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Quantitative Relations Holding in Coordination of (Tetraphenylporphyrinato)zinc(II) and Nucleophilic Substitution with Anilines

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Abstract—Thermodynamic parameters ($\Delta G°$, $\Delta S°$) of quasi-isoenthalpic coordination of (tetraphenylporphyrinato)zinc(II) with anilines (except for 4-halo derivatives) in chloroform at 273–313 K in the absence of steric factors are linearly related to shifts of their absorption bands in the electronic spectra in reactions with anilines, as well as with logarithms of the stability constants of the complexes, pK_a values of the ligands in water, and Hammett substituent constants σ^+. Linear relations were also found between thermodynamic and kinetic parameters of some nucleophilic substitution reactions and complex formation of (tetraphenylporphyrinato)zinc(II) with anilines.

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The present article continues our studies on quantitative relations between the stability constants of complexes formed by (tetraphenylporphyrinato)zinc(II) (Zn-TPP) with various organic compounds, rate constant of nucleophilic substitution, and physicochemical parameters characterizing these processes. We previously showed [1–3] that shifts of absorption maxima ($\Delta\lambda$) in the electronic spectra of Zn-TPP in chloroform upon reaction with 3- and 4-substituted pyridines, as well as with pyridine, quinoline, and acridine *N*-oxides, are linearly related to logarithms of the stability constants (K) of the complexes, pK_a of ligands (L) in water and other solvents, and Hammett constants σ of substituent in the heteroring.

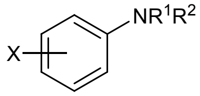
Using the extended Taft equation (1), modified by Litvinenko et al. [4] for amines, we succeeded [5] in obtaining correlation (2) between $\log K$ in benzene (determined by calorimetry), $\Sigma\sigma^*$, E_N, and $\log k$ for the reaction of phenacyl bromide with amines in benzene at 25°C.

$$\log k = \log k_0 + \rho^* \Sigma\sigma^* + \delta E_N, \qquad (1)$$

Here, k is the rate constant, the term $\rho^*\Sigma\sigma^*$ describes the inductive effect of all substituents on the nitrogen atom, and δE_N characterizes steric factor (δE_s in the Taft equation).

$$\log(K/k) = 2.77 + 2.73\,\Sigma\sigma^* - 0.94\,E_N;\ r = 0.983. \qquad (2)$$

The goal of the present work was to analyze kinetic and thermodynamic parameters of coordination of Zn-TPP with substituted anilines **Ia**–**Iv** in chloroform.



Ia–**Iv**

$R^1 = R^2 = H$, X = H (**a**), 3-Me (**b**), 4-Me (**c**), 4-Et (**d**), 3-MeO (**e**), 4-MeO (**f**), 4-H_2N (**g**), 3-O_2N (**h**), 4-F (**i**), 4-Cl (**j**), 4-Br (**k**), 4-I (**l**), 3-Cl (**m**), 2-Cl (**n**), 4-O_2N (**o**); $R^2 = X = H$, R^1 = Me (**p**), Et (**q**); Ph (**r**); $R^1 = R^2$ = Et, X = H (**s**); $R^1 = R^2$ = Me, X = H (**t**), 4-CHO (**u**), 4-EtOC(O) (**v**).

We found that shifts of the absorption maxima ($\Delta\lambda$) in the electronic spectra observed in reactions of Zn-TPP with anilines in chloroform are linearly related (r = 0.95–0.98) to logarithms of the stability constants of the complexes ($\Delta\lambda_{II} = 3.26\log K + 6.85$), p$K_a$ values of the ligands in water ($\Delta\lambda_{II} = 1.11\,pK_a + 9.15$), and Hammett constants σ of substituents in the benzene ring of anilines ($\Delta\lambda_{II} = 2.92\sigma + 14.12$) provided that steric factors are lacking (see table).

The experimental stability constants (K) of the Zn-TPP complexes with aniline derivatives in chloro-

Stability constants (K) and thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$) for the formation of molecular complexes of Zn-TPP with anilines in chloroform at 25°C, shifts of the absorption maxima of the *I*, *II*, and Soret bands ($\Delta\lambda$) in the spectra of Zn-TPP upon complex formation, substituent constants σ^+, and pK_a of anilines in water at 25°C

