ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 2, pp. 161–164. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © I.E. Tolpygin, E.N. Shepelenko, Yu.V. Revinskii, A.V. Tsukanov, A.D. Dubonosov, V.A. Bren', V.I. Minkin, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 2, pp. 175–178.

Chemosensors Based on *N*-(2-Aminophenyl)-*N*-(9-Anthrylmethyl)amine: II.*

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

[a] *Research Institute of Physical and Organic Chemistry at Southern Federal University, Rostov-on-Don, 344090 Russia*
e-mail: dubon@ipoc.rsu.ru
[b] *Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*

Received January 9, 2008

Abstract—A series of *N*-(9-anthrylmethyl)arylimines was prepared by condensation of *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)amine with aromatic aldehydes. The study of the luminescent and complexing properties of compounds obtained showed that 2-{[2-(9-anthrylmethylamino)phenylimino]methyl}-1-naphthol and 1-{[2-(9-anthrylmethylamino)phenylimino]methyl}-6-bromo-2-naphthol were efficient highly selective chemosensors of cations Hg^{2+}.

DOI: 10.1134/S1070428009020018

The designing of efficient fluorescent chemosensors requires special attention to the choice of the receptor part governing the selectivity of the created analytical reagent [1–3]. Previous investigations [4–7] demonstrated the fundamental possibility to use *N*-(9-anthrylmethyl)substituted polyamines and their derivatives as fluorescent chemosensors.

This study is an extension of the research of sensor systems based on *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)amine [8] aiming at the search for more efficient and selective fluorescent chemosensors for Hg^{2+} cations.

By reactions of *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)amine with a number of aldehydes we obtained a series of *N*-(9-anthrylmethyl)imines **I–V** (see the scheme). Compound **VI** was prepared with the use of 2-(hydroxymethylene)-1-benzothiophen-3(2*H*)-one as a "carbonyl" component.

In order to study the coordination center we obtained tosyl derivative **VII** by a reaction of equimolar amounts of 9-anthraldehyde and *N*-(2-aminophenyl)-4-methylbenzenesulfonamide [9] followed by reduction of the obtained *N*-[2-(9-anthrylmethyleneamino)phenyl]-4-methylbenzenesulfonamide with sodium borohydride in a mixture ethanol–DMF (see the scheme).

Owing to the presence in the composition of compounds under study of 9-aminomethylanthracene fragment the main mechanism of the sensor action is PET-effect [10, 11].

