N′*-disubstituted diamines can be used as chemosensors for zinc cations [1]. The results of DFT (B3LYP/LanL2DZ) quantum-chemical calculations of *N,N′*-bis(9-anthrylmethyl)-ethane-1,2-diamine as an example showed that the energy of complex formation decreases in the series $Zn^{2+} > Hg^{2+} > Cd^{2+}$ due to joint action of steric and orbital factors [2]. With a view to perform a detailed study on the interaction of chemosensors of that type with transition metal cations we synthesized *N,N′*-bis-(9-anthrylmethyl)-substituted diamines **I–V** and products of their cyclization by the action of salicylaldehydes, *N,N′*-bis(9-anthrylmethyl)imidazolidines **VI** and **VII** and *N,N′*-bis(9-anthrylmethyl)hexahydropyrimidines **VIII** and **IX** (Scheme 1).

Compounds **I–IX** have a three-module structure typical of PET (photoinduced electron transfer) chemosensors [3–8]: their molecules contain a fluorophore (anthracene fragment), receptor (amino groups), and spacer (methylene bridge). Such systems give rise to photoinduced electron transfer from the receptor to fluorophore, which leads to considerable (or in some cases complete) suppression of fluorescence. Addition of a metal cation to the receptor of a chemosensor makes PET unfavorable from the viewpoint of energy, and fluorescence intensity appreciably increases. It should be noted that in most cases polyamine-based systems are widely used as chemosensor fragments

responsible for complex formation [9–19]. The 9-anthryl signaling fragment frequently plays the role of fluorophore in chemosensor molecules [17, 18, 20–23]; nevertheless, no detailed studies on luminescence and complexing properties of the representative series of diamines **I–IX** were performed so far.

The electronic absorption spectra of compounds **I–IX** contained a long-wave maximum in the region λ 320–400 nm with a fine vibrational structure typical of anthracene derivatives. The intensity of these bands is twice as large as that intrinsic to model *N*-(9-anthrylmethyl)phenylmethanamine having only one anthracene fragment. Therefore, compounds **I–IX** can be regarded as bichromophore systems in which the anthracene fragments do not interact with each other in the ground state.

Photoexcitation of molecules **I–IX** at 293 K leads to a weak emission in a broad range from 390 to 550 nm. The fluorescence band has a complex shape; it shows a vibrational structure typical of local anthracene emission (λ 390–450 nm) and a diffuse structureless emission in the λ range from 460 to 550 nm with its maximum at λ 480 nm. The fluorescence excitation spectra in the regions of 400 and 480 nm are identical, and they coincide with the long-wave absorption of compounds **I–IX**, indicating similar initial excited states for the different emission bands. Presumably, the fluorescence band of compounds **I–IX** at λ 460–

