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Chemosensor Properties of Mono- and Bisthioureas Based on 9-Anthrylmethyl-Substituted Alkylamines and Diamines

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Abstract—Mono- and bisthioureas were synthesized based on *N*-(9-anthrylmethyl)-substituted alkylamines and diamines. Their luminescent and complexing properties were studied by the electronic, IR, and NMR ^{1}H spectroscopy. *N*-(9-Anthrylmethyl)-*N*-(6-{9-anthrylmethyl[(phenylamino)carbothioyl]amino}hexyl)-*N*'-phenylthiourea was shown to be a highly effective fluorescent chemosensor for Hg^{2+} cations.

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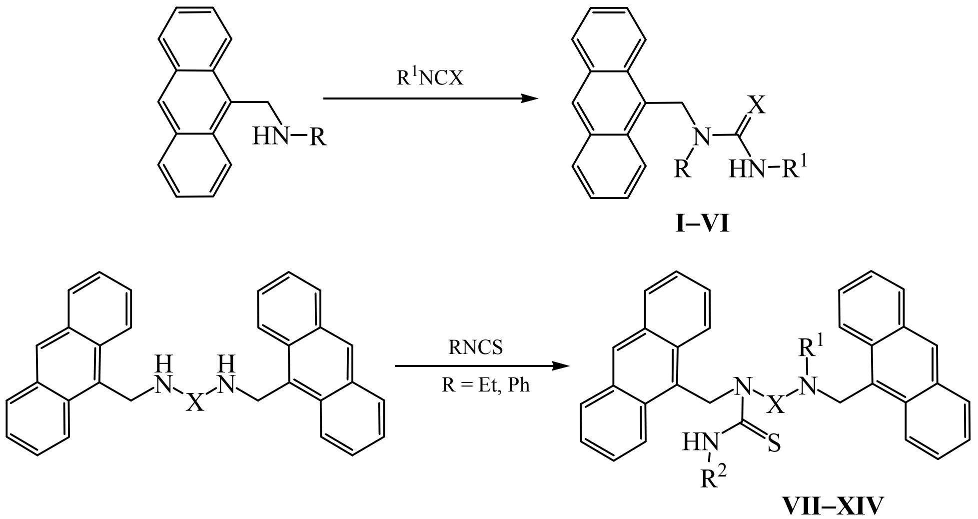
Fluorescent selective chemical sensors for determination of cations and anions in different media are the subject of ongoing fundamental and practical interest [1-3]. Most timely are the studies of chemosensors sensitive to highly toxic cations such as Hg^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, etc. [4–7]. The earlier prepared *N*-(9-anthrylmethyl)-*N*-benzyl-*N*'-phenylthiourea proved to be a selective fluorescent chemosensor to Hg^{2+} [8]. Aiming at further studies of the sensors on the basis of *N*-(9-anthrylmethyl)-substituted alkylamines and diamines we synthesized a series of thioureas **I–XIV** (Scheme 1).

Scheme 1.