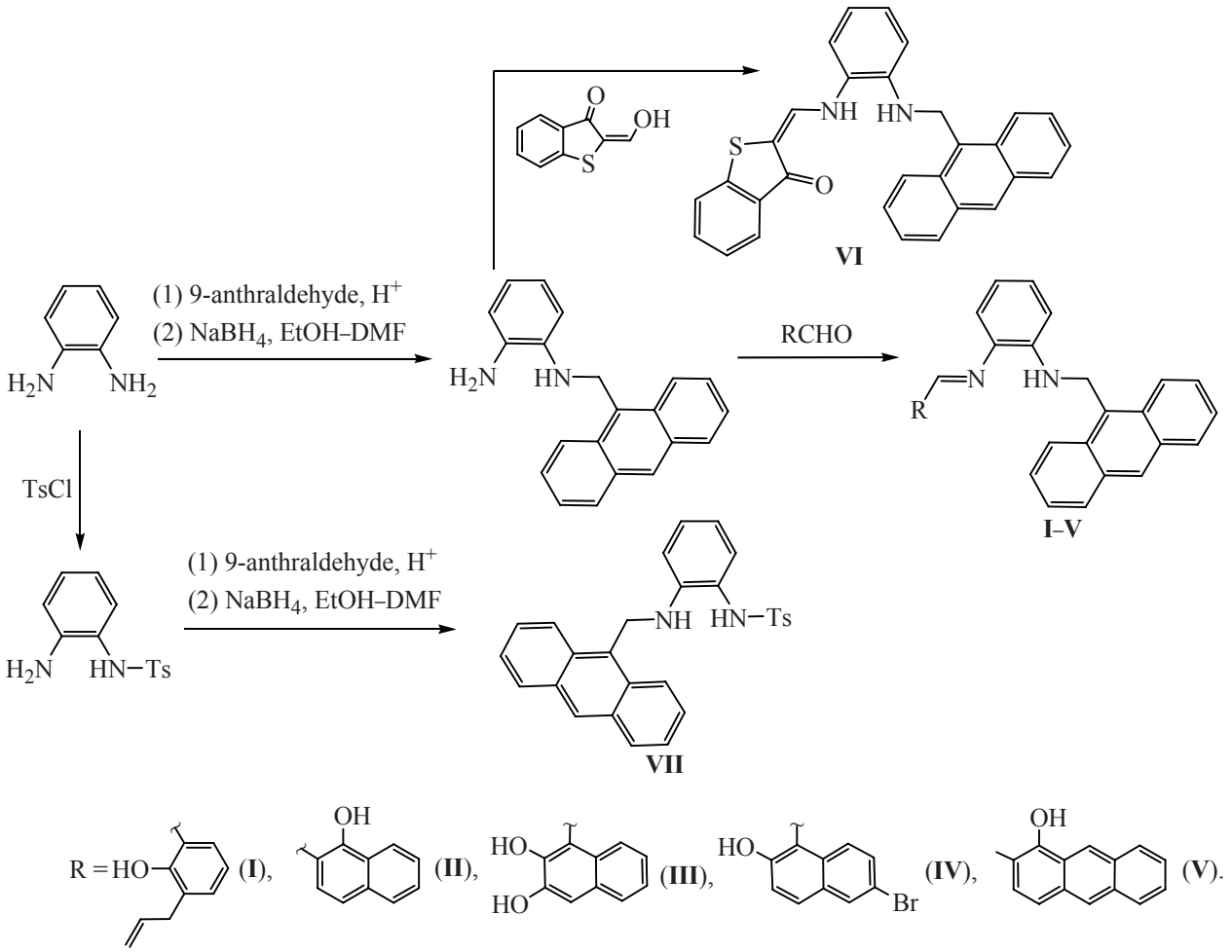
The sensor ability of compounds **I–VII** was estimated from the fluorescence spectra. To this end to the solution of compounds **I–VII** (c 5×10^{-6} mol l^{-1}) was added a calculated five-fold excess of a metal acetate (H^+, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}) or of their mixtures (for compound **II**).

The intensity of fluorescence of compounds **I, II, IV, V**, and **VII** increased 67, 591, 262, 3.7, and 3.6 times respectively on addition of mercury acetate (see the figure). At the addition of CF_3COOH to the solutions of the same compounds the fluorescence increased 13, 96, 9.7, 1.8, and 3-fold. In the case of imine **III** the fluorescence intensity increased only at the addition of cations of mercury(II) (I/I_0 5.1); at the addition of the other cations no fluorescence was observed.

The presence of a rigid coordination center in all compounds synthesized made it possible to form stable complexes of chelate type. The addition of acetates of zinc, lead, and copper in the molar ratio 1:5 to the acetonitrile solutions of compounds **I, IV**, and **VII** respectively resulted in the appearance of new fluorescence bands (λ_{max} 505, 505, and 465 nm) characteristic of complexes

* For communication I, see [8].

Scheme.



