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Chemosensors Based on *N*-(9-Anthrylmethyl)-benzene-1,2-diamine

I. E. Tolpygin[a], V. P. Rybalkin[b], E. N. Shepelenko[b], L. L. Popova[a], Yu. V. Revinskii[a], A. V. Tsukanov[a], O. I. Dmitrieva[a], A. D. Dubonosov[b], V. A. Bren'[a,b], and V. I. Minkin[a,b]

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

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

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Abstract—A number of *N*-(9-antrylmethyl)-*N*′-arylmethylidenebenzene-1,2-diamines and 1-(9-anthrylmethyl)-2-aryl-1*H*-benzimidazoles were synthesized by condensation of *N*-(9-anthrylmethyl)benzene-1,2-diamine with aromatic and heterocyclic aldehydes. Study on their luminescent properties and complexing ability showed that 2-{[2-(9-anthrylmethylamino)phenylimino]methyl}-5-methylphenol, 2-{[2-(9-anthrylmethylamino)phenylimino]methyl}-4-methoxyphenol, and 2-{[2-(9-anthrylmethylamino)phenylimino]methyl}-6-methoxy-4-nitrophenol are effective and highly selective chemosensors for H^+ and Hg^{2+} ions.

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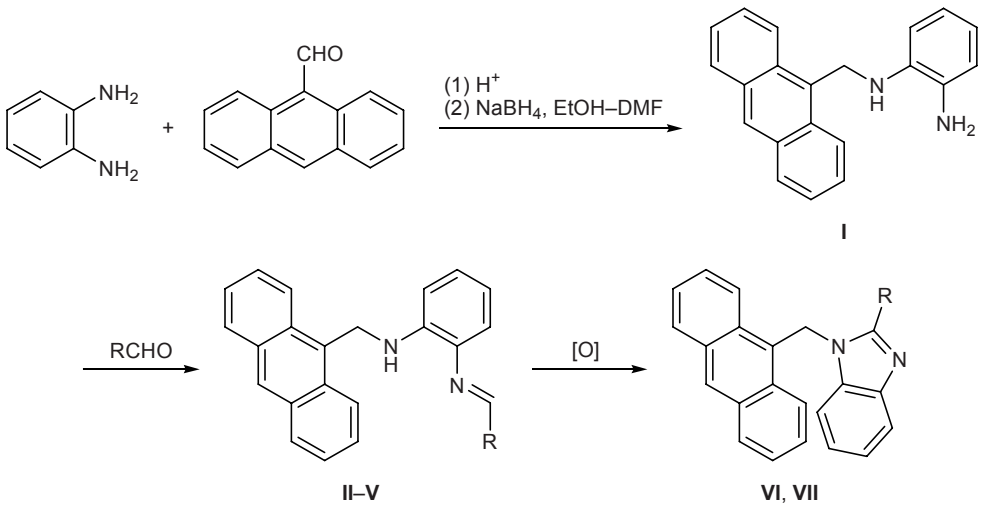
Design of effective chemosensors implies the use of molecules with a wide variety of receptor fragments. Our previous studies in this field [1, 2] demonstrated that *N*,*N*′-bis(9-antrylmethyl)substituted diamines can be used as fluorescent chemosensors which can be modified via introduction of a thiourea fragment. In the present work we made an attempt to obtain chemosensors on the basis of *N*-(9-anthrylmethyl)benzene-1,2-diamine (**I**); the presence of a primary amino group in the latter provides the possibility for subsequent modifications.

While trying to improve the procedure described in [3] for the synthesis of diamine **I** we found that benzene-1,2-diamine reacts with an equimolar amount of anthracene-9-carbaldehyde to give the corresponding Schiff base only at one amino group and that the con-

Scheme 1.