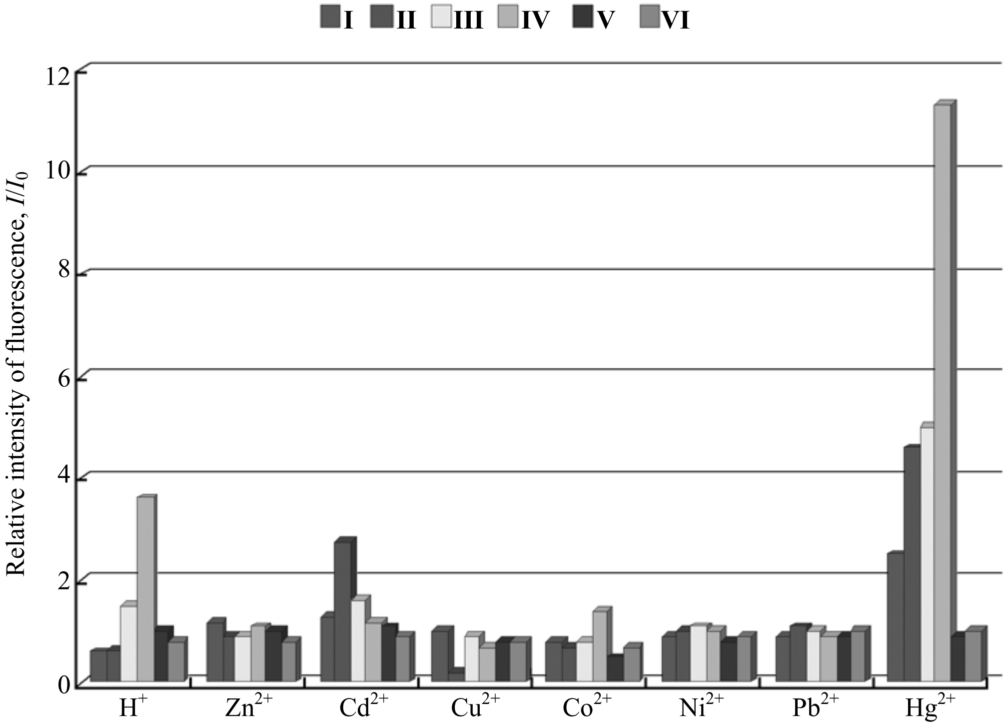
I, R = H, R^1 = Ph, X = S; **II**, R = CH_2CH_2OH, R^1 = Ph, X = S; **III**, R = H, R^1 = All, X = S; **IV**, R = CH_2Ph, R^1 = All; **V**, R = H, R^1 = C_6H_4Cl-4, X=O; **VI**, R = CH_2Ph, R^1 = C_6H_4Cl-4, X = O; **VII**, X = $(CH_2)_2$, R^1 = H, R^2 = Ph; **VIII**, X = $(CH_2)_3$, R^1 = C(S)NHPh, R^2 = Ph; **IX**, X = $(CH_2)_4$, R^1 = C(S)NHPh, R^2 = Ph; **X**, X = $(CH_2)_6$, R^1 = C(S)NHPh, R^2 = Ph; **XI**, X = $(CH_2)_2$, R^1 = C(S)NHEt, R^2 = Et; **XII**, X = $(CH_2)_3$, R^1 = C(S)NHEt, R^2 = Et; **XIII**, X = $(CH_2)_4$, R^1 = C(S)NHEt, R^2 = Et; **XIV**, X = $(CH_2)_6$, R^1 = C(S)NHEt, R^2 = Et.

Compounds **I–IV** possessing, apart from the nitrogen atom, a “soft” nucleophilic center, the sulfur atom, were obtained by the reaction of the corresponding 9-anthrylmethylamines [8] with phenyl or allyl isocyanate (Scheme 1). The diamines used for the synthesis of compounds **VII–XIV** have been earlier shown to be highly effective fluorescent chemosensors to zinc(II) cations [9], and phenyl or ethyl isothiocyanate were taken in a two-fold excess to avoid the formation of a mixture of the products of mono- and bis-addition (Scheme 1). In the case of *N*,*N*'-bis(9-anthrylmethyl)ethane-1,2-diamine regardless of the reaction conditions or the amount of the used PhNCS (but not EtNCS) only one fragment of thiourea can be introduced (compound **VII**), apparently, due to the arising steric hindrances for introduction of the second thiourea residue.

The sensory ability of compounds **I–XIV** with respect to cations H^+, Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+} in acetonitrile was estimated from the data of the fluorescence spectra in the region of the anthracene local fluorescence at 390 nm. Among the studied thiourea derivatives, effective and selective sensors for Hg^{2+} cations were found (Fig. 1).

