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A Voltammetric Study of the Chemosensor Activity of Aminoanthracene Derivatives

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Abstract—The redox activity of potent chemosensors based on anthryl-containing diamines, thioureas, and ureas in the absence and in the presence of complexing metal cations in solution was studied by cyclic and differential pulse voltammetry. The free energy of intramolecular electron transfer was calculated. The experimental conclusions were confirmed by ab initio RHF/6-31G** calculations. A correlation was found between the electrochemical and photophysical data for the compounds studied.

Determination of traces of metals in various natural objects became recently an urgent problem of environmental studies. A new approach to solving this problem is the use of highly sensitive chemosensors operating on the basis of the photoinduced electron transfer (PET) effect [1, 2]. The essence of this effect is as follows. In the absence of a substrate, photoexcitation of a chemosensor molecule consisting of a complexing fragment, a signaling fragment, and a bridge causes an intramolecular electron transfer from the highest occupied molecular orbital (HOMO) of the receptor to the vacant orbital of the fluorophore, quenching the fluorophore fluorescence. When a cation is bound, the receptor HOMO energy decreases, its oxidation potential increases, the electron transfer becomes more difficult, and the fluorescence of the signaling fragment is observed. Anthracene and its derivatives are often used as fluorophores.

If a chemosensor molecule contains "electrophore" groups, its activity can be evaluated electrochemically. This approach is based on a correlation between the HOMO and LUMO (lowest unoccupied molecular orbital) energies of a compound, on the one hand, and electrochemical potentials of its oxidation and reduction, on the other hand [3].

The free energy of electron transfer is estimated by the Rehm–Weller equation [4, 5]:

$$\Delta G_{et}^{0} = -E_{0-0}^{0} + (E_{d^{+}/d}^{0} - E_{a/a^{-}}^{0}) - \Delta G^{0}(\varepsilon).$$

where E_{0-0}^0 is the energy of the photoexcited state of the fluorophore, eV; E_{d/d^-}^0 , oxidation potential of the electron donor, V; E_{a/a^-}^0 , reduction potential of the

electron acceptor, V; and $\Delta G^0(\varepsilon)$, factor taking into account the dielectric premeability of the solvent (ε) and the distance between the centers of the donor and acceptor (*a*, Å) and calculated as $e^2/4\pi\varepsilon a$, eV.

As investigation objects we chose potent chemosensors, anthryl-containing diamines, thioureas, and ureas **I**-**XI**, and also compounds modeling separate fragments of the molecules under consideration: 9-aminomethylanthracene **XII**, thiourea **XIII**, and anthracene **XIV**.

Our goal was to determine the redox potentials of potent chemosensors, calculate the free energy of intramolecular electron transfer, and evaluate how these quantities correlate with the photophysical data reflecting the PET effect.

The synthesis of anthryl-containing derivatives **I**, **IV**, and **V** was described elsewhere [6]. The compounds were prepared along side Scheme 1.

The characteristics of the voltammograms of I-XI and of models XII-XV, determined by differential pulse voltammetry, are given in the table. The choice of this method is governed by the high accuracy of measuring the potentials in the case of reversible and irreversible systems and good resolving power [7]. The data obtained are well consistent with the halfpeak redox potentials $E_{1/2}$ determined by cyclic voltammetry under the same conditions.

As seen from the table, compounds **I**–**XII** are reduced under the experimental conditions, defined by the presence of the anthryl fragment. The reduction yields a stable radical anion and is characterized by a reversible one-electron peak in the cathodic branch of





 $X = (CH_2)_2$ (I), $(CH_2)_3$ (II), $(CH_2)_4$ (III), $(CH_2)_6$ (IV); R = H (V), $CH_2C_6H_5$ (VI),

 $(CH_2)_2NHCH_2 - \bigvee (VII), H (IX), CH_2C_6H_5 (X).$

the voltammogram (Fig. 1). The potential of this peak in most cases is close to that of unsubstituted anthracene **XIV** [8]. It is known that substituted aliphatic amines give no reduction waves on solid and mercury dropping electrodes [9]. The thioamide group (with thiourea used as model) did not undergo cathodic reduction under the experimental conditions (see table). An additional evidence of the assumption that the reduction involves primarily the anthryl fragment is the LUMO localization on this fragment, according to quantum-chemical calculations.