Ligand	K	σ^+ [6, 7]	pK_a, 25°C [8, 9]	$\Delta\lambda$, nm			$-\Delta H°$, kJ/mol	$\Delta S°$, J mol^{-1} K^{-1}	$-\Delta G°$,[d] kJ/mol
				I	*II*	Soret			
Ia	141±2	0	4.60	16.0	13.9	9.6	14.80±0.78	–8.27±2.35	12.26
Ib	174±3	–0.066[a] (–0.069)	4.72	17.0	14.5	10.0	14.82±0.1	–6.78±0.32	12.8
Ic	199±2	–0.311	5.07	16.8	14.8	10.2	15.06±0.5	–6.55±1.3	13.1
Id	161±8	–0.295	–	16.5	13.8	–	–	–	–
Ie	112±3	0.047[a] (0.115)	4.23	15.2	13.7	9.7	14.81±0.15	–10.63±0.66	11.64
If	343±3	–0.778	5.34	17.3	15.4	10.4	14.44±0.25	0.46±1.06	14.46
Ig	776±11	–1.3	6.16[b], 6.08[c]	18.6	15.8	11.2	14.75±0.15	5.86±0.27	16.51
Ih	49±1	0.674[a] (0.710)	2.46	14.9	12.0	–	14.87±0.19	–17.3±0.62	9.64
Ii	164±3	–0.073	4.65	17.2	14.4	9.4	13.47±0.05	–2.57±0.27	12.70
Ij	138±3	0.114	3.98	16.2	13.7	9.4	13.66±0.6	–4.68±2	12.20
Ik	109±3	0.150	3.88	16.0	13.5	8.9	15.62±0.15	–13.23±0.3	11.62
Il	124±4	0.135	3.79	14.8	13.0	8.8	14.24±0.6	–7.72±2	11.94
Im	72±2	0.399	3.52	15.4	13.1	9.0	14.59±0.1	–13.35±0.26	10.59
In	36±1	–	2.64	15.5	12.8	9.1	14.60±0.17	–19.51±0.5	8.87
Ip	103±2	–	4.85	15.7	13.3	–	14.81±0.27	–11.51±0.6	11.38
Iq	189±4	–	5.11	17.0	14.7	–	14.76±0.06	–5.69±0.04	12.98
It	20.4±0.8	–	5.06	15.0	12.2	10.2	14.78±0.48	–24.52±1.3	7.47
Iu	3.66±0.06	(0.22) CHO [8]	1.61[b]	11.3	7.9	7.9	12.30±1.23	–30.5±5	3.21
Iv	44.6±7	(0.45) COOEt	2.61 [10]	14.8	11.7	9.3	10.90±1	–5.0±2	9.4

[a] Substituent constant σ^+_{meta}; Hammett constants σ are given in parentheses.

[b] Ionic strength 0.10 (**Ig**) [11], 0.14 (**Iu**) [12].

[c] At 20°C [13].

[d] $\Delta G° = \Delta H° - T\Delta S°$.

form are concentration-dependent. On the other hand, taking into account low concentration of the initial compounds (2×10^{-5} M for Zn-TPP and 10^{-4} to 10^{-3} M for ligands, except for **In**, **It**, and **Iu**) and the absence of ionic species in solution, we presume that the experimental values insignificantly differ from the thermodynamic constants. We believe that the obtained stability constants of the Zn-TPP complexes with anilines (except for **Iu** and **Iv**) characterize 1 : 1 molecular *n*,*v*-complexes with a dative N–Zn bond. In particular, linear correlation between pK_a of the ligands in water and log$K$ in chloroform (see table), as well as the X-ray diffraction data [14] (CSD refcodes HAMLAI and JIVNIL), confirmed that protonation and coordination of ligands **Ia**–**It** with Zn-TPP involve the same center, i.e., nitrogen atom in the amino group.

In addition, crystalline 1 : 2 *n*,*v*-complexes of Zn-TPP with aniline and 2-methylaniline were reported [14] (HAMCIH, HAMMEN). As in the 1 : 1 adduct with isoquinoline *N*-oxide [3], the angle between the porphyrin macroring plane and aromatic ring in the ligand in the above complexes of both types is about 30°. However, in our case the formation of such adducts is hardly probable because of low concentration and weak nucleophilicity of anilines (even 1 : 1 complexes are very unstable). Furthermore, interaction of Zn-TPP with the second ligand molecule should return the zinc atom to the macroring cavity, so that the position and intensity of absorption bands in the electronic spectra of more symmetric 1 : 2 complexes should differ only slightly from the spectrum of Zn-TPP itself, and the stability constants of 1 : 1 complexes determined by electronic spectroscopy should not be affected. In fact, an isosbestic point was observed in the spectra upon gradual addition of a ligand to a solution of Zn-TPP ($c = 2\times10^{-5}$ M) until complete complexation, and the intensity of absorption bands belonging to the components occurring in equilibrium conformed to the Bouguer–Lambert–Beer law. The formation of crystalline 1:2 complexes is likely to be determined by the conditions of their isolation (slow evaporation in air of a solution containing metal porphyrin and aniline at a given ratio); in some cases, stable crystalline clathrates and solvates can be obtained in such a way.