Thus, the sensitivity and selectivity with respect to Hg^{2+} ions increases in the series of molecules **I** < **II** < **III** < **IV**, the *N*'-allyl-*N*-(9-anthrylmethyl)-*N*-benzylthiourea (**IV**) having the best sensor parameters among the prepared monothioureas (Fig. 1). Such a large sensitivity of thiourea to the mercury cation is due to high affinity of the sulfur-containing receptor to Hg^{2+} as well as to the possibility of complexes formation of the chelate type (Scheme 2) [10, 11]. The composition of the formed complexes with thioureas strongly depends on the nature of the metal cation and the substituents at the nitrogen atoms. Per one metal cation there may be from 1 to 6 thiourea residues [10–13].

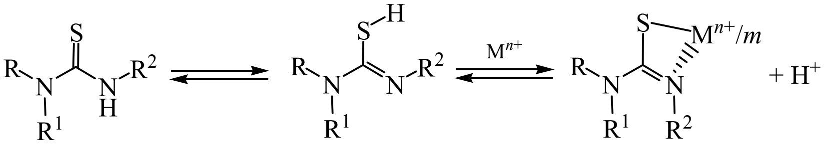
The replacement of a “soft” nucleophilic sulfur atom in monothioureas by more “hard” oxygen atom leads to ureas **V**, **VI**, respectively, which do not



	H^+	Zn^{2+}	Cd^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Hg^{2+}
I	0.6	1.2	1.3	1.0	0.8	0.9	0.9	2.5
II	0.7	0.9	2.8	0.2	0.7	1.0	1.1	4.6
III	1.5	0.9	1.6	0.9	0.8	1.1	1.0	5.0
IV	3.6	1.1	1.2	0.7	1.4	1.0	0.9	11.3
V	1.0	1.0	1.1	0.8	0.5	0.8	0.9	0.9
VI	0.8	0.8	0.9	0.8	0.7	0.9	1.0	1.0

Fig. 1. Relative variation of intensity of fluorescence of compounds **I–VI** (c = 5×10^{-6} M) in acetonitrile upon addition of trifluoroacetic acid or acetates of various cations ($c = 2.5\times10^{-5}$ M).

Scheme 2.

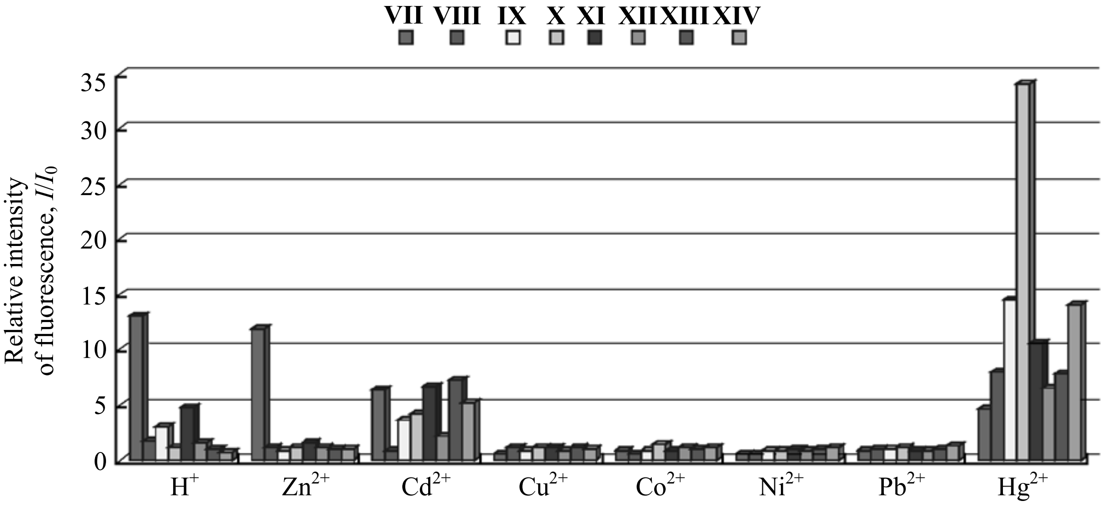


R, R^1, R^2 = H, Alk, Ar, m = 1, 2, 4, 6.

possess sensor properties with respect to any of the cations studied (Fig. 1). This effect can be explained by a sharp decrease in the ability of ureas to complex formation and by decrease of the heteroatom (oxygen) affinity to mercury cations.