Oxidation of the compounds under consideration occurs in one or two steps involving the anthryl fragment and the donor moiety (amino, thiourea, or urea group). Generally the anodic process corresponds to the *ECEC* mechanism (E, electrochemciial reaction; C, chemical reaction) [3] for two-step oxidation and *EC* mechanism for one-step oxidation.

The peaks in the anodic branch of the voltammograms at 0.95–1.05 V (e.g., signal A, Fig. 1) correspond to the electrooxidation of the receptors of the compounds whose potentials were taken into account in the subsequent calculations of ΔG_{el}^0 . This is confirmed by published data on oxidation of aliphatic amines in acetonitrile [10] and of urea derivatives [3], and also by the closeness to the values of the oxidation potentials of "model" compounds **XII** and **XIII**. Oxidation of these donor fragments is irreversible; an unstable radical cation is formed in the first step, which is followed by a fast chemical reaction.

As seen from the table, for I-X the second oxidation step is observed. As judged from the potentials and shape of the signals, this is the anodic branch of the anthryl fragment. It is known that anthracene is reversibly oxidized via formation of a stable radical

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Comp. no.	Ligand				Cation	Complex			
	E _{p.c} , V	E _{p.a} , V	Δg_{et}^0 , eV	I ₀	Cation	E _{p.c} , V	E _{p.a} , V	Δg_{et}^0 , eV	<i>I</i> / <i>I</i> ₀
Ι	-1.85	1.00 1.05	-0.25	5.2	H^+ Zn^{2+}	-2.05 -2.00	1.35 1.30	>>0 0.20	32.0 42.0
II	-1.85	0.93 1.58	-0.32	1.0	H^+ Zn^{2+}	-2.05 -2.00	1.45 1.35 1.25	>>0 0.15	15.0 10.0
Ш	-1.88	0.93 1.50	-0.29	4.1	H^+ Zn^{2+}	-2.00 -2.00	1.46 1.38 1.13 1.50	>>0 0.03	64.0 2.5
IV	-1.83	1.05 1.50	-0.22	7.4	H^+ Zn^{2+}	$-2.10 \\ -2.00$	1.30 1.38 1.10 1.28	>>0 0.18	36.0 26.0
V	-1.98	0.98	-0.14	27.6	Hg ²⁺	-1.83	- 1 43	>>0	2.5
VI	-1.45	1.00 1.38	-0.65	1.9	Hg ²⁺	-2.25	1.03	0.18	77.0
VII	-1.95	0.95 1.40	-0.20	5.9	${ m H^+} { m Zn^{2+}}$	$-2.08 \\ -1.98$	1.15 1.30	0.13 0.18	13.0 12.0
VIII	-1.98	0.95 1.30	-0.17	11.8	Hg ²⁺	-1.95	1.15	0.00	11.0
IX	-1.98	1.05 1.50	-0.07	142.9	Cu ²⁺	-2.08	1.00	-0.02	0.8
X	-2.07	1.00 1.63	-0.03	138.9	H^+ Co^{2+}	-2.28 -2.05	1.05 0.93	0.23 -0.12	0.8 0.9
XI XII	-1.85 -1.90	0.98 1.10 1.45	-0.27 -0.10	4.1 125.4	Hg^{2+} H^{+}	-1.88 -2.13	1.35 1.20	0.11 >>0	11.7 2.2
XIII XIV XV	 	0.94 1.35 0.38	_ _ _ L	_ _ _		L	L	L	

Redox potentials of compounds and complexes on platinum disk electrode in acetonitrile vs. saturated calomel electrode, calculated Gibbs energies of the electron transfer, and relative intensities of the fluorescence

^a XII, 9-aminomethylanthracene; XIII, thiourea; XIV, anthracene; XV, ferrocene.

cation in the first step [8]. The nature of the subsequent chemical steps was not examined.

