ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 9, pp. 1305–1309. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © I.E. Tolpygin, Yu.V. Revinskii, A.V. Tsukanov, A.D. Dubonosov, V.A. Bren', V.I. Minkin, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 9, pp. 1288–1292.

Chemosensors Based on N^2-(Anthracen-9-ylmethyl)-naphthalene-2,3-diamine

I. E. Tolpygin[a], Yu. V. Revinskii[a], A. V. Tsukanov[b], A. D. Dubonosov[b], V. A. Bren'[a], and V. I. Minkin[a, b]

[a] *Institute of Physical and Organic Chemistry, Southern Federal University, pr. Stachki 194/2, Rostov-on-Don, 344090 Russia*
e-mail: tolpygin@ipoc.sfedu.ru

[b] *Southern Research Center, Russian Academy of Sciences, Rostov-on-Don*

Received February 28, 2011

Abstract—Condensation of N^2-(anthracen-9-ylmethyl)naphthalene-2,3-diamine with aromatic and heterocyclic aldehydes gave a series of the corresponding Schiff bases and *N*-(anthracen-9-ylmethyl)-substituted naphtho-[2,3-*d*]imidazoles. Study on the luminescence spectra and complexing ability of the condensation products revealed their sensor properties toward some heavy metal cations.

DOI: 10.1134/S1070428011090077

Development of efficient optical chemosensor systems is primarily determined by proper choice of the receptor fragment responsible for selective recognition of an analyte [1–4]. Of particular interest are those sensors whose selectivity and efficiency can be varied over a wide range by changing the structure and properties of the coordination entity [5, 6]. The results of our previous studies [7–9] demonstrated prospects in using *N*-(anthracen-9-ylmethyl)benzene-1,2-diamine having a free amino group as a variable base for the synthesis of fluorescent reagents for different cations, e.g., H^+ and Hg^{2+}. The procedure developed in [7] for the preparation of *N*-(anthracen-9-ylmethyl)benzene-1,2-diamine was extended to naphthalene-2,3-diamine. The reaction of the latter with an equimolar amount of anthracene-9-carbaldehyde gave Schiff base **I** which was reduced with sodium tetrahydridoborate in EtOH–DMF to obtain amine **II** in high yield (Scheme 1). Protons in the NH_2 and NH groups of compound **II** appeared in the ^{1}H NMR spectrum as two broadened signals at δ 4.88 and 5.10–5.30 ppm, respectively.

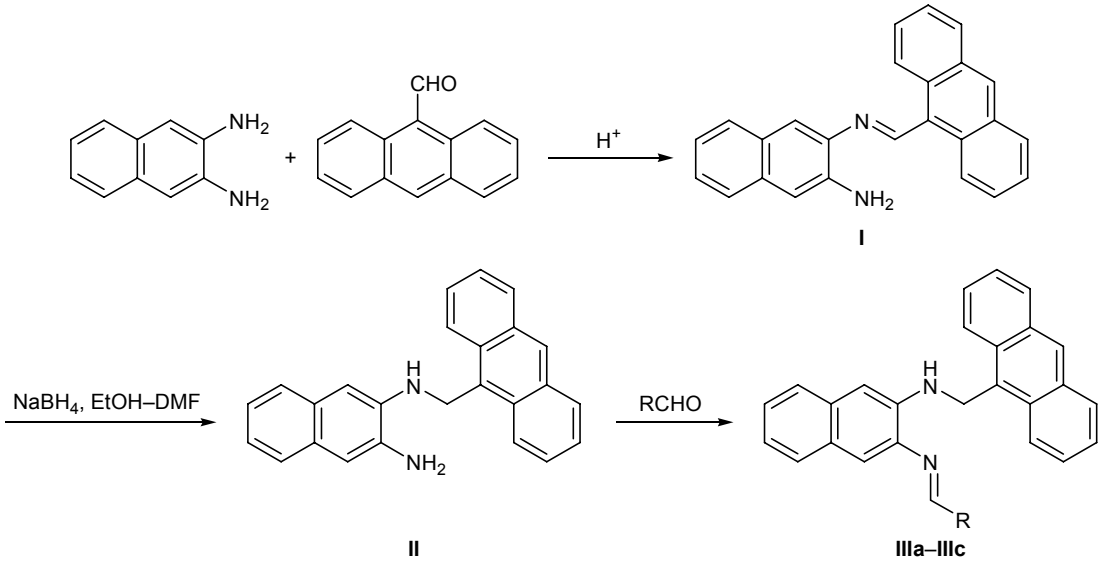
The free amino group in molecule **II** was modified with a view to obtain a chelating receptor moiety. By reaction of **II** with *ortho*-hydroxy-substituted aromatic aldehydes we synthesized the corresponding *ortho*-hydroxy Schiff bases **IIIa**–**IIIc** (Scheme 1). The ^{1}H NMR spectra of **IIIa**–**IIIc** lacked signal assignable to NH_2 group, whereas signals typical of CH=N (a singlet at δ 8.60–9.46 ppm) and OH protons (a singlet at δ 12.07–14.05 ppm) appeared.