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Scheme 1.
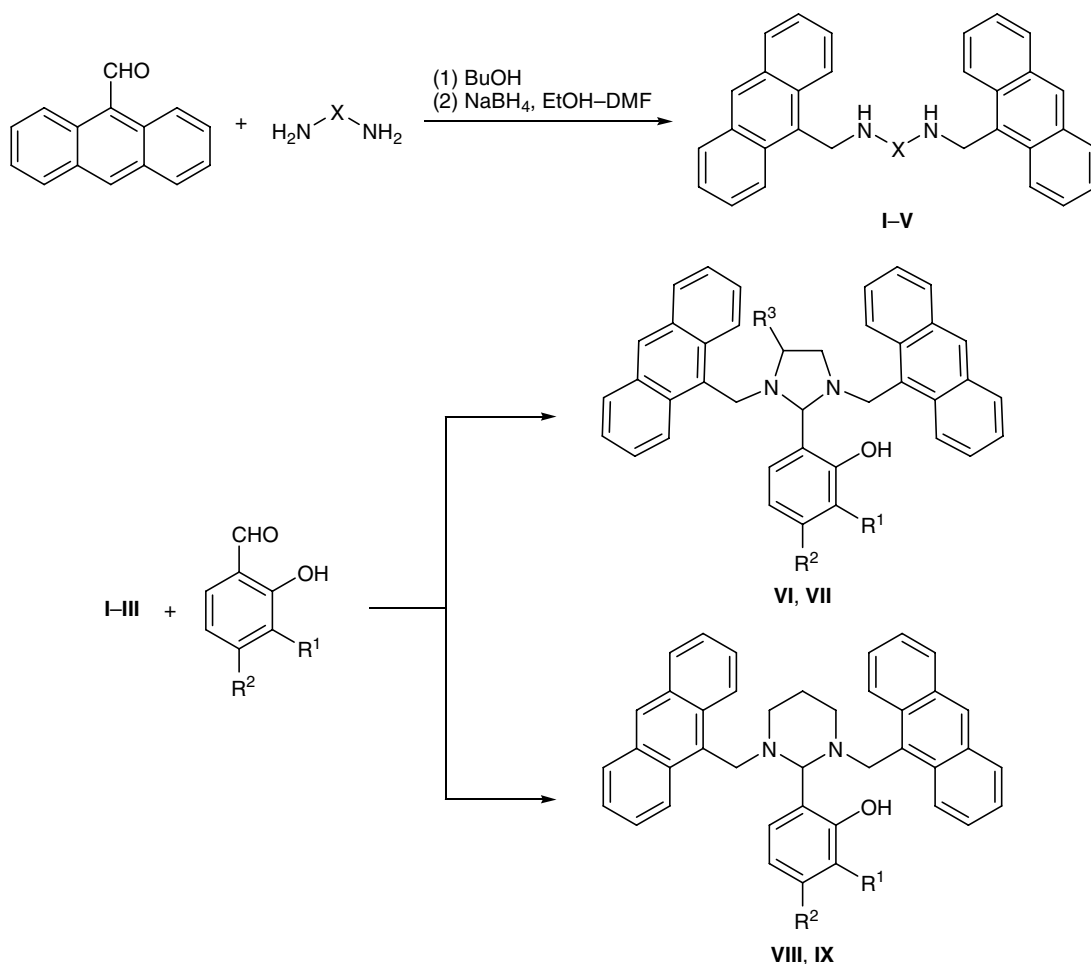
I, X = (CH$_2$)$_2$; **II**, X = CH(Me)CH$_2$; **III**, X = (CH$_2$)$_3$; **IV**, X = (CH$_2$)$_4$; **V**, X = (CH$_2$)$_6$; **VI**, R^1 = R^3 = H, R^2 = Me; **VII**, R^1 = H, R^2 = R^3 = Me; **VIII**, R^1 = H, R^2 = Me; **IX**, R^1 = MeO, R^2 = H.

550 nm corresponds to the interaction between the two anthracene fragments with formation of intramolecular excimer [24–27], and the position of its emission maximum (λ 480 nm) suggests that the anthracene fragments are overlapped through one benzene ring [24].

Complex formation with various metal cations strongly affects the thermodynamic parameters of photoinduced electron transfer via binding of lone electron pair on the nitrogen atom; as a result, the fluorescence intensity changes, and compounds **I**–**V** acquire sensor properties. Addition of bivalent transition metal acetates (Cu, Hg) to a solution of **I**–**V** in acetonitrile induces a small attenuation of the anthracene local emission, while addition of Zn^{2+} ions strongly increases the fluorescence intensity (Fig. 1).

Compounds **I** and **II** in neutral medium are highly efficient fluorescent chemosensors for Zn^{2+} ions, while diamine **IV**, unlike the other members of the examined

series, shows almost no sensor activity toward zinc cations (I/I_0 = 2.6) but is the most sensitive to pH.

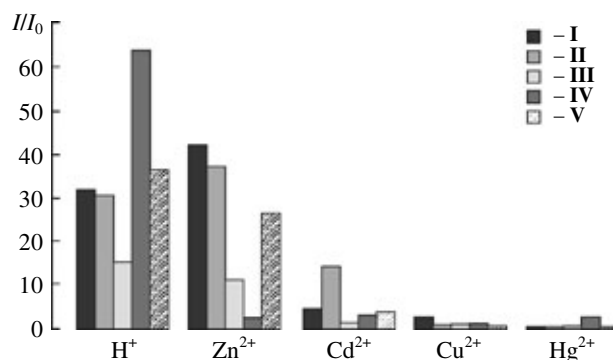Insofar as no analytical signal necessary for determination of the composition of complexes formed was