We failed to determine K and $\Delta\lambda$ values for the complex with 4-nitroaniline (**Io**) due to its poor solubility in chloroform (calculation of the molar absorption coefficient of the complex required a higher concentration of **Io** to convert all metal porphyrin molecules in solution into molecular complex). Diphenylamine (**Ir**) (pK_a 0.78 [15]), like 2,6-dimethyl-4-nitropyridine *N*-oxide (pK_a –0.86 [5]) and 2,6-dichloropyridine (pK_a –2.57 [16]), even in a saturated solution did not produce appreciable variations in the electronic absorption spectra of Zn-TPP, in contrast to such even weaker bases as 4-nitro- (pK_a –1.7), 3-methyl-4-nitro- (pK_a –0.97), and 2-methyl-4-nitropyridine *N*-oxides (pK_a –0.967) [5]. This may be due to joint effect of electronic and especially steric factors which sharply reduce nucleophilicity of the nitrogen atom and hamper bond formation with the metal ion. Probably, weakly basic and weakly nucleophilic anilines like diphenylamine react with Zn-TPP in solution to give only n,π- and π,π-complexes whose electronic absorption spectra differ insignificantly from the spectra of the metal porphyrin; therefore, such complexes could not be detected by electronic spectroscopy.

Unlike pyridines and heteroaromatic *N*-oxides [1–3], the behavior of anilines upon complexation with Zn-TPP is described much better with the use of substituent constants σ^+ ($\log K = -0.57\sigma^+ + 2.13$; $r = 0.99$, $n = 11$) rather than Hammett constants σ ($r = 0.91$). It was specially noted [6] that the necessity of using constants σ^+ is determined by the presence of just vacant orbital rather than positive charge on the reaction center. We must emphasize that the residual positive charge on the zinc atom in Zn-TPP is too small to polarize aniline molecules to an appreciable extent via Coulomb forces.

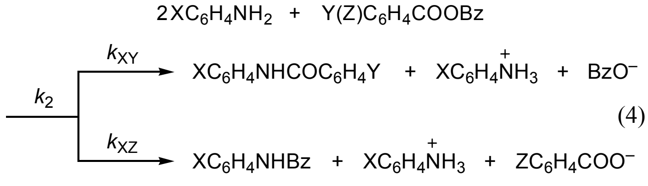
Exclusion of compounds **In**, **Ip**, **Iq**, **It** (steric factors), and **Il** (iodine atom very strongly differs from other substituents in polarizability) gives a good linear correlation between $\log K$ and $\Delta\lambda$ ($\log K = 0.307\Delta\lambda_I - 2.88$; $n = 13$, $r = 0.97$; $\log K = 0.27\Delta\lambda_{II} - 1.59$, $n = 13$, $r = 0.97$). Likewise, the complex formation is well described by the equation $\log K = 0.31\,\mathrm{p}K_a + 0.82$ ($n = 12$, $r = 0.97$) provided that N-substituted anilines **In**, **Ip**, **Iq**, and **It**–**Iv** are not taken into account.

The coordination process involving 2- or N-substituted anilines **In**, **Ip**, **Iq**, **Is**, and **It**, in which the substituent exerts steric shielding of the coordination center, cannot be described properly by the Hammett equation. In this case, steric constants should be used, e.g., as in modified Taft equation (1). The complexes formed by the above ligands with Zn-TPP (except for the most basic ligand **Iq**) are characterized by considerably lower stability constants as compared to aniline, whereas *N*,*N*-diethylaniline failed to bind all Zn-TPP molecules even at a ligand-to-Zn-TPP ratio of 150000:1; therefore, we were unable to determine the molar absorption coefficient ε and hence the K value for the complex.

Taking into account similarity in the structures of Zn-TPP complexes with anilines and transition states in nucleophilic substitution reactions [5] with the latter as nucleophiles, we made an attempt to reveal quantitative relations between the parameters characterizing these processes. It was found that the rate constants k for nucleophilic substitution by anilines in methanol–acetonitrile mixtures (50–100%) at 35°C [17] [Eq. (3)], rate constants k_2, k_{XY}, and k_{XZ} for the aminolysis of benzoic anhydrides in methanol at 25–45°C [18] [Eq. (4)], and rate constants for the reaction of *trans*-β-chlorovinyl 3-nitrophenyl ketone with anilines (X = 4-H_2N, 4-MeO, 4-Me, 4-Br, 3-Cl, 3-O_2N) in isopropyl alcohol at 25°C [19] are linearly related to the complex formation constants of anilines with Zn-TPP in chloroform at 25°C ($\log k = 2.69\log K - 6.29$; $r = 0.99$) and shifts of the absorption maxima ($\Delta\lambda$) of the metal porphyrin (Fig. 1).