In the case of the thiourea derivatives **VII–X** the efficiency of the sensor with respect to Zn^{2+} ions decreases relative to that of the starting diamines [9], and the dependence of the fluorescence on the pH of the solution practically disappears. The sensitivity to Hg^{2+} ions increases in the series **VII** < **VIII** < **IX** < **X** as proved by the corresponding flaring of fluorescence (Fig. 2). The relatively low sensitivity of sensor **VII** to Hg^{2+} ions can be explained by the presence of only one thiourea fragment in the molecule. Therefore, in the case of thioureas **VII–X** the most selective for the series of cations is the reaction to Hg^{2+} ions, the sensitivity of the sensors increases with the length of the alkyl chain **X**, and the most effective is compound **X** on the basis of 1,6-diaminohexane (I/I_0 = 34.0). A similar effect is observed also for the series of ethylthioureas **XI–XIV**: the maximum flaring of fluorescence upon the reaction with mercury(II) ions occurs in the case of *N*-(9-anthrylmethyl)-*N*-(6-{9-anthrylmethyl[(ethylamino)carbothioyl]amino}hexyl)-*N*'-ethylthiourea (**XIV**) (I/I_0 = 14.0). As compared to the phenyl derivatives, the selectivity and efficiency of the ethyl derivatives with respect to mercury(II) ions decreases, however, sharply increases the sensitivity to Cd^{2+} ions (Fig. 2).

Therefore, thioureas on the basis of *N*-(9-anthrylmethyl)derivatives of alkylamines and diamines



	H^+	Zn^{2+}	Cd^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Hg^{2+}
VII	13.0	11.8	6.4	0.5	0.9	0.6	0.8	4.6
VIII	1.7	1.1	0.9	1.1	0.5	0.6	1.0	7.9
IX	3.0	0.9	3.6	0.8	0.9	0.8	1.0	14.5
X	1.2	1.1	4.2	1.2	1.4	0.9	1.1	34.0
XI	4.7	1.6	6.6	1.1	0.9	1.0	0.9	10.5
XII	1.6	1.2	2.2	0.8	1.2	0.8	0.8	6.5
XIII	1.0	1.0	7.2	1.1	1.0	1.0	1.0	7.8
XIV	0.7	1.0	5.2	1.0	1.1	1.2	1.3	14.0

Fig. 2. Relative variation of intensity of fluorescence of compounds **VII–XIV** (c = 5×10^{-6} M) in acetonitrile upon addition of trifluoroacetic acid or acetates of various cations (c = 2.5×10^{-5} M).

as chemosensors display sensor activity with respect to a series of cations Zn^{2+}, Cd^{2+}, Hg^{2+}, and *N*-(9-anthrylmethyl)-*N*-(6-{9-anthrylmethyl[(phenylamino)-carbothioyl]amino}hexyl)-*N'*-phenylthiourea (**X**) is a highly effective chemosensor for Hg^{2+} cations.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Varian Unity 300 spectrometer (300 MHz). Residual signals of $CHCl_3$ (δ = 7.25 ppm) and $(CH_3)_2SO$ (δ = 2.50 ppm) were used as an internal reference. Electron absorption spectra were taken on a Specord M-40 spectrophotometer, luminescence spectra were measured on a Hitachi 650-60 and Varian Eclipse spectrofluorimeters. Vibrational spectra were recorded on a Specord 75IR instrument in mineral oil. Melting points were determined in glass capillaries on a PTP(M) device. The reactions were followed and the purity of the obtained compounds was checked by TLC (Silufol U254 plates, eluent–chloroform, development with iodine vapors in a wet chamber).

General procedure for preparation of ureas and thioureas. To the solution of 2.0 mmol of the corresponding amine in 30 ml of benzene 2.2 mmol (for **I–VI**) and 4.4 mmol (for **VII–XIV**) of the corresponding isocyanate (for **V, VI**) or isothiocyanate was added and the obtained mixture was heated on a water bath for 2 h, cooled, the precipitate formed was filtered off, washed with ether and crystallized from the appropriate solvent, and dried in air.