As with *ortho*-phenylenediamine derivative [7], the reaction of amine **II** with pyridine-2-carbaldehyde did not stop at the stage of formation of the corresponding Schiff base, but subsequent oxidative cyclization with participation of atmospheric oxygen afforded naphtho-[2,3-*d*]imidazole **IV** (Scheme 2). In the ^{1}H NMR spectrum of **IV** we observed a strong downfield shift of the CH_2 proton signal (by ~1.6 ppm relative to the corresponding signal of the initial amine), while neither NH_2 nor NH signal was present.

We also tried to modify the structure of coordination entity (and hence the selectivity of sensor system) via introduction of thiourea fragment [10]. As in the previous case, the reaction of compound **II** with phenyl isothiocyanate gave cyclic derivative, 1-(anthracen-9-ylmethyl)-2,3-dihydro-1*H*-naphtho[2,3-*d*]-imidazole-2-thione (**V**) [11, 12]. The formation of cyclic structure followed from the downfield shift of the NCH_2 signal by 1.1 ppm, the lack of signals from phenyl ring, and the presence of a downfield signal at δ 12.93 ppm, which is typical of NHC(S) proton.

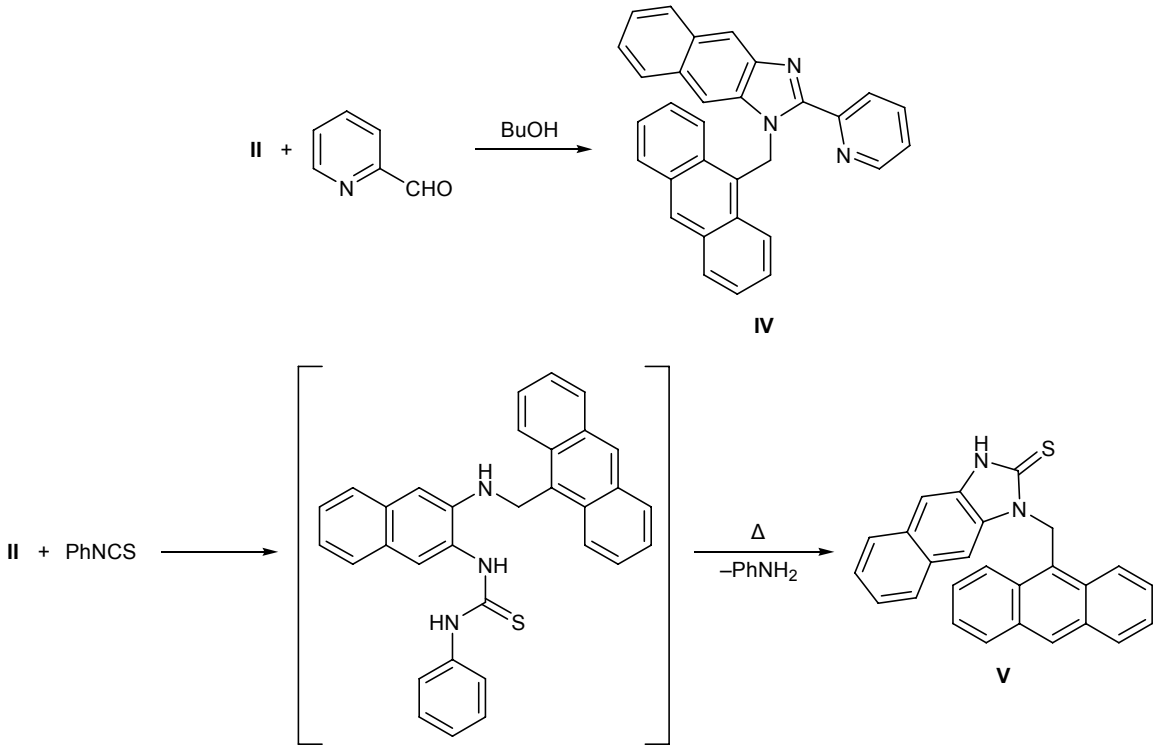
The complexing power of the newly synthesized compounds was studied by measuring their fluorescence spectra in acetonitrile. Unlike analogous *N*-(anthracen-9-ylmethyl)benzene-1,2-diamine derivatives, in most cases complexation of **II**–**V** with cations led to