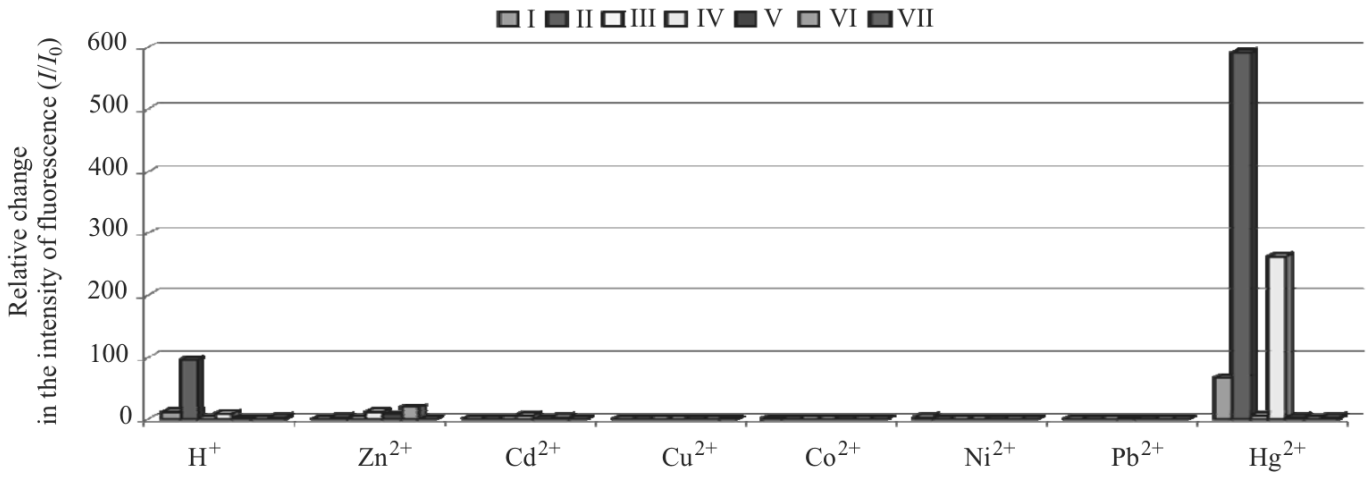
of chelate type [12]. In the case of azomethine **II** the changes in the fluorescence spectrum occurred at the action of more cations (Zn^{2+}, Cd^{2+}, and CO^{2+}). At the interaction of dianthryl derivative **V** with Hg^{2+} the classic type of the anthracene spectrum was recovered, λ_{max} 415 nm (three individual maxima in the region 390–440 nm) apparently due to the destruction of the excimer structure on the complex formation [13, 14]. In the spectrum of compound **VI** possessing fluorescence, λ_{max} 547 nm, the addition of cations Zn^{2+} and Cd^{2+} resulted not only in the intensification of the fluorescence (19 and 4.2-fold), but also to a blue shift of the fluorescence maximum by 30 nm. The selectivity of the most efficient among the compounds obtained, 2-{[2-(9-anthrylmethylamino)phenylimino]methyl}-1-naphthol (**II**), was shown by adding to its acetonitrile solution (c 5×10^{-6} mol l^{-1}) a mixture of cations; therewith each cation was taken in a five-fold molar excess with respect to compound **II**. In this case the relative fluorescence intensity increased 570 times. Thus the deviation of the fluorescence intensity of the compound **II** solution at the addition of the mixture of cations from the fluorescence intensity of the compound **II** solution at the addition of only mercury acetate was ~3% demonstrating the high selectivity of this fluorescence chemosensor with respect to ions Hg^{2+} in neutral environment.

Thus new fluorescent chemosensors based on the derivatives of *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)-amine show the sensor activity with respect to a number of cations, and 2-{[2-(9-anthrylmethylamino)phenylimino]methyl}-1-naphthol and 1-{[2-(9-anthrylmethylamino)phenylimino]methyl}-6-bromo-2-naphthol are efficient highly selective chemo-sensors with respect to Hg^{2+} cations.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Varian Unity 300 (300 MHz) in $CDCl_3$ or DMSO-d_6. As

Relative change in the intensity of fluorescence (I/I_0) of compound **I** (C 5 × 10^{-6} mol l^{-1}) in acetonitrile on addition of various cations (C 2.5 × 10^{-5} mol l^{-1}), "–" means the absence of fluorescence.