***N*-(9-Anthrylmethyl)-*N'*-phenylthiourea (I)** was prepared from 9-aminomethylanthracene and phenyl - isothiocyanate. Yield 82%, mp 191–192°C (1-butanol). IR spectrum, ν, cm^{-1}: 3295, 3145, 1547, 1513, 1475. ^{1}H NMR spectrum, δ, ppm: 5.63 d (2H, CH_2, *J* = 5.2 Hz); 6.97-8.62 m (15H, NH + H_{Ar}); 9.18 s (1H, NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 414. Found, %: C 77.18; H 5.30; N 8.25; S 9.27. $C_{22}H_{18}N_2S$. Calculated, %: C 77.16; H 5.30; N 8.18; S 9.36.

***N*-(9-Anthrylmethyl)-*N*-(2-hydroxyethyl)-*N'*-phenylthiourea (II)** was prepared from 2-[(9-anthrylmethyl)amino]ethanol and phenyl isothiocyanate. Yield 70%, mp 183–184°C (1-butanol). IR spectrum, ν, cm^{-1}: 3435, 3195, 1633, 1574, 1467, 1366. ^{1}H NMR spectrum, δ, ppm: 2.92 q (2H, CH_2); 3.41 t (2H, CH_2); 5.65 t (1H, OH); 6.20 s (2H, CH_2); 6.98–8.65 m (14H, H_{Ar}); 10.14 s (1H, NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 416. Found, %: C 74.65; H 5.70; N 7.20; S 8.38. $C_{24}H_{22}N_2OS$. Calculated, %: C 74.58; H 5.74; N 7.25; S 8.30.

***N*-Allyl-*N'*-(9-anthrylmethyl)thiourea (III)** was prepared from 9-aminomethylanthracene and allylisothiocyanate. Yield 88%, mp 194–195°C (1-butanol). IR spectrum, ν, cm^{-1}: 3300, 1550, 1475. ^{1}H NMR spectrum, δ, ppm: 3.73–3.94 m (2H, CH_2); 5.00–5.20 m (2H, CH_2); 5.58–5.85 m (4H, CH_2 + NH + CH); 6.00 br.s (1H, NH); 7.40-8.50 m (9H, H_{Ar}). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 414. Found, %: C 74.54; H 5.98; N 9.10; S 10.38. $C_{19}H_{18}N_2S$. Calculated, %: C 74.47; H 5.92; N 9.14; S 10.47.

***N*-Allyl-*N'*-(9-anthrylmethyl)-*N'*-benzylthiourea (IV)** was prepared from *N*-(9-anthrylmethyl)-*N*-benzylamine and allyl isothiocyanate. Yield 75%, mp 140–141°C (1-butanol). IR spectrum, ν, cm^{-1}: 3315, 1465, 1370. ^{1}H NMR spectrum, δ, ppm: 4.25–4.40 m (4H, $2CH_2$); 4.83–5.05 m (2H, CH_2); 5.55 t (1H, NH, *J* = 5.6 Hz); 5.65–5.85 m (1H, CH); 6.38 s (2H, CH_2); 6.75–8.50 m (14H, H_{Ar}). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 417. Found, %: C 78.72; H 6.10; N 7.00; S 8.18. $C_{26}H_{24}N_2S$. Calculated, %: C 78.75; H 6.10; N 7.06; S 8.09.

***N*-(9-Anthrylmethyl)-*N'*-(4-chlorophenyl)urea (V)** was prepared from 9-aminomethylanthracene and phenyl isocyanate. Yield 87%, mp >325°C (subl., 1-butanol–DMF). IR spectrum, ν, cm^{-1}: 3300, 1627, 1555, 1464. ^{1}H NMR spectrum, δ, ppm: 5.30 d (2H, CH_2); 6.52 t (1H, NH); 7.05-8.60 m (14H, H_{Ar} + NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 413. Found, %: C 73.16; H 4.80; Cl 9.77; N 7.84. $C_{22}H_{17}ClN_2O$. Calculated, %: C 73.23; H 4.75; Cl 9.83; N 7.76.