Scheme 1.

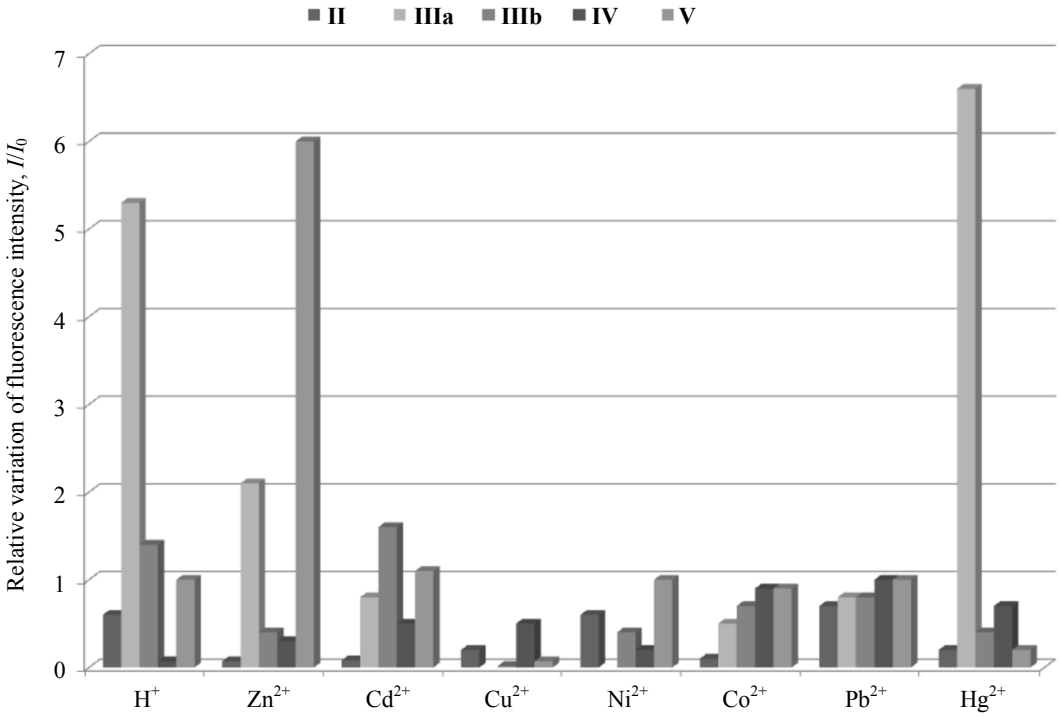


R = 2-HO-5-MeC_6H_3 (**a**), 2-hydroxynaphthalen-1-yl (**b**), 1-hydroxynaphthalen-2-yl (**c**).