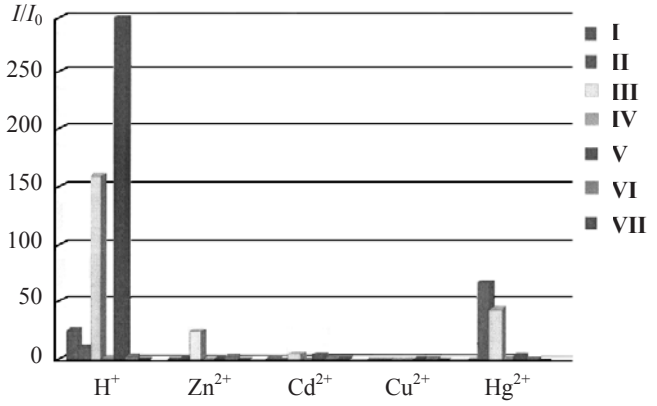
II, R = 2-HO-4-MeC_6H_3; **III**, R = 2-HO-5-MeOC_6H_3; **IV**, R = 2-HO-5-$O_2NC_6H_3$; **V**, R = 2-HO-3-MeO-5-$O_2NC_6H_2$; **VI**, R = 2-HO-3,5-$(O_2N)_2C_6H_2$; **VII**, R = pyridin-2-yl.

densation product readily undergoes reduction with sodium tetrahydridoborate in ethanol–dimethylformamide (3:2) to afford the target compound **I** in high yield. By reactions of **I** with a series of substituted salicylaldehydes we obtained *N*-(9-anthrylmethyl)-*N*′-arylmethylidenebenzene-1,2-diamines **II**–**V** as potential chelating ligands (Scheme 1).

The reactions of diamine **I** with 2-hydroxy-3,5-dinitrobenzaldehyde and pyridine-2-carbaldehyde did not stop at the stage of formation of the corresponding Schiff base: Intermediate *N*-(9-anthrylmethyl)-*N*′-arylmethylidenebenzene-1,2-diamines underwent oxidation with atmospheric oxygen to the corresponding benzimidazole derivatives **VI** and **VII** which were isolated as the major product (Scheme 1).

Amine **I** showed a low sensitivity and selectivity for most cations, except for protons (see figure). Compounds **II**–**V** are capable of acting as chemosensors according to two mechanism. The first of these involves formation of stable chelates with participation of the azomethine and hydroxy groups in the *ortho* position with respect to each other, which exhibit intrinsic fluorescence [4]. The second mechanism is photoinduced electron transfer due to the presence of a 9-aminomethylanthracene fragment [5–9].

The sensor properties of compounds **II**–**VII** were estimated on the basis of the fluorescence spectra in the region corresponding to local fluorescence of anthracene (λ 390 nm). The fluorescence intensity of compounds **II**, **III**, and **V** increased by a factor of 68, 46, and 4, respectively, upon addition of mercury acetate and by a factor of 11, 160, and 300, respectively, upon addition of trichloroacetic acid (see figure). In all cases, the structure of the fluorescence spectra remained unchanged (PET effects). A necessary condition for photoinduced electron transfer is the presence of an electron-donating group in the arylmethylidene moiety.



Relative change in the fluorescence intensity (I/I_0) of compounds **I**–**VII** in acetonitrile ($c = 5\times10^{-5}$ mol/l) in the presence of various cations (acetate as counterion, $c = 5\times10^{-4}$ M, λ 390 nm).

Addition of a solution of zinc or copper acetate to a solution of compound **II** or **V** in acetonitrile (to a molar ratio of 1:10) resulted in appearance of new fluorescence bands (λ_{max} 471 and 474 nm, respectively), which are typical of chelate compounds [4]. The fluorescence spectrum of methoxy derivative **III** changed upon addition of a wider variety of metal cations, including Zn^{2+}, Cd^{2+}, etc. Compound **IV** showed fluorescence at λ_{max} 342 nm but exhibited no appreciable sensor properties (see figure). The sensitivity to protons sharply increases in the series **II** < **III** < **V** (see figure), while the sensitivity to Hg^{2+} ions simultaneously decreases.

