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Nucleophilicity of *N*-Propargylanilines in the Coordination to Zinc Tetraphenylporphyrin in Chloroform

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Abstract—Thermodynamic parameters (ΔG^0 and ΔS^0) of the isoenthalpic (except for 4-halo derivatives) coordination of (tetraphenylporphyrinato)zinc(II) with anilines in chloroform at 273–313 K linearly correlate with the shift of their electronic absorption maxima in the reaction with anilines, as well as with the logarithms of the stability constants of the complexes, pK_a values of the ligands in water, and substituent constants σ^+. The 2 : 1 complex of (tetraphenylporphyrinato)zinc(II) with *p*-phenylenediamine was characterized by the X-ray diffraction data

Keywords: zinc tetraphenylporphyrin, *N*-propargylanilines, coordination, electronic spectroscopy, X-ray analysis

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It is currently a common practice to compare the behavior of pyridines and the corresponding oxidized derivatives (pyridine *N*-oxides) while studying coordination and nucleophilic substitution processes. However, the nature of “supernucleophilicity” of heteroaromatic *N*-oxides generally remains unclear [1].

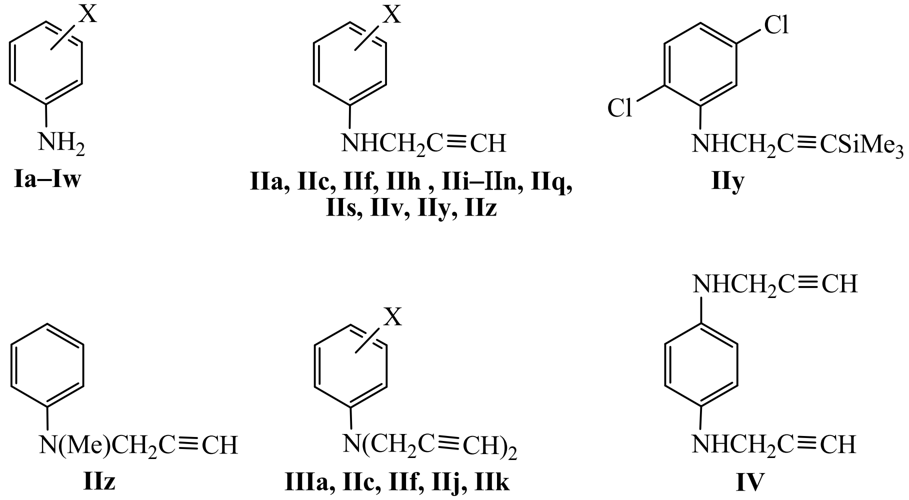
Our previous studies have shown [2, 3] that the thermodynamic parameters of coordination of pyridines and their *N*-oxides to (tetraphenylporphyrinato)-zinc(II) (Zn-TPP) in chloroform are substantially different. In the case of pyridines, the $\Delta H^0/\Delta S^0$ ratio is constant, whereas the ΔH^0 value is constant in the reactions with pyridine *N*-oxides. If the reason is that the formation of new *n*,*v*-dative bond with pyridine *N*-oxides is possible with participation of the oxygen *p* orbital [4], the thermodynamic parameters of the coordination and S_N reactions of anilines and pyridine *N*-oxides should be similar (unlike the nitrogen atom in pyridines, the nitrogen atom in amino group NR_2 and the oxygen atom in N→O group are capable of undergoing $sp^2\rightarrow sp^3$-rehybridization [5, 6]).

In fact, our studies on the coordination of Zn-TPP with ligands **Ia**–**In** revealed fairly similar values of ΔH^0 for primary 2-, 3-, and 4-substituted anilines [except for 4-haloanilines **Ii**–**Il**]: $\Delta H^0_{av} = -14.8\pm0.1$ kJ/mol, $n = 12$ [7]). Specific behavior of 4-haloanilines is well known [7]. For example, their basicity in water decreases in the series F > Cl > Br > I, whereas the stability constants of the corresponding complexes with Zn-TPP in chloroform [7] fit a different series: F > Cl > I > Br (in accordance with the substituent constants σ^+).