***N*-(9-Anthrylmethyl)-*N*-benzyl-*N'*-(4-chlorophenyl)urea (VI)** was prepared from *N*-(9-anthrylmethyl)-*N*-benzylamine and phenyl isocyanate. Yield 77%, mp 174–175°C (1-butanol). IR spectrum, ν, cm^{-1}: 3287, 1625, 1460, 1367. ^{1}H NMR spectrum, δ, ppm: 4.24 s (2H, CH_2); 5.81 s (2H, CH_2); 6.33 s (1H, NH); 6.87–8.50 m (18H, H_{Ar}). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 414. Found, %: C 77.18; H 5.20; Cl 7.90; N 6.28. $C_{29}H_{23}ClN_2O$. Calculated, %: C 77.24; H 5.14; Cl 7.86; N 6.21.

***N*-(9-Anthrylmethyl)-*N*-[2-(9-anthrylmethylamino)-ethyl]-*N'*-phenylthiourea (VII)** was prepared from *N*,*N'*-bis(9-anthrylmethyl)ethane-1,2-diamine and phenyl isothiocyanate. Yield 87%, mp 202–203°C (1-butanol–

DMF 2:1). IR spectrum, ν, cm^{-1}: 1605, 1507, 1475, 1315. ^{1}H NMR spectrum, δ, ppm: 1.93–2.06 m (2H, CH_2); 3.38–3.55 m (2H, CH_2); 4.00 s (2H, CH_2); 6.28 s (2H, CH_2); 6.45–8.82 m (23H, H_{Ar}). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 415. Found, %: C 81.34; H 5.75; N 7.37; S 5.54. $C_{39}H_{33}N_3S$. Calculated, %: C 81.36; H 5.78; N 7.30; S 5.56.

***N*-(9-Anthrylmethyl)-*N*-(3-{9-anthrylmethyl[(phenylamino)carbothioyl]amino}-propyl)-*N*'-phenylthiourea (VIII)** was prepared from *N*,*N*'-bis(9-anthrylmethyl)propane-1,3-diamine and phenyl isothiocyanate. Yield 70%, mp 201–202ºC (1-butanol–DMF 2:1). IR spectrum, ν, cm^{-1}: 3250, 1600, 1505, 1467. ^{1}H NMR spectrum, δ, ppm: 1.68–1.84 m (2H, CH_2); 2.86-3.11 m (4H, $2CH_2$); 5.80 s (4H, $2CH_2$); 7.02–8.57 m (28H, H_{Ar}); 8.95 s (2H, 2NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 416. Found, %: C 77.83; H 5.60; N 7.77; S 8.80. $C_{47}H_{40}N_4S_2$. Calculated, %: C 77.86; H 5.56; N 7.73; S 8.85.

***N*-(9-Anthrylmethyl)-*N*-(4-{9-anthrylmethyl[(phenylamino)carbothioyl]amino}butyl)-*N*'-phenylthiourea (IX)** was prepared from *N*,*N*'-bis(9-anthrylmethyl)butane-1,4-diamine and phenyl isothiocyanate. Yield 85%, mp 187–188ºC (1-butanol–DMF 2:1). IR spectrum, ν, cm^{-1}: 3260, 1600, 1500, 1475, 1453, 1300. ^{1}H NMR spectrum, δ, ppm: 1.17–1.37 m [4H, $(CH_2)_2$]; 2.85–3.07 m (4H, $2CH_2$); 6.00 s (4H, $2CH_2$); 7.03–8.60 m (28H, H_{Ar}); 9.1 s (2H, 2NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 419. Found, %: C 78.06; H 5.74; N 7.50; S 8.70. $C_{48}H_{42}N_4S_2$. Calculated, %: C 78.01; H 5.73; N 7.58; S 8.68.