$$\mathrm{XC_6H_4NH_2 + YC_6H_4CH_2OSO_2C_6H_4Z \longrightarrow XC_6H_4\overset{+}{N}H_2CH_2C_6H_4Y + ZC_6H_4SO_3^-} \quad (3)$$

X = H, Me, 4-MeO, 4-Cl, 3-O_2N; Y = H, 4-Cl;
Z = H, 4-Me, 4-Cl, 3-O_2N.



$$\mathrm{2XC_6H_4NH_2 + Y(Z)C_6H_4COOBz} \xrightarrow{k_2} \begin{cases} \xrightarrow{k_{XY}} \mathrm{XC_6H_4NHCOC_6H_4Y + XC_6H_4\overset{+}{N}H_3 + BzO^-} \\ \xrightarrow{k_{XZ}} \mathrm{XC_6H_4NHBz + XC_6H_4\overset{+}{N}H_3 + ZC_6H_4COO^-} \end{cases} \quad (4)$$

X = H, 4-MeO, 4-Me, 4-Br, 3-Cl; Y (Z) = H, 4-MeO,
4-Me, 3-Cl, 4-O_2N.

The experimental stability constants of the Zn-TPP complexes with anilines, determined at different temperatures (273–313 K), were used to calculate thermodynamic parameters of the complex formation process (see table). It should be noted that the $\Delta H°$ values for anilines **Ia**–**Ih**, **Im**, **In**, **Ip**, **Iq**, and **It** are fairly similar (–14.5 to –15 kJ/mol; ΔH°_{av} –14.76±0.14 kJ/mol; n = 12), i.e., the complexation of anilines with Zn-TPP is a quasi-isoenthalpic process (in the complexation with pyridines, ΔH° ranges from –8 to –25 kJ/mol and is linearly related to the ligand basicity [2]). Presumably, the reason is much weaker nucleophilicity (basicity) of anilines compared to pyridines.

In going from most basic *p*-phenylenediamine (**Ig**) to least basic 3-nitroaniline (**Ih**), the parameter ΔS° changes from positive (for anilines **Ia**–**Ih** and **Im** with primary amino group) to negative and shows a linear correlation with the substituent constants σ^+ ($\Delta S^\circ = -11.46\sigma^+ - 8.84$; $r = 0.995$, $n = 8$). For the anilines constituting a quasi-isoenthalpic series, including 2-chloroaniline, ΔS° is linearly related to log$K$ ($\Delta S^\circ = 19.35\log K - 49.9$; $r = 0.999$, $n = 12$). Thus, even though the possibility for coordination is enthalpy-controlled (major contribution to ΔG°), the selectivity of complex formation (i.e., the relation between K and aniline structure) is determined by variation of the entropy. In the coordination with pyridines, ΔS° is linearly related to the ligand basicity [2], but it varies over a broader range, from –27 to 54 J mol^{-1} K^{-1}.

The fact that ΔS° for coordination with primary anilines **Ia**–**Ih** and **Im** changes in parallel with electron-donor power of substituents in the benzene ring may be attributed to some extent (unlike pyridines) to gradual increase in the *p*-character of the lone electron pair on the nitrogen atom due to electron density transfer to the benzene ring ($sp^3 \rightarrow sp^2$ rehybridization). This should change steric environment of the reaction center (ligand molecule becomes more planar), while N→Zn dative bonding should require stronger structural rearrangement to ensure the reverse rehybridization ($sp^2 \rightarrow sp^3$). Analogous pattern was observed by us previously for the oxygen atom in heteroaromatic *N*-oxides upon formation of *n*,*v*-complexes with BF_3, $CuCl_2$, $ZnCl_2$, and Zn-TPP [3, 20, 21].

Analysis of the X-ray diffraction data [14] for anilines, their salts, and molecular complexes showed that the formation of a new bond involving LEP on the amino nitrogen atom is accompanied by extension of the C–N bond from 1.340–1.406 to 1.433–1.485 Å and that the bond angles α at the nitrogen atom correspond to sp^3 hybridization (~109°). The distances r_{C-N} and angles α and θ in free aniline ligands can be used to estimate the degree of sp^3 ($\alpha \approx 109^\circ$, $\theta = 20$–50°) and sp^2 hybridization ($\alpha = 120^\circ$, $\theta = 0^\circ$) of the nitrogen atom. For example, introduction of a nitro group into the benzene ring of 4-methylaniline (EDACUI, ISAYAC01) or of an acetyl group into 4-bromoaniline (PBRANL01, ICAMUU, ICANAB) [14] shortens the C–N bond and reduces the angle θ (α approaches 120°), indicating $sp^3 \rightarrow sp^2$ rehybridization of the nitrogen atom.