Fig. 1. Relative increase in the fluorescence intensity of diamines **I**–**V** in acetonitrile ($c = 5 \times 10^{-5}$ M) upon addition of metal cations ($c = 2.5 \times 10^{-4}$ M); λ 390 nm.
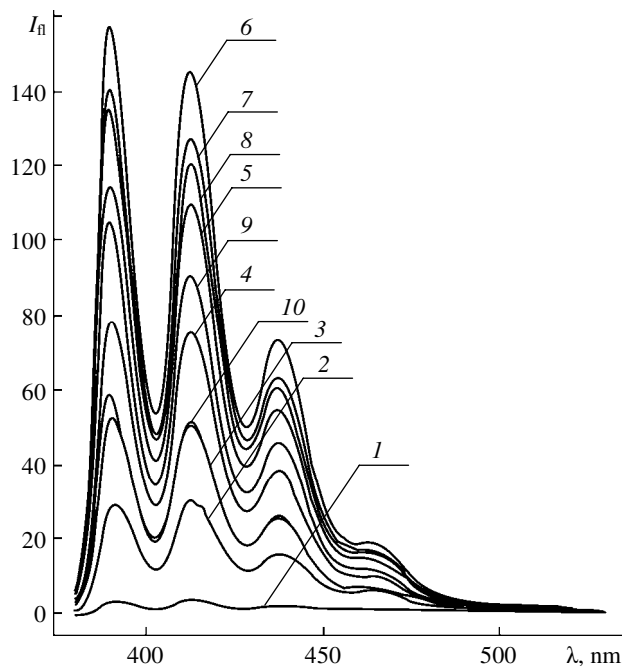
Fig. 2. Plot of the fluorescence intensity of compound **III** in acetonitrile (λ_{excit} 365 nm) versus mole fraction of Zn(OAc)$_2 \cdot$ 2H$_2$O ($c = 2 \times 10^{-5}$ M). Curves *1–10* correspond to mole fractions of Zn^{2+} from 0 to 0.9 through a step of 0.1.

observed in the electronic absorption spectra of compounds **I–V**, the stoichiometry of their complex formation with Zn^{2+} ions was established by measuring the fluorescence of their isomolar solutions (Fig. 2). The isomolar diagram (Fig. 3) indicates that the composition of the resulting complex is 1:1 [1 mol of diamine **III** per mole of Zn(OAc)$_2 \cdot$2H$_2$O]. Cyclic diamines
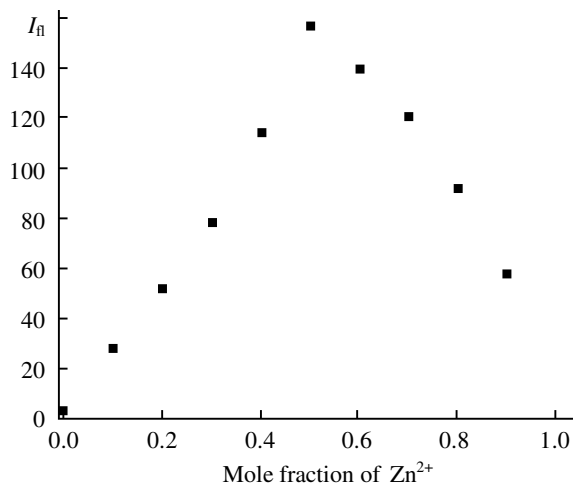

Fig. 3. Isomolar diagram for the determination of the composition of the complex formed by compound **III** with zinc(II) acetate [dependence of the fluorescence intensity of compound **III** in acetonitrile upon mole fraction of Zn(OAc)$_2 \cdot$2H$_2$O, $c = 2 \times 10^{-5}$ M; λ_{excit} 365 nm, λ_{fl} 390 nm].

VI–IX turned out to be less selective for transition metal cations (Fig. 4), except for compound **IX** which is a selective sensor for Hg^{2+} ions.