Scheme 2.



abrupt fluorescence quenching (see figure). In addition, a fairly strong difference in the complexing properties of Schiff bases **IIIa**–**IIIc** was observed. Initial amine **II** showed a low selectivity for most cations; depending on the latter, fluorescence intensity decreased by a factor of 1.7 to 14.3. Addition of H^+ and Hg^{2+} to a solution of Schiff base **IIIa** increases fluorescence intensity by a factor of 5.3 and 6.6, respectively; simultaneously, the fluorescence maximum was displaced by 68 and 67 nm, respectively, to shorter wavelengths. Copper(II) and nickel(II) cations induced complete fluorescence quenching. Compound **IIIc** alone shows no fluorescence, and fluorescence was observed only in the presence of H^+ and Hg^{2+}.



Relative variation of fluorescence intensity of compounds **II**–**V** ($c = 5.0 \times 10^{-6}$ M) in acetonitrile upon addition of different cations ($c = 2.5 \times 10^{-5}$ M).

Schiff base **IIIb** turned out to be the most promising as analytical reagent: addition of copper(II) acetate induced considerable fluorescence quenching (by a factor of 60) and 50-nm blue shift of the fluorescence maximum. Addition of Zn^{2+}, Ni^{2+}, and Hg^{2+} ions reduced the fluorescence intensity by a factor of 2.5, whereas the other examined cations almost did not affect the fluorescence pattern. Thione **V** showed response to Zn^{2+} ($I/I_0 = 6.0$), Cu^{2+} ($I/I_0 \approx 0.07$), and Hg^{2+} ($I/I_0 = 0.2$); mercury(II) ions also induced red shift of the fluorescence maximum ($\Delta\lambda = 28$ nm). Reactions of cyclic derivative **IV** with cations showed insufficient selectivity.

Thus fluorescent chemosensors based on N^2-(anthracen-9-ylmethyl)naphthalene-2,3-diamine derivatives exhibited sensor activity toward a large number of cations, and 1-[3-(anthracen-9-ylmethylamino)naphthalen-2-yliminomethyl]naphthalen-2-ol (**IIIb**) can be recommended as analytical reagent for detection of copper(II) ions.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) from solutions in $CDCl_3$ or DMSO-d_6 using the residual solvent signal as reference ($CHCl_3$, δ 7.25 ppm; DMSO-d_5, δ 2.50 ppm). The electronic absorption spectra were measured on a Varian Cary 100 spectrophotometer. The luminescence spectra were recorded on Hitachi 650-60 and Varian Eclipse spectrofluorimeters. The IR spectra were obtained on a Specord 75IR instrument. The melting points were determined in glass capillary on a PTP (M) melting point apparatus. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates using chloroform as eluent; spots were visualized by treatment with iodine vapor in a moist chamber.

***N*^{2}-(Anthracen-9-ylmethylidene)naphthalene-2,3-diamine (I).** Acetic acid, 0.2 ml, was added to a solution of 1.6 g (10 mmol) of naphthalene-2,3-diamine in 40 ml of toluene, and a solution of 2.1 g (10 mmol) of anthracene-9-carbaldehyde in 20 ml of toluene was added dropwise over a period of 10 min on heating under stirring. The mixture was heated for 2 h under reflux, the solvent was removed under reduced pressure, and the residue was recrystallized from butan-1-ol. Yield 3.3 g (95%), mp 237–238°C. IR spectrum, ν, cm^{-1}: 1580, 1460, 1380. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.55–8.23 m (13H, H_{arom}, NH_2), 8.60–9.00 m (4H, H_{arom}), 9.90 s (1H, CH). Found, %: C 86.72; H 5.18; N 8.10. $C_{25}H_{18}N_2$. Calculated, %: C 86.68; H 5.23; N 8.09.

