

SHORT
COMMUNICATIONS

New Fluorescent Chemosensors on the Basis of 9-Aminomethylantracene

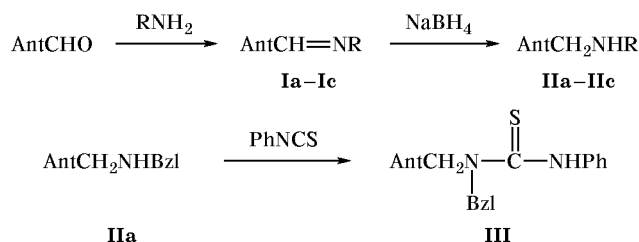
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Received April 9, 2003

Fluorescent chemosensors whose action is based on the PET (photoinduced electron transfer) effect are widely used in the determination of various substances in the environment [1, 2]. 9-Aminomethylantracene derivatives could give rise to PET in the excited state from lone electron pair on the nitrogen atom to the anthracene fragment, which leads to quenching of fluorescence in the latter [3, 4]. Interaction of such compounds with metal cations or proton inhibits PET, thus inducing strong fluorescence of the sensor [5, 6].

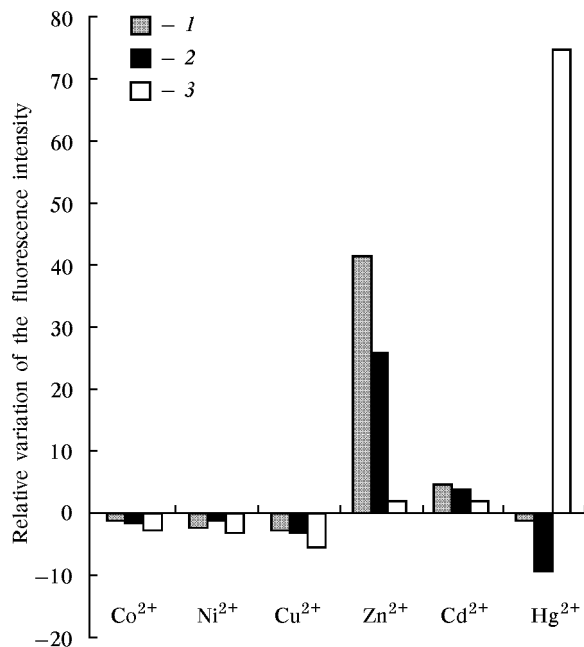
By reduction of Schiff bases **Ia–Ic** we obtained the corresponding N-substituted 9-aminomethylantracene derivatives **IIa–IIc**. Compound **IIa** was brought into reaction with phenyl isothiocyanate to obtain sensor **III** having a thiourea fragment.



R = Bzl (**a**), (CH₂)₂NHCH₂Ant (**b**), (CH₂)₆NHCH₂Ant (**c**);
Ant = 9-anthryl.

Chemosensors **IIb**, **IIc**, and **III** show a very weak anthracene-like fluorescence in acetonitrile solution on excitation at λ_{excit} 355 nm (three maxima in the region 390–440 nm and a shoulder at 460–470 nm are observed). The emission spectrum of diamine **IIb** also contains a weak band at 470–600 nm, which is likely to correspond to formation of exiplex [7]. Addition of various *d*-metal acetates to solutions of compounds **IIb** and **IIc** (5×10^{-5} M) favors further fluorescence decay, while Zn²⁺ ions (and, to a lesser extent,

Cd²⁺ ions) sharply increase the relative fluorescence intensity (see figure). In this case, the emission band corresponding to exiplex completely disappears from the spectrum of **IIb**. Compound **III** having a thiourea fragment and hence capable of coordinating heavy metal cations [8–10] selectively reacts with Hg²⁺ ions, resulting in a 77-fold increase in the fluorescence intensity. We can thus conclude that the obtained 9-aminomethylantracene derivatives are new effective fluorescent chemosensors selective for Zn²⁺ (**IIb** and **IIc**) and Hg²⁺ ions (**III**).



Variation of the fluorescence intensity of compounds (1) **IIb**, (2) **IIc**, and (3) **III** ($c = 5 \times 10^{-5}$ M) upon complex formation with metal cations in acetonitrile (λ_{excit} 355 nm, λ_{fluor} 418 nm).

***N*-(1*E*)-9-Anthrylmethylene]-*N*-benzylamine (Ia).** A mixture of 4.12 g (20 mmol) of 9-anthraldehyde, 2.15 g (20 mmol) of benzylamine, and 50 ml of toluene was heated for 2 h under reflux in a flask equipped with a Dean–Stark trap. The solvent was distilled off under reduced pressure (water-jet pump), and the residue was recrystallized from 1-butanol. Yield 5.15 g (87%). mp 177–178°C. IR spectrum, ν , cm^{-1} : 1455, 1360. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 5.38 s (2H, CH_2), 6.93–8.64 m (14H, H_{arom}), 9.61 s (1H, CH). Found, %: C 89.4; H 5.8; N 4.7. $\text{C}_{22}\text{H}_{17}\text{N}$. Calculated, %: C 89.5; H 5.8; N 4.7.