I	13.0	1.6	1.3	0.2	1.7	2.9	1.3	**67.0**
II	96.0	2.1	1.3	0.5	0.7	1.2	1.1	**591.0**
III	–	–	–	–	–	–	–	5.1
IV	9.7	11.6	6.8	0.6	0.8	0.9	1.8	**262.0**
V	1.8	7.5	1.0	0.8	1.5	1.2	1.2	3.7
VI	–	**19.0**	**4.2**	–	–	–	–	–
VII	3.0	0.3	0.2	1.9	0.2	0.2	0.9	3.6

internal references served residual signals of $CHCl_3$ and DMSO (δ 7.25 and 2.50 ppm respectively). IR spectra were obtained on a spectrophotometer Specord 75IR (from mulls in mineral oil). Electron absorption spectra were recorded on a spectrophotometer M-40, fluorescence spectra, on a spectrofluorimeter Hitachi 650-60. Melting points were measured in glass capillaries on a PTP (M) device. The completion of reaction was monitored and the purity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluent chloroform, development by iodine vapor in a moist chamber.

***N*-(9-Anthrylmethyl)arylimines.** *General procedure.* In 5 ml of 1-butanol was dissolved 0.3 g (1 mmol) of *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)amine, 2–3 drops of glacial acetic acid, and 1 mmol of an appropriate aldehyde was added. The mixture was heated for 30 min, cooled, the precipitate was filtered off and crystallized from an appropriate solvent.

2-Allyl-6-{[2-(9-anthrylmethylamino)phenylimino]methyl}phenol (I) was obtained from *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)amine and 3-allyl-2-hydroxybenzaldehyde. Yield 79%, mp 230–231°C (1-butanol). IR spectrum, ν, cm^{-1}: 1600, 1465, 1380. ^{1}H NMR spectrum, δ, ppm: 3.00–3.24 m (2H, CH_2), 4.76–5.00 m (2H, CH_2), 5.26 s (2H, CH_2), 5.63–5.88 m (1H, CH), 6.64–8.76 m (17H, H_{arom} + CH), 12.58 s (1H, OH). Fluorescence spectrum in acetonitrile: λ_{max} 415 nm (c 5 × 10^{-5} mol l^{-1}). Found, %: C 84.05; H 5.97; N 6.30. $C_{31}H_{26}N_2O$. Calculated, %: C 84.13; H 5.92; N 6.33.

2-{[2-(9-Anthrylmethylamino)phenylimino]methyl}-1-naphthol (II) was obtained from *N*-(2-amino-phenyl)-*N*-(9-anthrylmethyl)amine and 1-hydroxy-2-naphthaldehyde. Yield 88%, mp 236–237°C (1-butanol–DMF). IR spectrum, ν, cm^{-1}: 1605, 1460, 1375. ^{1}H NMR spectrum, δ, ppm: 5.04 s (1H, NH), 5.24 s (2H, CH_2), 6.77–8.80 m (19H, H_{arom} + CH), 14.05 s (1H, OH). Fluorescence spectrum in acetonitrile: λ_{max} 531 nm (c 5 × 10^{-5} mol l^{-1}). Found, %: C 84.86; H 5.42; N 6.25. $C_{32}H_{24}N_2O$. Calculated, %: C 84.93; H 5.35; N 6.19.

1-{[2-(9-Anthrylmethylamino)phenylimino]methyl}naphthalene-2,3-diol (III) was obtained from *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)amine and 2,3-dihydroxy-1-naphthaldehyde. Yield 90%, mp 242–243°C (1-butanol–DMF). IR spectrum, ν, cm^{-1}: 3400, 1625, 1605, 1560, 1480. ^{1}H NMR spectrum, δ, ppm: 4.20 s (1H, NH), 5.27 s (2H, CH_2), 6.97 s (1H, NH), 6.80–8.95 m (18H, H_{arom} + CH), 14.71 s (1H, OH). Fluores-

cence spectrum in acetonitrile: λ_{max} 555 nm (c 5 × 10^{-5} mol l^{-1}). Found, %: C 82.00; H 5.22; N 5.93. $C_{32}H_{24}N_2O_2$. Calculated, %: C 82.03; H 5.16; N 5.98.