***N*^{2}-(Anthracen-9-ylmethyl)naphthalene-2,3-diamine (II).** Sodium tetrahydridoborate, 0.9 g (25 mmol), was added under stirring to a hot solution of 1.7 g (5 mmol) of Schiff base **I** in 100 ml of EtOH–DMF (3:2). The mixture was stirred for 2 h and diluted with water, and the precipitate was filtered off, washed with water, dried in air, and recrystallized from butan-1-ol–DMF (3:1) with addition of activated charcoal. Yield 1.5 g (86%), mp 262–263°C. IR spectrum, ν, cm^{-1}: 1590, 1500, 1460, 1435. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.88 br.s (2H, NH_2), 5.10–5.30 br.s (3H, CH_2, NH), 6.87 s (1H, H_{arom}), 7.00–7.17 m (3H, H_{arom}), 7.35–7.62 m (6H, H_{arom}), 8.07 d (2H, H_{arom}, J = 7.4 Hz), 8.30 d (2H, H_{arom}, J = 7.4 Hz), 8.54 s (1H, H_{arom}). Fluorescence spectrum (acetonitrile): λ_{max} 413 nm ($c = 5\times10^{-5}$ M). Found, %: C 86.18; H 5.82; N 8.00. $C_{25}H_{20}N_2$. Calculated, %: C 86.18; H 5.78; N 8.04.

Schiff bases IIIa–IIIc (*general procedure*). Amine **II**, 0.17 g (0.5 mmol), was dissolved in 10 ml of a 3:1 butan-1-ol–DMF mixture, 0.05 ml of acetic acid and 0.5 mmol of the corresponding aldehyde were added, the mixture was heated for 30 min and cooled, and the precipitate was filtered off and recrystallized from appropriate solvent.

2-[3-(Anthracen-9-ylmethylamino)naphthalen-2-yliminomethyl]-4-methylphenol (IIIa) was synthesized from amine **II** and 2-hydroxy-5-methylbenzaldehyde. Yield 78%, mp 247–248°C (from butan-1-ol–DMF, 3:1). IR spectrum, ν, cm^{-1}: 1600, 1467, 1380. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 s (3H, CH_3), 4.63 br.s (1H, NH), 5.35 s (2H, CH_2), 6.50–6.73 m (2H, H_{arom}), 7.10–7.60 m (9H, H_{arom}), 7.70–7.90 m (2H, H_{arom}), 8.05 d (2H, H_{arom}, J = 7.8 Hz), 8.30 d (2H, H_{arom}, J = 7.8 Hz), 8.52 s (1H, H_{arom}), 8.60 s (1H, CH), 12.07 s (1H, OH). Fluorescence spectrum (acetonitrile): λ_{max} 487 nm ($c = 5\times10^{-5}$ M). Found, %: C 84.90; H 5.68; N 5.95. $C_{33}H_{26}N_2O$. Calculated, %: C 84.95; H 5.62; N 6.00.

1-[3-(Anthracen-9-ylmethylamino)naphthalen-2-yliminomethyl]naphthalen-2-ol (IIIb) was synthesized from amine **II** and 2-hydroxynaphthalene-1-carbaldehyde. Yield 87%, mp 302–303°C (from butan-1-ol–DMF, 3:1). IR spectrum, ν, cm^{-1}: 1600, 1460, 1385. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.78 br.s (1H, NH), 5.38 s (2H, CH_2), 6.94 d (1H, H_{arom}, J = 8.7 Hz), 7.20–7.57 m (10H, H_{arom}), 7.66–7.90 m (4H, H_{arom}), 8.04 d (2H, H_{arom}, J = 7.9 Hz), 8.14 d (1H, H_{arom}, J = 8.2 Hz), 8.32 d (2H, H_{arom}, J = 7.8 Hz), 8.49 s (1H, H_{arom}), 9.46 s (1H, CH), 14.05 s (1H, OH). Fluorescence spectrum (acetonitrile): λ_{max} 480 nm ($c = 5\times10^{-5}$ M): 480. Found, %: C 86.00; H 5.27; N 5.60. $C_{36}H_{26}N_2O$. Calculated, %: C 86.03; H 5.21; N 5.57.