Benzimidazole derivatives **VI** and **VII** turned out to be less efficient chemosensors as compared to *ortho*-hydroxy-substituted Schiff bases. Compound **VI** having two nitro groups displayed a weak anthracene type fluorescence, and the fluorescence pattern almost did not change upon addition of various cations (see figure). The sensitivity of 1-(9-anthrylmethyl)-2-(pyridin-2-yl)-1*H*-benzimidazole (**VII**) to H^+ and Hg^{2+} ions is related to fluorescence quenching by the action of these cations; in the presence of excess H^+ and Hg^{2+} ions, the fluorescence intensity decreases by a factor of 77 and 50, respectively (see figure). Presumably, the anthryl fragment in **VII** acts as the strongest electron donor in the complex formation.

Thus chemosensors based on *N*-(9-anthrylmethyl)-benzene-1,2-diamine (**I**) are sensitive to a number of cations, while 2-{[2-(9-anthrylmethylamino)phenylimino]methyl}-5-methylphenol (**II**), 2-{[2-(9-anthrylmethylamino)phenylimino]methyl}-4-methoxyphenol (**III**), and 2-{[2-(9-anthrylmethylamino)phenylimino]-methyl}-6-methoxy-4-nitrophenol (**V**) are highly effective chemosensors for protons and mercury(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 proton signals of the solvent as reference (δ 7.25 and 2.50 ppm, respectively). The IR spectra were measured on a Specord 75IR instrument from samples dispersed in mineral oil. The electronic absorption spectra were obtained on a Specord M-40 spectrophotometer. The fluorescence spectra were recorded on a Hitachi 650-

60 spectrofluorimeter from solutions in acetonitrile with a concentration of 5×10^{-5} M. The melting points were determined in glass capillaries on a PTP (M) melting point apparatus. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent; spots were visualized by treatment with iodine vapor in a moist chamber.

***N*-(9-Anthrylmethyl)benzene-1,2-diamine (I).** Acetic acid, 0.5 ml, was added to a solution of 2.38 g (22 mmol) of benzene-1,2-diamine in 40 ml of toluene, and a solution of 4.12 g (20 mmol) of anthracene-9-carbaldehyde in 20 ml of toluene was added dropwise under stirring over a period of 10 min. 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 of *N*-(9-anthrylmethylidene)benzene-1,2-diamine quantitative. The product was dissolved in 100 ml of a 3:2 ethanol–dimethylformamide mixture, the solution was heated, and 1.9 g (50 mmol) of sodium tetrahydridoborate was added in portions under stirring. The mixture was stirred for 2 h, diluted with 200 ml of water, and treated with dilute acetic acid to decompose excess $NaBH_4$. The precipitate was filtered off, washed with water, and dried in air. Compound **I** was recrystallized from butan-1-ol with addition of charcoal (10 wt %). Yield 5.38 g (82%), mp 183–184°C (from butan-1-ol); published data [3]: mp 178–180°C. IR spectrum, ν, cm^{-1}: 1595, 1500, 1460, 1435. ^1H NMR spectrum, δ, ppm: 3.38 m (3H, NH, NH_2), 5.17 s (2H, CH_2), 6.65–8.53 m (13H, H_{arom}). Fluorescence spectrum: λ_{max} 416 nm. Found, %: C 84.57; H 5.98; N 9.45. $C_{21}H_{18}N_2$. Calculated, %: C 84.53; N 6.08; N 9.39.

2-{[2-(9-Anthrylmethylamino)phenylimino]-methyl}-5-methylphenol (II) was synthesized from compound **I** and 2-hydroxy-4-methylbenzaldehyde. Yield 78%, mp 209–210°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 1600, 1467, 1380. ^1H NMR spectrum, δ, ppm: 2.20 s (3H, CH_3), 4.50 s (1H, NH), 5.20 d (2H, CH_2), 6.50–8.54 m (17H, H_{arom}), 12.23 s (1H, NH). Fluorescence spectrum: λ_{max} 417 nm. Found, %: C 83.70; H 5.75; N 6.64. $C_{29}H_{24}N_2O$. Calculated, %: C 83.63; H 5.81; N 6.73.