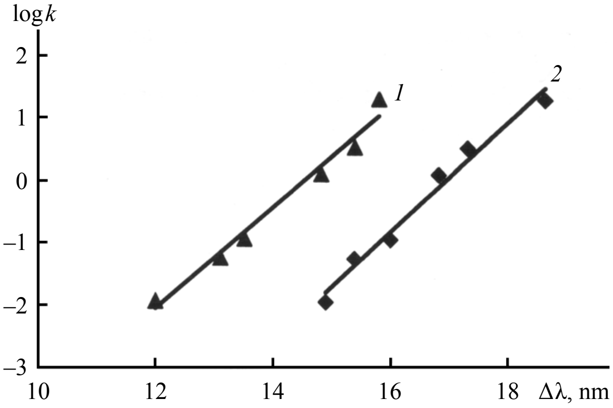


Fig. 1. Plots of log$k$ for the reaction of *trans*-β-chlorovinyl 3-nitrophenyl ketone ($3\text{-}O_2NC_6H_4COCH{=}CHCl$) with anilines **Ic**, **If**–**Ih**, **Ik**, and **Im** in isopropyl alcohol at 25°C [19] versus shifts of the absorption maxima of the (*1*) first ($\Delta\lambda_I$, $\log k = 0.82\Delta\lambda_I - 11.83$; $r = 0.99$) and (*2*) second bands ($\Delta\lambda_{II}$, $\log k = 0.89\Delta\lambda_{II} - 14.94$; $r = 0.99$) in the electronic spectrum of Zn-TPP upon complex formation with anilines in chloroform.

In molecules of anilines having alkyl groups or +*M*-substituents, the angle θ between the benzene ring plane and the amino group ranges from 22 to 49°, and it increases as the size of the neighboring substituents increases, reaching 89.74° in hexakis(dimethylamino)-benzene (GENFAG) [14]. By contrast, accumulation of –*M*-substituents in the benzene ring [NO_2, COOH, C≡CH, C≡N, CHO, C(O)R] reduces the angle θ to 0–10°, the molecule becomes more planar, and the nitrogen atom approaches sp^2 hybridization.

Thus, according to the X-ray diffraction data, hybridization of the amino nitrogen atom in anilines (sp^2 or sp^3) in crystal is determined by electronic properties of substituents in the benzene ring. Subsequently, we would like to demonstrate by complex formation of Zn-TPP with various ligands that the parameters operative in X-ray analysis are applicable to characterization of chemical and biochemical processes occurring in solution with participation of low-molecular compounds. For instance, X-ray diffraction data obtained for crystalline samples are widely used in the determination of native structures of high-molecular substances such as proteins [22].

Obviously, coordination of metal porphyrins with anilines having sp^2-nitrogen atom ($sp^2 \rightarrow sp^3$ rehybridization during complex formation) should be accompanied by electron density transfer from the benzene ring with charge localization on the nitrogen atom. As the degree of conjugation between the amino group and π-system of the aromatic ring decreases (electron-donor power of substituents increases), the entropy $\Delta S°$ for the complexation with Zn-TPP gradually becomes less and less negative, approaches zero for compound **If** (X = 4-OMe), and becomes positive for ligand **Ig** (X = 4-H_2N). In the latter case, the degree of electron density localization on the nitrogen atom is sufficient (for some reason) to make the initial state of the system more ordered than the final state. This may be due to solvation of the reactants.

Decrease of $\Delta S°$ in the series aniline > *N*-methylaniline > *N*,*N*-dimethylaniline from –8.27 to –24.52 J× mol^{-1} K^{-1} (sp^3-hybridization) is likely to result primarily from steric interactions, for the number of degrees of freedom of atoms adjacent to the amino group in the complex should decrease as the size of substituents on the nitrogen atom increases.

The alkyl groups in *N*,*N*-diethylaniline (**Is**, pK_a 6.56 [13]) are so bulky that the stability constant of its complex with Zn-TPP (we failed to determine its value) is much lower than for *p*-dimethylaminobenzaldehyde (K = 3.66) having an electron-withdrawing CH=O group (σ^- = +1.13, σ_p = +0.44 [6, 23]). Unfortunately, compound **It** is liquid under normal conditions, but the X-ray diffraction data showed that *N*,*N*-diethyl-3,4-dinitroaniline molecules in crystal exist as two conformers with *cis* and *trans* arrangement of methyl groups in the ethyl fragments relative to the aromatic ring plane, which hampers coordination of nitrogen to the zinc atom.