Similar oxidation pattern was reported for chemosensors, 9,10-bis(1,3-dithiol-2-ylidine)-9,10-dihydroanthracene derivatives, in which the sulfur-containing ionophore was oxidized at about 0.35 V, and the oxidation peak of the anthracene moiety was observed at 1.62 V (vs. Ag/AgCl) [11].

The experimentally determined redox potentials were subsequently used for calculating ΔG_{el}^0 by the above equation. For **I**–**XII**, we observed a small PET effect compared to systems in which both electron donors and acceptors are aromatic [12]. There is no apparent correlation between the ease of the donor

oxidation and ΔG_{el}^0 . Generally, the free energy of the electron transfer is determined by the difference between the redox potentials of the donor and acceptor in the molecule and by their mutual electronic effects. It should be noted that the PET effect is the strongest for **VI**, and with this compound the increase in the relative fluorescence intensity in the presence of Hg²⁺ ions is the most pronounced (see table). The low absolute value of ΔG_{el}^0 for **IX** and **X** may be due to the presence of the electronegative chlorine atom decreasing the donor power of the receptor.

We found an empirical correlation between the free energies of electron transfer (electrochemical parameters) and relative fluorescence intensities (photophysical data). Theoretically, the stronger the PET effect, the more efficient should be the intramolecular fluorescence quenching and the lower should be the fluorescence intensity, which is reflected in Fig. 2. As seen, an exponential dependence is observed.

In the second part of our study, we examined the redox behavior of the compounds in acetonitrile solution on adding cations. We considered cations whose coordination caused the most significant changes in the relative fluorescence intensity (see I/I_0 values in the table).

The electrochemical pattern changed on adding H^+ , Zn^{2+} , Hg^{2+} , Cu^{2+} , and Co^{2+} ions (table, Fig. 1), owing to protonation or complexation. For the complexes, the peak potentials are given in the table for the anthryl fragment.

Upon protonation of the amino groups in **I**–**IV** and **XII**, only the oxidation peak of the anthryl fragment was observed at sweeping anodic potential within the working potential range; the parameters of this peak were not taken into account in the calculation of ΔG_{el}^0 . It is known that tetrasubstituted amines undergo electrooxidation at potentials higher than 2 V vs. saturated calomel electrode.

The table shows that in most cases, as expected, the photoinduced electron transfer becomes thermodynamically unfavorable in the presence of cations, except the complexes of **IX** and **X** with Cu^{2+} and Co^{2+} . Apparently, in these complexes the electron is transferred from the central metal atom to the fluorophore; such cases were described in the literature [12].

To interpret theoretically the effects of intramolecular electron transfer examined electrochemically, we analyzed in this study the orbital interactions in diamines **I–III** and compound **VI**. The efficiency of various intra- and intermolecular interactions is largely determined by the efficiency of orbital ionteractions in this molecular system and can be qualitatively estimated by molecular-orbital analysis.

The calculations showed that diamines **I–III** can exist in the form of various *cisoid* and *transoid* conformers differing in the energy by no more than 2 kcal mol⁻¹. The most stable complexes with metal cations, according to quantum-chemical calculations, are formed by the conformers shown in Fig. 3.

The efficiency of orbital interactions determining the transfer of the electron density from the donor (amino group) to acceptor (anthracene substituent) fragment is detfined by the width of the energy gap between the frontier orbitals of the fragment and by their overlap integral. According to the calculations,

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Fig. 1. Differential pulse voltammogram of oxidation–reduction of **II** in acetonitrile (*1*) in the absence and (*2*) in the presence of Zn^{2+} ions. Supporting electrolyte 0.1 M tetraethylammonium perchlorate. (*A* and *B*) are the signals oxidation of amino groups and anthryl fragment in **II**, respectively.



Fig. 2. Empirical correlation between the calculated free energies of intramolecular electron transfer and photophysical data (logarithms of relative fluorescence intensities) for **I–XII**.

the HOMOs of the donor fragment of the diamines are the orbitals of the lone electron pairs of the nitrogen centers, and LUMO of the acceptor fragment is the π orbital of the anthracene moiety. The shapes of the corresponding orbitals of diamine **I** are shown in Fig. 4a; similar topology of the frontier orbitals of the donor and acceptor fragments is characteristic of diamines **II** and **III**.