Thus our results showed that *N,N'*-bis(9-anthrylmethyl)ethane-1,2-diamine (**I**) and *N,N'*-bis(9-anthrylmethyl)butane-1,4-diamine (**IV**) are efficient and selective PET chemosensors for Zn^{2+} and H$^+$ ions, respectively, and that 2-[1,3-bis(9-anthrylmethyl)hexahydropyrimidin-2-yl]-6-methoxyphenol (**IX**) may be used as fluorescent chemosensor for mercury(II) ions.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz); the chemical shifts were measured relative to signals from residual protons in the deuterated solvent (CDCl$_3$, δ 7.25 ppm; DMSO-d_6, δ 2.50 ppm). The electronic absorption spectra were recorded on a Specord M-40 spectrophotometer. The luminescence spectra were measured on Hitachi 650-60 and Varian Eclipse spectrofluorimeters. The IR spectra were obtained on a Specord 75IR instrument from samples dispersed in mineral oil. The melting points were determined in glass capillaries using a PTP (M) melting point apparatus. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates using chloroform as eluent; development with iodine vapor in a moist chamber.

N,N'-Bis(9-anthrylmethyl)ethane-1,2-diamine (**I**) and *N,N'*-bis(9-anthrylmethyl)hexane-1,6-diamine (**V**) were synthesized previously [1].

N,N'-**Bis(9-anthrylmethyl)propane-1,2-diamine** (**II**) was prepared according to the procedure described in [1] from anthracene-9-carbaldehyde and propane-1,2-diamine. Yield 69%, mp 147–148°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 1465, 1370. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.27 d (3H, CH$_3$, $J = 6.2$ Hz), 2.70–3.22 m (3H, CH, CH$_2$), 4.55–4.88 m (4H, CH$_2$), 7.16–8.43 m (20H, H$_{arom}$, NH). Found, %: C 87.00; H 6.71; N 6.29. C$_{33}$H$_{30}$N$_2$. Calculated, %: C 87.19; H 6.65; N 6.16.

N,N'-**Bis(9-anthrylmethyl)propane-1,3-diamine** (**III**) was prepared in a similar way [1] from anthracene-9-carbaldehyde and propane-1,3-diamine. Yield 71%, mp 112–113°C (from butan-1-ol); published data [24]: mp 109–110°C. IR spectrum, ν, cm^{-1}: 3405, 1465, 1367. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.78 t (2H, CH$_2$, $J = 6.3$ Hz), 2.92 t (4H, CH$_2$, $J = 6.6$ Hz),

4.61 s (4H, CH$_2$), 7.31–8.49 m (18H, H$_{arom}$). Found, %: C 87.11; H 6.73; N 6.12. C$_{33}$H$_{30}$N$_2$. Calculated, %: C 87.19; H 6.65; N 6.16.

N,N′-Bis(9-anthrylmethyl)butane-1,4-diamine (IV) was prepared in a similar way [1] from anthracene-9-carbaldehyde and butane-1,4-diamine. Yield 85%, mp 120–121°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 1465, 1367. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.65 s [4H, (CH$_2$)$_2$], 2.92 s (4H, CH$_2$), 4.71 s (4H, CH$_2$), 7.33–8.62 m (18H, H$_{arom}$). Found, %: C 87.05; H 6.94; N 6.10. C$_{34}$H$_{32}$N$_2$. Calculated, %: C 87.14; H 6.88; N 5.98.

Compounds VI–IX (*general procedure*). A solution of 2 mmol of diamine **I**, **II**, or **III** and 2 mmol of the corresponding substituted salicylaldehyde in 10 ml of butan-1-ol (or benzene) was heated for 15–20 min in the presence of an acid catalyst (acetic acid or *p*-toluenesulfonic acid). The solvent was removed under reduced pressure, and the precipitate was filtered off, washed with petroleum ether, dried in air, and recrystallized from butan-1-ol.

2-[1,3-Bis(9-anthrylmethyl)imidazolidin-2-yl]-5-methylphenol (VI) was synthesized from diamine **I** and 2-hydroxy-4-methylbenzaldehyde. Yield 75%, mp 219–220°C. IR spectrum, ν, cm^{-1}: 1645, 1600, 1465, 1390. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.41 s (3H, CH$_3$), 2.44–2.78 m [4H, (CH$_2$)$_2$], 4.45 s (1H, CH), 4.65 d.d (4H, CH$_2$, J_1 = 29.0, J_2 = 12.7 Hz), 6.68–8.51 m (21H, H$_{arom}$), 10.12 s (1H, OH). Found, %: C 85.87; H 6.18; N 4.96. C$_{40}$H$_{34}$N$_2$O. Calculated, %: C 85.99; H 6.13; N 5.01.