2-{[2-(9-Anthrylmethylamino)phenylimino]-methyl}-4-methoxyphenol (III) was synthesized from compound **I** and 2-hydroxy-5-methoxybenzaldehyde. Yield 72%, mp 198–199°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 1615, 1465. ^1H NMR spectrum, δ, ppm: 3.70 s (3H, CH_3), 4.48 s (1H, NH), 5.22 s (2H, CH_2), 6.60–8.54 m (17H, H_{arom}, N=CH), 11.80 s (1H, OH). Fluorescence spectrum: λ_{max} 416 nm. Found, %: C 80.58; H 5.69; N 6.50. $C_{29}H_{24}N_2O_2$. Calculated, %: C 80.53; H 5.60; N 6.48.

2-{[2-(9-Anthrylmethylamino)phenylimino]-methyl}-4-nitrophenol (IV) was synthesized from compound **I** and 2-hydroxy-5-nitrobenzaldehyde. Yield 86%, mp 254–255°C (from butan-1-ol–DMF). IR spectrum, ν, cm^{-1}: 3435, 1605, 1590, 1460, 1335. ^1H NMR spectrum, δ, ppm: 5.00–5.45 m (2H, CH_2), 5.80–8.60 m (17H, H_{arom}), 8.9–10.22 m (1H, OH, NH). Fluorescence spectrum: λ_{max} 342 nm. Found, %: C 75.21; H 4.66; N 9.32. $C_{28}H_{21}N_3O_3$. Calculated, %: C 75.15; H 4.73; N 9.39.

2-{[2-(9-Anthrylmethylamino)phenylimino]-methyl}-6-methoxy-4-nitrophenol (V) was synthesized from compound **I** and 2-hydroxy-3-methoxy-5-nitrobenzaldehyde. Yield 81%, mp 240–241°C (from butan-1-ol–DMF). IR spectrum, ν, cm^{-1}: 3380, 1600, 1460. ^1H NMR spectrum, δ, ppm: 3.60–3.96 m (3H, CH_3), 4.90–5.42 m (2H, CH_2), 5.80–9.00 m (16H, H_{arom}, N=CH). Fluorescence spectrum: λ_{max} 425 nm. Found, %: C 72.87; H 4.94; N 8.81. $C_{29}H_{23}N_3O_4$. Calculated, %: C 72.94; H 4.86; N 8.86.

2-[1-(9-Anthrylmethyl)-1*H*-benzimidazol-2-yl]-4,6-dinitrophenol (VI). Compound **I**, 0.3 g (1 mmol), was dissolved in 5 ml of butanol, a few drops of glacial acetic acid and 0.21 g (1 mmol) of 2-hydroxy-3,5-dinitrobenzaldehyde were added, and the mixture was heated for 15 min under reflux and cooled. The precipitate was filtered off and recrystallized from butan-1-ol–DMF (1:1). Yield 0.2 g (41%), mp >270°C (decomp., from butan-1-ol–DMF). IR spectrum, ν, cm^{-1}: 3350, 1605, 1450. ^1H NMR spectrum, δ, ppm: 6.65 s (2H, CH_2), 6.76–8.68 m (15H, H_{arom}). Fluorescence spectrum: λ_{max} 416 nm. Found, %: C 68.67; H 3.62; N 11.50. $C_{28}H_{18}N_4O_5$. Calculated, %: C 68.57; H 3.70; N 11.42.

1-(9-Anthrylmethyl)-2-(pyridin-2-yl)-1*H*-benzimidazole (VII). Compound **I**, 0.6 g (2 mmol), was dissolved in 10 ml of toluene, a few drops of glacial acetic acid and 0.21 ml (2 mmol) of pyridine-2-carbaldehyde were added, and the mixture was heated for 1 h under reflux. The solvent was distilled off under reduced pressure, and the residue was recrystallized from petroleum ether–benzene (3:1). Yield 0.49 g (64%), mp 278–279°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 1600, 1465, 1380. ^1H NMR spectrum, δ, ppm: 7.22 s (2H, CH_2), 6.26–8.80 m (17H, H_{arom}). Fluorescence spectrum: λ_{max} 415 nm. Found, %: C 84.07; H 5.05; N 11.94. $C_{27}H_{19}N_3$. Calculated, %: C 84.13; H 4.97; N 10.90.

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