***N*-(9-Anthrylmethyl)-*N*-(6-{9-anthrylmethyl[(phenylamino)carbothioyl]amino}-hexyl)-*N*'-phenylthiourea (X)** was prepared from *N*,*N*'-bis(9-anthrylmethyl)hexane-1,6-diamine and phenyl isothiocyanate. Yield 76%, mp 192–193ºC (1-butanol–DMF 2:1). IR spectrum, ν, cm^{-1}: 3255, 1680, 1633, 1600, 1533, 1467, 1447. ^{1}H NMR spectrum, δ, ppm: 0.17–0.35 m [4H, $(CH_2)_2$]; 0.80–1.05 m (4H, $2CH_2$); 2.80–3.05 m (4H, $2CH_2$); 6.10 s (4H, $2CH_2$); 7.05–8.75 m (28H, H_{Ar}.); 9.15 s (2H, 2NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 416. Found, %: C 78.22; H 6.09; N 7.30; S 8.39. $C_{50}H_{46}N_4S_2$. Calculated, %: C 78.29; H 6.05; N 7.30; S 8.36.

***N*-(9-Anthrylmethyl)-*N*-(3-{9-anthrylmethyl-[(ethylamino)carbothioyl]amino}ethyl)-*N*'-ethylthiourea (XI)** was prepared from *N*,*N*'-bis(9-anthrylmethyl)ethane-1,2-diamine and ethyl isothiocyanate. Yield 73 %, mp 213–214ºC (1-butanol–DMF 4:1). IR spectrum, ν, cm^{-1}: 3250, 1600, 1500, 1475. ^{1}H NMR spectrum, δ, ppm: 1.23 t (6H, $2CH_3$, $J = 6.5$ Hz); 2.98–3.27 m (4H, CH_2CH_2); 3.54–3.76 m (4H, $2CH_2$); 5.50 s (4H, $2CH_2$); 7.20–8.33 m (20H, H_{Ar} + 2NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 414. Found, %: C 74.28; H 6.18; N 9.04; S 10.50. $C_{38}H_{38}N_4S_2$. Calculated, %: C 74.23; H 6.23; N 9.11; S 10.43.

***N*-(9-Anthrylmethyl)-*N*-(3-{9-anthrylmethyl [(ethylamino)carbothioyl]amino}-propyl)-*N*'-ethylthiourea (XII)** was prepared from *N*,*N*'-bis(9-anthrylmethyl)propane-1,3-diamine and ethyl isothiocyanate. Yield 68%, mp 190–191ºC (1-butanol). IR spectrum, ν, cm^{-1}: 3250, 1610, 1505, 1465. ^{1}H NMR spectrum, δ, ppm: 1.18 t (6H, $2CH_3$, $J = 7.2$ Hz); 1.28–1.48 m (2H, CH_2); 2.72 t (4H, $2CH_2$, $J = 7.0$ Hz); 3.50–3.72 m (4H, $2CH_2$); 5.66 s (4H, $2CH_2$); 7.06–8.54 m (20H, H_{Ar} + 2NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 415. Found, %: C 74.55; H 6.35; N 8.97; S 10.13. $C_{39}H_{40}N_4S_2$. Calculated, %: C 74.48; H 6.41; N 8.91; S 10.20.

***N*-(9-Anthrylmethyl)-*N*-(4-{9-anthrylmethyl [(ethylamino)carbothioyl]amino}butyl)-*N*'-ethylthiourea (XIII)** was prepared from *N*,*N*'-bis(9-anthrylmethyl)butane-1,4-diamine and ethyl isothiocyanate. Yield 88%, mp 165–166ºC (1-butanol–DMF 4:1). IR spectrum, ν, cm^{-1}: 3260, 1600, 1500, 1470, 1455, 1300. ^{1}H NMR spectrum, δ, ppm: 0.88–1.08 m (4H, $2CH_2$); 1.15 t (6H, $2CH_3$, $J = 6.5$ Hz); 2.57–2.78 m (4H, $2CH_2$); 3.51–3.73 m (4H, $2CH_2$); 5.87 s (4H, $2CH_2$); 7.07–8.54 m (20H, H_{Ar} + 2NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 415. Found, %: C 74.74; H 6.64; N 8.72; S 9.90. $C_{40}H_{42}N_4S_2$. Calculated, %: C 74.74; H 6.58; N 8.71; S 9.97.