2-[1,3-Bis(9-anthrylmethyl)-4-methylimidazolidin-2-yl]-5-methylphenol (VII) was synthesized from diamine **II** and 2-hydroxy-4-methylbenzaldehyde. Yield 72%, mp 259–260°C. IR spectrum, ν, cm^{-1}: 1640, 1600, 1470, 1380. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.13 d (3H, CH$_3$, J = 6.4 Hz), 2.17 d.d (2H, CH$_2$, J_1 = 9.1, J_2 = 2.3 Hz), 2.44 s (3H, CH$_3$), 2.89 t (2H, CH$_2$, J = 8.8 Hz), 3.07–3.24 m (1H, CH), 4.33–4.67 m (3H, CH$_2$, CH), 4.80 d.d (2H, CH$_2$, J_1 = 22.4, J_2 = 13.0 Hz), 6.61–8.42 m (21H, H$_{arom}$), 10.22 s (1H, OH). Found, %: C 86.13; H 6.30; N 4.93. C$_{41}$H$_{36}$N$_2$O. Calculated, %: C 85.98; H 6.34; N 4.89.

2-[1,3-Bis(9-anthrylmethyl)hexahydropyrimidin-2-yl]-5-methylphenol (VIII) was synthesized from diamine **III** and 2-hydroxy-4-methylbenzaldehyde. Yield 70%, mp 236–237°C. IR spectrum, ν, cm^{-1}: 1600, 1467, 1385. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.08–1.60 m (2H, CH$_2$), 2.18–2.52 m (7H, CH$_2$, CH$_3$),
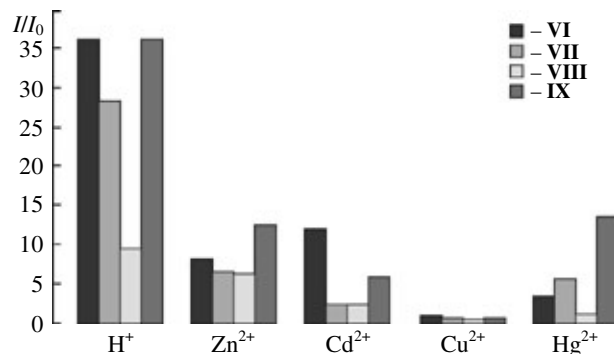

Fig. 4. Relative increase in the fluorescence intensity of compounds **VI–IX** in acetonitrile ($c = 5 \times 10^{-5}$ M) upon addition of metal cations ($c = 2.5 \times 10^{-4}$ M); λ 390 nm.

4.22 s (1H, CH), 4.50 d.d (4H, CH$_2$, J_1 = 38.8, J_2 = 12.7 Hz), 6.69–8.62 m (21H, H$_{arom}$), 9.80 s (1H, OH). Found, %: C 86.02; H 6.39; N 4.91. C$_{41}$H$_{36}$N$_2$O. Calculated, %: C 85.98; H 6.34; N 4.89.

2-[1,3-Bis(9-anthrylmethyl)hexahydropyrimidin-2-yl]-6-methoxyphenol (IX) was synthesized from diamine **III** and 2-hydroxy-3-methoxybenzaldehyde. Yield 68%, mp 260–261°C. IR spectrum, ν, cm^{-1}: 1630, 1465, 1485. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.11–1.65 m (2H, CH$_2$), 2.22–2.57 m (4H, CH$_2$), 4.08 s (3H, CH$_3$), 4.32 s (1H, CH), 4.48 d.d (4H, CH$_2$, J_1 = 57.3, J_2 = 12.8 Hz), 6.86–8.6 m (21H, H$_{arom}$), 10.0 s (1H, OH). Found, %: C 83.49; H 6.35; N 4.80. C$_{41}$H$_{36}$N$_2$O$_2$. Calculated, %: C 83.36; H 6.48; N 4.74.

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