2-[3-(Anthracen-9-ylmethylamino)naphthalen-2-yliminomethyl]naphthalen-1-ol (IIIc) was synthesized from amine **II** and 1-hydroxynaphthalene-2-carbaldehyde. Yield 84%, mp 246–247°C (from butan-1-ol–DMF, 3:1). IR spectrum, ν, cm^{-1}: 1610, 1460, 1375. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.70 br.s (1H, NH), 5.38 s (2H, CH_2), 6.80 d (1H, H_{arom}, J = 7.4 Hz), 7.00–8.20 m (17H, H_{arom}), 8.34 d (2H, H_{arom}, J = 8.0 Hz), 8.50 s (1H, H_{arom}), 8.72 s (1H, CH), 13.68 s (1H, OH). No fluorescence was observed in acetonitrile. Found, %: C 85.94; H 5.23; N 5.62. $C_{36}H_{26}N_2O$. Calculated, %: C 86.03; H 5.21; N 5.57.

1-(Anthracen-9-ylmethyl)-2-(pyridin-2-yl)-1*H*-naphtho[2,3-*d*]imidazole (IV). Amine **II**, 0.17 g (0.5 mmol), was dissolved in 10 ml of butan-1-ol–DMF (3:1), 0.05 ml of acetic acid and 0.1 ml (1.0 mmol) of pyridine-2-carbaldehyde were added, the mixture was heated for 1 h, the solvent was distilled off under reduced pressure, and the residue was recrystallized from butan-1-ol. Yield 0.14 g (64%), mp 256–257°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 1600, 1465, 1380. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.88 s (1H, CH_2), 7.08–7.30 m (5H, H_{arom}, CH_2), 7.33–7.52 m (5H, H_{arom}), 7.80–8.10 m (4H, H_{arom}), 8.20 s (1H, H_{arom}), 8.40–8.53 m (4H, H_{arom}), 8.68–8.74 m (1H, H_{arom}). Fluorescence spectrum (acetonitrile): λ_{max} 455 nm ($c = 5\times10^{-5}$ M). Found, %: C 85.55; H 4.82; N 9.63. $C_{31}H_{21}N_3$. Calculated, %: C 85.49; H 4.86; N 9.65.

1-(Anthracen-9-ylmethyl)-2,3-dihydro-1*H*-naphtho[2,3-*d*]imidazole-2-thione (V). A solution of 0.5 g (1.5 mmol) of amine **II** in 2 ml (13 mmol) of phenyl isothiocyanate was heated for 1 h. The mixture was cooled, and the precipitate was filtered off and recrystallized from butan-1-ol–DMF. Yield 0.5 g (84%), mp 244–245°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 3170, 1455, 1445, 1380. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.40 s (2H, CH_2), 6.60 s (1H, H_{arom}), 6.80–7.22 m (3H, H_{arom}), 7.40–7.77 m (6H, H_{arom}), 8.11 d (2H, H_{arom}, J = 7.8 Hz), 8.64 s (1H, H_{arom}), 8.72 d (2H, H_{arom}, J = 7.8 Hz), 12.93 s (1H, NH). Fluorescence spectrum (MeCN): λ_{max} 418 nm ($c = 5\times10^{-5}$ M). Found, %: C 80.05; H 4.71; N 7.09; S 8.15. $C_{26}H_{18}N_2S$. Calculated, %: C 79.97; H 4.65; N 7.17; S 8.21.

This study was performed under financial support by the Russian Foundation for Basic Research (project

no. 09-03-00052), by the Ministry of Education and Science of the Russian Federation (project no. VSh 2.2.1.1/12630), and by the Council for Grants at the President of the Russian Federation (project no. NSh-3233.2010.3).

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