1-{[2-(9-Anthrylmethylamino)phenylimino]-methyl}-6-bromo-2-naphthol (IV) was obtained from *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)-amine and 2-hydroxy-6-bromo-1-naphtaldehyde. Yield 83%, mp 275–276°C (toluene). IR spectrum, ν, cm^{-1}: 1600, 1465, 1385. ^1H NMR spectrum, δ, ppm: 4.52 s (1H, NH), 5.24 s (2H, CH_2), 6.80–8.55 (18H, H_{arom}), 9.27 s (1H, CH), 14.30 s (1H, OH). Fluorescence spectrum in acetonitrile: λ_{max} 416 nm (c 5 × 10^{-5} mol l^{-1}). Found, %: C 72.40; H 4.33; Br 15.11; N 5.30. $C_{32}H_{23}BrN_2O$. Calculated, %: C 72.32; H 4.36; Br 15.04; N 5.27.

2-{[2-(9-Anthrylmethylamino)phenylimino]-methyl}-1-anthrol (V) was obtained from *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)amine and 1-hydroxyanthracene-2-carbaldehyde. Yield 91%, mp 315–316°C (DMF). IR spectrum, ν, cm^{-1}: 3410, 1620, 1460, 1390. ^1H NMR spectrum, δ, ppm: 5.20 d (2H, CH_2, J 4.1 Hz), 5.65 t (1H, NH, J 3.5 Hz), 6.75–8.78 m (22H, H_{arom} + CH), 13.64 C (1H, OH). Fluorescence spectrum in acetonitrile: λ_{max} 545 nm (c 5 × 10^{-5} mol l^{-1}). Found, %: C 85.96; H 5.25; N 5.55. $C_{36}H_{26}N_2O$. Calculated, %: C 86.03; H 5.21; N 5.57.

2-{[2-(9-Anthrylmethylamino)phenylamino]-methylene}-1-benzo[*b*]thiophen-3(2*H*)-one (VI) was obtained from *N*-(2-aminophenyl)-*N*-(9-anthrylmethyl)-amine and 2-(hydroxymethylene)-1-benzothiophen-3(2*H*)-one. Yield 85%, mp 208–209°C (toluene). IR spectrum, ν, cm^{-1}: 1645, 1600, 1470. ^1H NMR spectrum, δ, ppm: 5.00–5.60 m (3H, NH + CH_2), 6.70–9.20 m (19H, H_{arom} + CH), 11.80 br.s (1H, NH). Fluorescence spectrum in acetonitrile: λ_{max} 547 nm (c 5 × 10^{-5} mol l^{-1}). Found, %: C 78.56; H 4.89; N 6.06; S 7.05. $C_{30}H_{22}N_2OS$. Calculated, %: C 78.57; H 4.84; N 6.11; S 6.99.

***N*-[2-(9-Anthrylmethylamino)phenyl]-4-methylbenzenesulfonamide (VII)**. In 30 ml of toluene was dissolved 2.62 g (10 mmol) of *N*-(2-aminophenyl)-4-methylbenzenesulfonamide [9], 2–3 drops of glacial acetic acid, and 2.06 g (10 mmol) of 9-anthraldehyde was added. The reaction mixture was heated for 1 h, the solvent was removed in a vacuum, the residue was crystallized from 1-butanol. Yield of *N*-[2-(9-anthrylmethyleneamino)-phenyl]-4-methylbenzenesulfonamide 4.37 g (97%). To 2.25 g (5 mmol) of this product dissolved in 50 ml of a mixture ethanol–DMF, 3:2, at heating was added while stirring by small portions 0.48 g (12.5 mmol) of sodium borohydride. The mixture was stirred for 2 h, cooled, diluted with 200 ml of water, and the excess borohydride was decomposed by diluted acetic acid. The separated precipitate was filtered off, washed with water, and dried in air. Yield 2.0 g (89%), mp 276–277°C (1-butanol). IR spectrum, ν, cm^{-1}: 3440, 1610, 1460, 1385. ^1H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3), 4.51 s (1H, NH), 5.07 d (2H, CH_2, J 4.8 Hz), 5.77 s (1H, NH), 6.53–8.60 m (17H, H_{arom}). Fluorescence spectrum in acetonitrile: λ_{max} 405 nm (c 5 × 10^{-5} mol l^{-1}). Found, %: C 74.35; H 5.30; N 6.14; S 7.16. $C_{28}H_{24}N_2O_2S$. Calculated, %: C 74.31; H 5.35; N 6.19; S 7.09.