***N,N*-Bis[(1*E*)-9-anthrylmethylene]ethane-1,2-diamine (Ib).** A mixture of 4.12 g (20 mmol) of 9-anthraldehyde, 0.5 ml of acetic acid, and 0.6 g (10 mmol) of ethylenediamine in 50 ml of ethanol was heated for 2 h under reflux. The precipitate was filtered off and recrystallized from 1-butanol–DMF (1:1). Yield 4.09 g (94%). mp 145–146°C. IR spectrum, ν , cm^{-1} : 1633, 1447, 1360. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 4.43 s [4H, $(\text{CH}_2)_2$], 7.12–8.62 m (18H, H_{arom}), 9.52 s (2H, 2CH). Found, %: C 88.0; H 5.4; N 6.3. $\text{C}_{32}\text{H}_{24}\text{N}_2$. Calculated, %: C 88.0; H 5.5; N 6.4.

***N,N*-Bis[(1*E*)-9-anthrylmethylene]hexane-1,6-diamine (Ic)** was synthesized as described above for compound **Ib**. Yield 4.47 g (91%). mp 151–152°C. IR spectrum, ν , cm^{-1} : 1620, 1460, 1360. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.67 m [4H, $(\text{CH}_2)_2$], 1.96 m (4H, 2 CH_2), 3.95 t (4H, 2 CH_2), 7.38–8.62 m (18H, H_{arom}), 9.42 s (2H, 2CH). Found, %: C 87.9; H 6.5; N 5.6. $\text{C}_{36}\text{H}_{32}\text{N}_2$. Calculated, %: C 87.8; H 6.5; N 5.7.

***N*-(9-Anthrylmethyl)-*N*-benzylamine hydrochloride (IIa·HCl).** Sodium tetrahydridoborate, 1.13 g (30 mmol), was added with stirring to a suspension of 2.95 g (10 mmol) of Schiff base **Ia** in 100 ml of ethanol. The mixture was stirred for 4 h and diluted with water (200 ml), and excess NaBH_4 was decomposed with acetic acid. Product **IIa** was extracted into chloroform (3×50 ml), the extract was washed with water and dried over anhydrous Na_2SO_4 , the solvent was distilled off, and the residue was dissolved in 50 ml of benzene. The solution was saturated with hydrogen chloride over a period of 2 h, and the precipitate was filtered off, dried, and recrystallized from 1-butanol. Yield 2.45 g (73%). mp 225–226°C. IR spectrum, ν , cm^{-1} : 3435, 3200, 1457, 1385. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 4.38 t (2H, CH_2), 5.08 t (2H, CH_2), 7.40–8.70 m (14H, H_{arom}), 9.96 br.s (2H, NH_2). Found, %: C 79.0; H 6.0; Cl 10.4; N 4.1. $\text{C}_{22}\text{H}_{20}\text{ClN}$. Calculated, %: C 79.1; H 6.0; Cl 10.6; N 4.2.

***N*-Bis(9-anthrylmethylene)ethane-1,2-diamine (IIb).** Sodium tetrahydridoborate, 1.13 g (30 mmol), was added in small portions to a suspension of 2.18 g (5 mmol) of Schiff base **Ib** in 100 ml of ethanol–DMF (3:1), stirred at 60–70°C. The mixture was stirred for 3 h at that temperature and diluted with water (200 ml), and excess NaBH_4 was decomposed with acetic acid. The precipitate was filtered off, dried, and recrystallized from 1-butanol. Yield 1.67 g (76%). mp 183–184°C. IR spectrum, ν , cm^{-1} : 1330, 1235. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 3.06 s [4H, $(\text{CH}_2)_2$], 4.71 s (4H, 2 CH_2), 7.20–8.45 m (18H, H_{arom}). Found, %: C 87.1; H 6.4; N 6.2. $\text{C}_{32}\text{H}_{28}\text{N}_2$. Calculated, %: C 87.2; H 6.4; N 6.4.

***N*-Bis(9-anthrylmethylene)hexane-1,6-diamine (IIc)** was synthesized as described above for compound **IIb**. Yield 2.02 g (81%). mp 137–138°C. IR spectrum, ν , cm^{-1} : 3385, 1485, 1328, 1220. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.22–1.72 m [8H, $(\text{CH}_2)_4$], 2.87 t (4H, 2 CH_2), 4.71 s (4H, 2 CH_2), 7.18–8.45 m (18H, H_{arom}). Found, %: C 87.1; H 7.3; N 5.7. $\text{C}_{36}\text{H}_{36}\text{N}_2$. Calculated, %: C 87.0; H 7.3; N 5.6.

***N*-(9-Anthrylmethyl)-*N*-benzyl-*N'*-phenylthiourea (III).** A mixture of 1.48 g (5 mmol) of amine **IIa** and 0.68 g (5 mmol) of phenyl isothiocyanate in 30 ml of benzene was heated for 2 h under reflux. It was then cooled, and the product was filtered off and recrystallized from 1-butanol. Yield 85%. mp 191–192°C. IR spectrum, ν , cm^{-1} : 3320, 1455, 1378, 1305. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 4.56 s (2H, CH_2), 6.17 s (2H, CH_2), 6.88–8.60 m (19H, H_{arom}), 9.46 s (1H, NH). Found, %: C 80.6; H 5.6; N 6.3; S 7.4. $\text{C}_{29}\text{H}_{24}\text{N}_2\text{S}$. Calculated, %: C 80.5; H 5.6; N 6.4; S 7.4.

The IR spectra were recorded on a Specord 75IR spectrometer from samples pelleted with KBr. The fluorescence spectra were measured from solutions in acetonitrile on a Hitachi 650-60 spectrofluorimeter. The ^1H NMR spectra were obtained on a Varian Unity-300 instrument (300 MHz) using tetramethylsilane as reference.

This study was financially supported by the Ministry of Education of the Russian Federation (project no. E02-12.6-259) and by the CRDF (project no. REC-004).

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