Unlike other anilines, the complexation with *p*-dimethylaminobenzaldehyde (**Iu**) is characterized by considerably lower $\Delta H°$ value (–12.3 KJ/mol) and very low value of $\Delta S°$ (–30.5 J mol^{-1} K^{-1}; see table). We believe that ligand **Iu** is coordinated with participation of a different donor center, carbonyl oxygen atom.

It is known that the LEP on the nitrogen atom directly linked to a strong –*M*-substituent is displaced toward the electronegative atom so considerably that dative bonds with Lewis acids involve just that atom [6]. We showed that 4-(4-dimethylaminostyryl)pyridine *N*-oxide reacts with HCl, BF_3, $CuCl_2$, $ZnCl_2$, and Zn-TPP in various organic solvents at the *N*-oxide oxygen atom rather than at the nitrogen atom in the dimethylamino group [3]. Nevertheless, first protonation of this compound occurs at the dimethylamino group [24, 25]. According to the X-ray diffraction data, *p*-dimethylaminobenzaldehyde hydrobromide (MABZAL10) is protonated at the amino group, whereas the reaction of **Iu** with a softer and bulkier Lewis acid, dichloro(diphenyl)tin (BUHKEU) [14] gives rise to *n*,*v*-dative bond with participation of the carbonyl oxygen atom.

Coordination through the carbonyl oxygen atom is indirectly supported by the facts that the stability constant of the complex with ethyl *p*-dimethylaminobenzoate (**Iv**) is twice as high as that found for *N*,*N*-dimethylaniline, though ethoxycarbonyl group is electron-withdrawing, and that the $\Delta H°$ value (–10.9 kJ× mol^{-1}) is even higher than $\Delta H°$ for *p*-dimethylaminobenzaldehyde (it differs from the average $\Delta H°$ values for other anilines coordinated to Zn-TPP at the amino nitrogen atom). The $\Delta S°$ value for ester **Iv** (–5.0 J × mol^{-1} K^{-1}) considerably differs from the corresponding value for *p*-dimethylaminobenzaldehyde, which may be due to replacement of the aldehyde hydrogen atom by +*M* ethoxy group. Dative bonds between the zinc atom in Zn-TPP and benzoic acid esters in crystal (SEMRAD, SEMREH, SEMRIL) [14] are formed through the carbonyl oxygen atom in the ligand.

As might be expected, the stability constants of the Zn-TPP complexes with anilines in chloroform increase as the temperature decreases. On the other hand, the data in Fig. 2 suggest that ΔG and the stability constants at 0 K should not depend on the ligand structure. The plots of ΔG versus substituent constants σ^+ at different temperatures (Fig. 3) cross each other at $\sigma^+ \approx -0.8$ ($\Delta H \approx -14.5$ KJ/mol), i.e., for the corresponding ligand $\Delta G_T = \Delta G° = \Delta H°$ ($\Delta S° = 0$), and variation of the Gibbs energy for the coordination process should not depend on the temperature. In fact, the ΔG value for 4-methoxyaniline ($\sigma^{+}_{\mathrm{OMe}} = -0.778$) changes very weakly with temperature.

Specific attention should be given to 4-haloanilines **Ii**–**Il**, for which $\Delta H°$ ranges from –13.47 to –15.62 kJ× mol^{-1}. Figure 4 shows that anilines **Ii**–**Il** do not fit $\Delta S°$—σ^+ and $\Delta G°$—σ^+ correlations found for other 4- and 3-substituted anilines with primary amino group. The temperature dependence of ΔG indicates that ΔG values and the stability constants become independent of the nature of 4-haloaniline at about 180 K rather than at 0 K.

At first glance, extrapolation of thermodynamic data obtained for a narrow temperature range for complexation in solution to a temperature beyond phase transition of the solvent may seem improper. However, we only emphasize very high accuracy of crossing of the straight lines at a single point (Fig. 2) near 0 K for most 3- and 4-substituted anilines and quite different temperature dependence of ΔG for 4-haloanilines.

Furthermore, the basicity of 4-haloanilines in water at 25°C decreases in the series F > Cl > Br > I (see table), while the stability constants of their complexes with Zn-TPP in chloroform at the same temperature show a somewhat different order, F > Cl > I > Br (in keeping with the substituent constants σ^+). Unlike C, N, and O atoms belonging to the second row of the Periodic Table, halogen atoms differ considerably in the size of their orbitals; therefore, specificities of static (electronic effects) and dynamic (e.g., solvation by aprotic solvents) polarization of molecules containing different halogen substituents cannot be interpreted in a simple fashion.