***N*-(9-Anthrylmethyl)-*N*-(6-{9-anthrylmethyl [(ethylamino)carbothioyl]amino}-hexyl)-*N*'-ethylthiourea (XIV)** was prepared from *N*,*N*'-bis(9-anthrylmethyl)hexane-1,6-diamine and ethyl isothiocyanate. Yield 84%, mp 197–198ºC (1-butanol–DMF 4:1). IR spectrum, ν, cm^{-1}: 3255, 1670, 1600, 1535, 1470. ^{1}H NMR spectrum, δ, ppm: 0.15–0.36 m (4H, $2CH_2$); 0.71–0.94 m (4H, $2CH_2$); 1.20 t (6H, $2CH_3$, $J = 7.6$ Hz); 2.61–2.84 m (4H, $2CH_2$); 3.57–3.77 m (4H, $2CH_2$); 5.97 s (4H, $2CH_2$); 7.15–8.60 m (20H, H_{Ar} + 2NH). Spectrum of fluorescence in acetonitrile, λ_{max}, nm ($c = 5\times10^{-5}$ M): 416. Found, %: C 78.09; H 6.96;

N 8.40; S 9.55. $C_{42}H_{46}N_4S_2$. Calculated, %: C 75.18; H 6.91; N 8.35; S 9.56.

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REFERENCES

1. Callan, J.F., de Silva, A.P., and Magri, D.C., *Tetrahedron,* 2005, vol. 61, p. 8551.
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. Kumar, S., Kaur, S., and Singh, G., *Supramol. Chem.*, 2003, vol. 15, p. 65.
5. Prodi, L., Bargossi, C., Montalti, M., Zaccheroni, N., Su, N., Bradshaw, J.S., Izatt, R.M., and Savage, P.B., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 6769.
6. Beeby, A., Parker, D., and Williams, J.A.G., *J. Chem. Soc. Perkin Trans. 2*, 1996, p. 1565.
7. Costero, A.M., Banuls, M.J., Aurella, M.J., and Domenech, A., *Tetrahedron*, 2006, vol. 62, p. 11972.
8. Tolpygin, I.E., Dubonosov, A.D., Bren', V.A., Minkin, V.I., and Pybalkin, V.P., *Zh. Org. Chem.,* 2003, vol. 39, no. 9, p. 1435.
9. Tolpygin, I.E., Pybalkin, V.P., Shepelenko, E.N., Makarova, N.I., Metelitsa, A.V., Revinskii, Yu.V., Tsukanov, A.V., Dubonosov, A.D., Bren', V.A., and Minkin, V.I., *Zh. Org. Chem.,* 2007, vol. 43, no. 3, p. 390.
10. Toropova, V.F., *Zh. Neorg. Khim.*, 1956, vol. 1, no. 5, p. 930.
11. Umland, F., Jansen, A., Tirig, D., and Wunsch, G., *Kompleksnye soedimemiya v analiticheskoi khimii* (Complexes in Analytical Chemistry), Moscow: Mir, 1975.
12. Yatsimirskii, K.B., Kostromina, N.A., Sheka, Z.A., Davidenko, N.K., Kriss, E.E., and Ermolenko, V.I., *Khimiya kompleksnykh soedinenii redkozemel'nykh elementov* (Chemistry of Complex Compounds of Rate-Earth Elements), Kiev: Naukova Dumka, 1966.
13. Losev, V.N., Bakhtina, M.P., Bakhvalova, I.P., Trofimchuk, A.K., and Runov, V.K., *J. Anal. Chem.*, 2001, vol. 56, p. 341.