Fig. 3. Geometric characteristics of I-III and VI, according to ab initio RHF/6-31G** calculations (bond lengths in Å).

An NBO analysis [13] of the electronic structure of diamines **I**-**III** shows that the efficiency of donation of the electron density from the lone electron pairs of the nitrogen centers to the anthracene fragment is very low (the energies of the corresponding orbital interactions do not exceed 1 kcal mol⁻¹), which is confirmed by the experimental conclusion that the free energies of intramolecular electron transfer in these systems are low in absolute values. The low efficiency of the intramolecular donor-acceptor interaction is caused by the large energy gap between the HOMO level of the donor fragment and LUMO level of the acceptor fragment ($\Delta E_{\text{HOMO-LUMO}}$): According to RHF/6-31G** calculations, $\Delta E_{\text{HOMO-LUMO}}$ for diamines I-III is approximately the same, ~11.6 eV. More favorable orientation of the interacting orbitals in II provides increased overlap integral and higher efficiency of the

electron donation compared to I and III, which is confirmed by the experimental data (see table).

In the case of **VI**, HOMO of the donor fragment is the orbital of the lone electron pair of the S atom, and LUMO of the accceptor fragment, as in **I–III**, is the π orbital of the anthracene fragment (Fig. 4b). In **VI**, according to the calculations, the HOMO level of the donor fragment and the LUMO level of the acceptor fragment are appreciably closer ($\Delta E_{\text{HOMO-LUMO}} \sim 9.6 \text{ eV}$), which accounts for the experimentally observed increase in the absolute value of the free energy of the intramolecular electron transfer in **VI** (see table). Structure and some geometric parameters of **VI** are shown in Fig. 3.

Thus, we demonstrated the possibility of using voltammetric methods for evaluating the chemosensor



Fig. 4. Shapes of HOMO of the donor fragment and LUMO of the acceptor fragment in (a) I and (b) VI.

activity of anthryl-containing derivatives **I**–**XI**. Their electrochemical properties in acetonitrile were studied. From the potential difference for the first anodic and first cathodic redox transitions, associated with the relative arrangement and energies of the frontier orbitals, we calculated the free energy of the intramolecular electron transfer. We found that the compounds show a small PET effect (from -0.03 to -0.65 eV), which, however, allows them to be considered as promising chemosensors for H⁺, Zn²⁺, and Hg²⁺ ions. The experimental data were confirmed by quantum-chemical calculations.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrophotometer (mulls in mineral oil). The ¹H NMR spectra were taken on a Varian Unity-300 spectrometer (300 MHz), external reference TMS. The electronic absorption spectra were measured on a Specord M-40 spectrometer, and the fluoresence spectra, on a Hitachi-650-60 spectrofluorimeter in acetonitrile. The melting points were determined in glass capillaries with a PTP(M) device.

Cyclic and differential pulse voltammograms were recorded by standard procedures [14, 15] in acetonitrile containing $\leq 10^{-3}$ M water with a platinum disk electrode 2 mm in diameter, saturated calomel reference electrode, and platinum wire as auxiliary electrode; the supporting electrolyte was 0.1 M tetraethylammonium perchlorate. The concentrations of the compounds tested were 5×10^{-3} M, and those of the cations added, 5×10^{-2} M; electrochemical measurements were performed under Ar.

The voltammograms were taken on a PA-2 polarograph equipped with a two-coordinate recorder; the potential sweeping rate was 0.5 V s⁻¹ in cyclic voltammetry and 0.005 V s⁻¹ in differential pulse voltammetry, at a pulse amplitude of 12.5 mV.

Quantum-chemical calculations were performed by the ab initio RHF/6-31G** method [16] using the GAMESS program [17]. The geometries of the molecular structures were optimized to a gradient of 10^{-4} Hartree/Bohr; the stationary points were identified by calculating the force constant matrix.