Unusual basicity series of 4-haloanilines in water (F > Cl > Br > I; i.e., fluorine atom appears to be the strongest electron donor) is explained by the fact that the +*M*-effect of halogen atoms (which is maximal for fluorine) is stronger than the –*I*-effect which changes in the opposite direction [26]. However, such interpretation cannot rationalize the observed variations of the stability constants and thermodynamic parameters. Presumably, the reason should be sought among specificities of dynamic polarization of the reactants [protonation of anilines in water (pK_a) and coordination of anilines to Zn-TPP in chloroform (log$K$)]. In terms of the Pearson hard and soft acids and bases principle, bromine atom is likely to be solvated best with chloroform (better than other halogens and amino group), which leads to additional displacement of electron density from the nitrogen atom to bromine and hence reduces nucleophilicity of the amino group as compared to 4-iodoaniline. An indirect support is that 4-bromoaniline molecule in crystal is characterized by the smallest angle between the benzene ring and amino group planes (CLANIC05, EJAYET, IDAHUR, PBRANL01) [14], i.e., it is the most planar. Therefore, 4-bromoaniline (minimal *K* value in the series of 4-haloanilines) requires the highest energy for complexation with Zn-TPP ($sp^2 \rightarrow sp^3$ rehybridization). Solvation of amino group in water is much stronger than solvation of halogen atom, and the basicity series in water differs from the series of the stability constants in chloroform. This problem will be the subject of our further studies.

We also compared thermodynamic parameters for the aminolysis of benzoic anhydrides in methanol and complexation of anilines with Zn-TPP in chloroform. The nucleophilic substitution process [k_2, k_{XY}, k_{XZ}; Eq. (4)] [18] is characterized by fairly low enthalpies of activation $\Delta H^{\neq}$ (21–63 kJ/mol) and high negative entropies of activation $\Delta S^{\neq}$ (–105 to –196 J mol^{-1} K^{-1}), which is consistent with published data for S_N2 reactions [6, 7, 27]. The parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ give rise to isokinetic relationship. Unlike the parameters characterizing coordination of anilines to Zn-TPP, the $\Delta H°$ value for the aminolysis is constant (–14.8 kJ/mol) and $\Delta S°$ is small in absolute value (6 to –17 J mol^{-1} K^{-1}); the reason is that S_N2 reactions involve more essential reorganization of electron shells of atoms in the substrate and nucleophile upon formation of transition state as compared to complex formation with Zn-TPP. High negative $\Delta S^{\neq}$ values are intrinsic to reactions in which the transition state is much more ordered and compact than the initial system. Therefore, a linear correlation exists between $\Delta G^{\neq}$ for the aminolysis of benzoic anhydrides in methanol and $\Delta G°$ for the com-

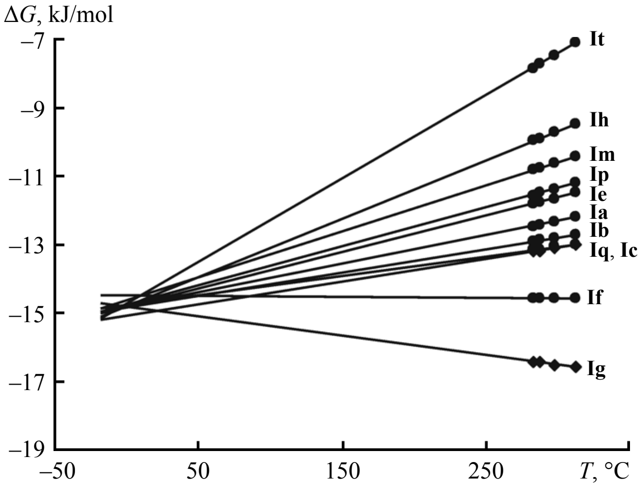


Fig. 2. Temperature dependences of ΔG for complex formation of Zn-TPP with anilines in chloroform.

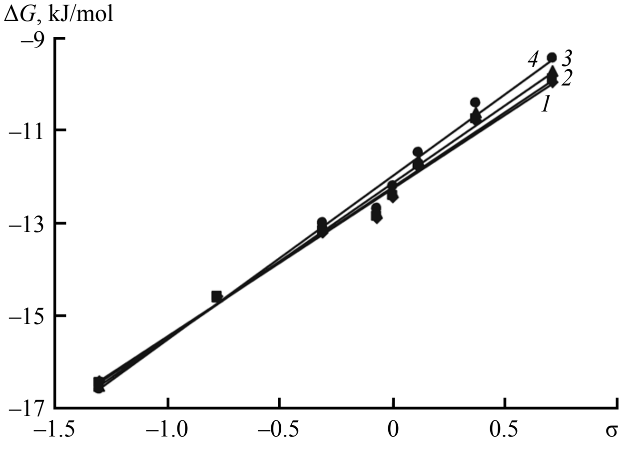


Fig. 3. Plots of ΔG for complex formation of Zn-TPP with anilines **Ia**–**Ic**, **Ie**–**Ih**, and **Im** versus substituent constants σ^+ at (*1*) 283, (*2*) 288, (*3*) 298, and (*4*) 313 K.