The study was carried out under a financial support of the Russian Foundation for Basic Research (grant no. 05-03-32470), Ministry of Education and Science of the Russian Federation [national project "Education" (the program of development of the Southern Federal University), RNP.2.2.2.2.5592 and RNP.2.2.1.1.2348], of Foundation CRDF (grants REC-004/BP1M04 and REC-004/BF5M04), and a grant of the President of Russian Federation (NSh-363.2008.3).

REFERENCES

1. Hancock, R.D. and Martell, A.E., *Chem. Rev.,* 1989, vol. 89, p. 1875.
2. Bren', V.A., *Usp. Khim.,* 2001, vol. 70, p. 1152.
3. Rurack, K. and Resch-Genger, U., *Chem. Soc. Rev.,* 2002, vol. 31, p. 116.
4. Sclafani, J.A., Maranto, M.T., Sisk, T.M., and van Arman, S.A., *Tetrahedron Lett*., 1996, vol. 37, p. 2193.
5. Fabbrizzi, L., Licchelli, M., Pallavicini, P., and Taglietti, A., *Inorg. Chem*., 1996, vol. 35, p. 1733.
6. Pina, F., Bernardo, M.A., and Garcia-Espana, E., *Eur. J. Inorg. Chem*., 2000, p. 2143.
7. Alves, S., Pina, F., Albelda, M.T., Garcia-Espana, E., Soriano, C., and Luis, S.V., *Eur. J. Inorg. Chem*., 2001, p. 405.
8. Tolpygin, I.E., Rybalkin, V.P., Shepelenko, E.N., Popova, L.L., Revinskii, Yu.V., Tsukanov, A.V., Dmitrieva, O.I., Dubonosov, A.D., Bren', V.A., and Minkin, V.I., *Zh. Org. Khim*., 2008, vol. 44, p. 562.
9. Busev, A.I., *Sintez novykh organicheskikh reagentov dlya neorganicheskogo analiza* (Synthesis of the New Reagents for Inorganic Analysis), Moscow: Izd. MGU, 1972.
10. De Silva, A.P., McClean, G.D., Moody, T.S., and Weir, S.M., *Handbook of Photochemistry and Photobiology*, Nalwa, Ed., ASP, CA; Stevenson, Ranch, 2003.

11. De Silva, A.P., Gunaratne, H.Q.N., Gunnlaugsson, T., Huxley, A.J.M., McCoy, C.P., Rademacher, J.T., and Rice, T.E., *Chem. Rev*., 1997, vol. 97, p. 1515.
12. Knyazhanskii, M.I. and Metelitsa, A.V., *Fotoinitsiirovannye protsessy v molekulakh azometinov i ikh strukturnykh analogov* (Photochemical Processes in Molecules of Amomethines and Their Structural Analogs), Rostov-na-Donu: Izd. RGU, 1992.
13. Lin, Z., Priyadarshy, S., Bartko, A., and Waldeck, D.H., *J. Photochem. Photobiol. A*, 1997, vol. 110, p. 131.
14. Hayashi, T., Mataga, N., Sakata, Y., Misumi, S., Morita, M., and Tanaka, J., *J. Am. Chem. Soc*., 1976, vol. 98, p. 5910.