N,N'-Bis(9-anthrylmethyl)alkanediamines II and III (general procedure). A 4.12-g portion of

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9-anthraldehyde was dissolved in 50 ml of ethanol, and 10 mmol of appropriate diamine and 0.5 ml of glacial acetic acid were added. The mixture was heated to reflux and cooled. The precipitate was filtered off, washed with hot ethanol, dried in air, and recrystallized from 1-butanol–DMF, 2:1. Bisazomethines were obtained in a quantitative yield.

A 1.9-g portion of finely divided NaBH₄ was added with stirring over a period of 2 h to a suspension of 5 mmol of azomethine in 100 ml of ethanol– DMF, 3 : 1, heated to $60-70^{\circ}$ C. The mixture was stirred at $60-70^{\circ}$ C for an additional 2 h, the solution was diluted with a twofold volume of water, and excess borohydride was decomposed with dilute CH₃COOH. The precipitate was filtered off, dried, and recrystallized from 1-butanol.

N,*N*'-**Bis**(9-anthrylmethyl)propane-1,3-diamine **II.** Yield 71%, mp 112–113°C (1-butanol). IR spectrum, ν, cm⁻¹: 1340, 1270. ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 1.78 t (2H, CH₂), 2.92 t (4H, 2CH₂), 4.61 s (2H, CH₂), 7.3–8.5 m (18H arom.). Found, %: C 87.1; H 6.8; N 6.1. $C_{33}H_{30}N_2$. Calculated, %: C 87.2; H 6.6; N 6.2.

N,*N*'-**Bis(9-anthrylmethyl)butane-1,4-diamine III.** Yield 85%, mp 120–121°C (1-butanol). IR spectrum, ν, cm⁻¹: 1480, 1335, 1220. ¹H NMR spectrum (CDCl₃), δ, ppm: 1.65 s [4H, (CH₂)₂], 2.9 s (4H, 2CH₂), 4.7 s (4H, 2CH₂), 7.3–8.6 m (18H arom.). Found, %: C 87.0; H 6.9; N 6.1. $C_{34}H_{32}N_2$. Calculated, %: C 87.1; H 6.9; N 6.0.

N-(9-Anthrylmethyl-*N*-R-*N*'-phenylthioureas VI and VII (general procedure). A 0.26-ml portion of phenyl isothiocyanate was added to a solution of 2 mmol of appropriate amine in 30 ml of benzene. The mixture was heated on a water bath for 2 h. The precipitate was filtered off, washed with petroleum ether, recrystallized from appropriate solvent, and dried in air.

N-(9-Anthrylmethyl)-*N*-benzyl-*N*'-phenylthiourea VI was prepared starting from *N*-(9-anthrylmethyl)-*N*-benzylamine [12] and phenyl isothiocyanate. Yield 85%, mp 181–182°C (1-butanol). IR spectrum, v, cm⁻¹: 3320, 1455, 1378, 1305. ¹H NMR spectrum (DMSO- d_6), δ, ppm: 4.56 s (2H, CH₂), 6.17 s (2H, CH₂), 6.88–8.6 m (19H arom.), 9.46 s (1H, NH). Found, %: C 80.5; H 5.7; N 6.5; S 7.3. C₂₉H₂₄N₂S. Calculated, %: C 80.5; H 5.6; N 6.5; S 7.4.

N-(9-Anthrylmethyl)-*N*-[2-(9-anthrylmethylamino)-ethyl]-*N*'-phenylthiourea VII was prepared starting from amine XII and phenyl isothiocyanate. Yield 87%, mp 202–203°C (1-butanol–DMF, 2 : 1). IR spectrum, v, cm⁻¹: 1607, 1475, 1315. ¹H NMR spectrum (DMSO- d_6), δ , ppm: 1.9–2.1 m (2H, CH₂), 3.41–3.55 m (2H, CH₂), 4.0 s (2H, CH₂), 6.28 s (2H, CH₂), 6.45–8.82 m (23H arom.). Found, %: C 81.3; H 5.7; N 7.3; S 5.7. C₃₉H₃₃N₃S. Calculated, %: C 81.3; H 5.8; N 7.3; S 5.6.