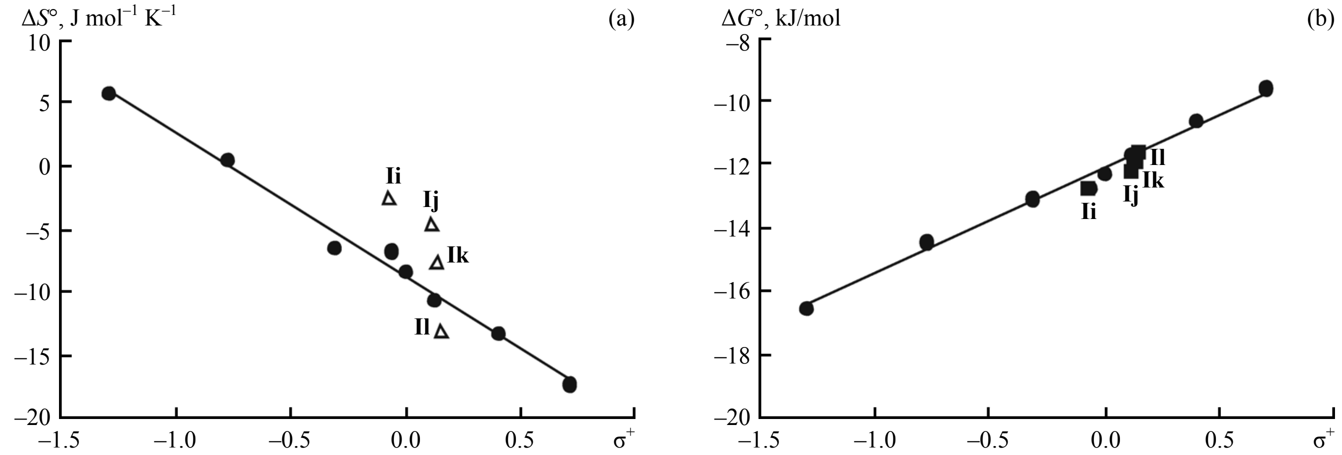


Fig. 4. Plots of (a) $\Delta S°$ ($\Delta S° = –11.46\sigma^+ – 8.84$; $r = 0.995$, $n = 8$) and (b) $\Delta G°$ ($\Delta G° = 3.36\sigma^+ – 12.11$; $r = 0.997$, $n = 8$) for complex formation of Zn-TPP with anilines **Ia**–**Ic**, **Ie**–**Ih**, and **Im** and 4-haloanilines **Ii**–**Il** in chloroform versus substituent constants σ^+.

plexation of anilines with Zn-TPP in chloroform, whereas $\Delta H^{\neq}$ ($\Delta S^{\neq}$) shows no correlation with $\Delta H°$ ($\Delta S°$). Nevertheless, the data on complex formation of anilines with Zn-TPP may be used to predict relative rate constants *k* and Gibbs energies of activation $\Delta G^{\neq}$ for nucleophilic substitution with participation of anilines.

We previously presumed [3] that the X-ray diffraction data for 1 : 1 complexes, namely the distances from the centroid of the Zn-TPP macroring to the zinc atom and from the latter to the ligand nitrogen atom, may be used as parameters characterizing nucleophilicity of the ligand. In fact, 3-nitroaniline forms a stronger complex with Zn-TPP than 2-chloroaniline (see table) and is characterized by longer distance r_1 and shorter distance r_2 [14]. We plan to examine the structure of Zn-TPP complexes with various ligands by X-ray diffraction with a view to check the above hypothesis for generality.

EXPERIMENTAL

Aniline and its derivatives were purified as described in [28]; their physical constants coincided with published data. The electronic absorption spectra were measured on an SF 2000-02 spectrophotometer. The stability constants of the complexes of Zn-TPP with anilines in chloroform were determined as reported in [1]. The thermodynamic parameters for the complex formation process were determined graphically with account taken of the first Ulich approximation [29]:

$$\ln K_T = –\Delta H^\circ_{298}/RT + \Delta S^\circ_{298}/R,$$

assuming that ΔH and ΔS remain constant in the examined temperature range (273–313 K).

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