N-Allyl-*N*⁻(9-anthrylmethyl)-*N*⁻benzylthiourea VIII. A mixture of 0.6 g of *N*-(9-anthrylmethyl)-*N*benzylamine and 0.22 ml of allyl isothiocyanate in 10 ml of benzene was heated on a water bath for 2 h and then cooled. The precipitate was filtered off, washed with petroleum ether, and dried in air. Yield 67%, mp 140–141°C (1-butanol). IR spectrum, v, cm⁻¹: 3290, 1450, 1375. ¹H NMR spectrum (DMSOd₆), δ , ppm: 4.25–4.4 m (4H, 2CH₂), 4.83–5.05 d.d (2H, CH₂=), 5.55 t (1H, NH), 5.65–5.85 m (1H, CH=), 6.38 s (2H, CH₂), 6.75–8.5 m (14H arom.). Found, %: C 78.6; H 6.2; N 7.1; S 8.1. C₂₆H₂₄N₂S. Calculated, %: C 78.7; H 6.1; N 7.1; S 8.1.

N-(9-Anthrylmethyl)-*N*'-(4-chlorophenyl)urea IX. A 0.82-g portion of 9-aminomethylanthracene XII was dissolved in 20 ml of benzene, and 0.48 ml of phenyl isocyanate was added. The mixture was heated for 15 min; the precipitate was filtered off, washed with benzene, and dried in air. Yield 87%, mp >325°C (sublimes, 1-butanol–DMF). IR spectrum, v, cm⁻¹: 3300, 1627, 1555, 1464. ¹H NMR spectrum (DMSO- d_6), δ , ppm: 5.3 d (2H, CH₂), 6.52 t (1H, NH), 7.05–8.6 m (14H, arom. + NH). Found, %: C 73.1; H 4.7; Cl 9.7; N 7.8. C₂₂H₁₇ClN₂O. Calculated, %: C 73.2; H 4.8; Cl 9.8; N 7.8.

N-(9-Anthrylmethyl)-*N*-benzyl-*N*-(4-chlorophenyl)urea **X** was prepared starting from *N*-(9-anthrylmethyl)-*N*-benzylamine and phenyl isocyanate, as described above for the synthesis of **IX**. Yield 77%, mp 174–175°C (1-butanol). IR spectrum, v, cm⁻¹: 3287, 1625, 1460, 1367. ¹H NMR spectrum (DMSO d_6), δ , ppm: 4.24 s (2H, CH₂), 5.81 s (2H, CH₂), 6.33 s (1H, NH), 6.87–8.5 m (18H atom.). Found, %: C 77.2; H 5.1; Cl 7.7; N 6.2. C₂₉H₂₃ClN₂O. Calculated, %: C 77.2; H 5.1; Cl 7.9; N 6.2.

N-(9-Anthrylmethyl)-*N*'-benzoylthiourea XI. A 0.55-g portion of ammonium thiocyanate was dissolved in 15 ml of absolute acetonitrile, 0.56 ml of benzoyl chloride was added, and the mixture was heated to reflux and left for 10–15 min. After that, a solution of 0.83 g of amine XII in 5 ml of absolute CH₃CN was added; the mixture was stirred, heated to reflux, and left at room temperature for 30 min. The resulting mixture was poured into 50 ml of water; the precipitate was filtered off, washed with water, and dried in a vacuum desiccator over P₂O₅. Yield 74%, mp 186–187°C (1-butanol). IR spectrum, v, cm⁻¹:

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3200, 1650, 1385. ¹H NMR spectrum (DMSO-d₆), δ , ppm: 5.83 d (2H, CH₂), 7.28–8.57 m (14H arom.), 9.06 s (1H, NH), 10.83 s (1H, NH). Found, %: C 74.6; H 4.8; N 7.6; S 8.6. C₂₃H₁₈N₂OS. Calculated, %: C 74.6; H 4.9; N 7.6; S 8.6.

9-Aminomethylanthracene **XII** was prepared by the published procedure [18].

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