The basicity of 4-haloanilines in water is usually rationalized taking into account that in this series the +*M*-effect of the substituent (the highest value is observed for fluorine) prevails over the –*I* effect which changes in the opposite direction [8]. However, this explanation cannot be applied to the stability constants of the complexes (F > Cl > I > Br) and thermodynamic parameters determined by us. It should be noted that there are no such anomalies in the complexation of Zn-TPP with 4-halopyridine and quinoline *N*-oxides [2]: these ligands conform to the same relations as those found for other 3- and 4-substituted derivatives.

In order to get a deeper insight into the effect of substituents in aniline molecule on the coordination to Zn-TPP, in the present work we examined the complexation of the latter with *N*-mono- (**II**) and *N*,*N*-

Scheme 1.

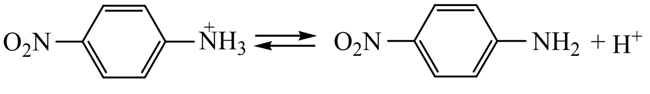


X = H (**a**), 3-Me (**b**), 2-Me (**c**), 4-Et (**d**), 3-MeO (**e**), 4-MeO (**f**), 4-NH_2 (**g**), 3-NO_2 (**h**), 4-F (**i**), 4-Cl (**j**), 4-Br (**k**), 4-I (**l**), 3-Cl (**m**), 2-Cl (**n**), 4-NO_2 (**o**); 3-F (**p**); 3-Br (**q**); 2-F (**r**); 2-Br (**s**); 2-I (**t**); 2,4-Cl_2 (**u**); 2,5-Cl_2 (**v**); 2,6-Cl_2 (**w**); 2-Me-4-Cl (**x**).

dipropargylanilines (**III**, **IV**) and extended the series of primary halo anilines (**Io**–**Ix**) (Scheme 1).

Like compounds **Ia**–**In**, shifts of the electronic absorption maxima ($\Delta\lambda$) of Zn-TPP in chloroform in the reactions with anilines **Io**–**Ix** were found to correlate linearly with the logarithms of the stability constants of the respective complexes, pK_a of the ligands in water, and substituent constants σ^+ for *meta* and *para* positions of the benzene ring (Table 1) [7]; the constant σ^-_{para} (+1.27) should be used for 4-nitroaniline.

It should be noted that constants σ^- were introduced to describe dissociation of phenols and anilinium ions [9] with *para* substituents possessing a large –*M* effect, i.e., to correlate the rate and equilibrium constants for reactions where the electron-withdrawing substituent is directly conjugated with the reaction center (furthermore, the degree of this conjugation should change in the course of the process). In the considered case (complex formation with anilines), zinc atom of Zn-TPP acts as acceptor, and constants σ^+ should be used for substituents with a large +*M* effect.



We believe that the stability constants of complexes formed by anilines **I**–**IV** with Zn-TPP correspond to the 1 : 1 *n*,ν-type molecular complexes with dative N→Zn bond. From the complex formation equilibrium (1), the slope of the straight line in the coordinates log{[Zn-TPPL$_n$]/[Zn-TPP]}—log[L] (where [Zn-TPPL$_n$], [Zn-TPP], and [L] are, respectively, the equilibrium concentrations of the complex, Zn-TPP, and ligand) is equal to the number (*n*) of ligand molecules involved in the coordination.

$$\text{Zn-TRR} + n\text{L} \rightleftarrows \text{Zn-TPP}\cdot\text{L}_n. \qquad (1)$$

The *n* value for the complexes with ligands **I**–**IV** is equal to unity. In addition, the linear relation between pK_a of anilines in water and log$K$ in chloroform (log$K$ = 0.34pK_a + 0.69; $n = 23$, $r = 0.96$ [7]; Table 1), as well as the X-ray diffraction data (CSD refcodes: HAMLAI, JIVNIL, HAMCIH, HAMMEN [16]), confirms that protonation and coordination of ligands **I** to metalloporphyrin involves the same center, nitrogen atom of the amino group.

Taking into account that ligand **Ig** was *a priori* expected to give rise to adducts with a somewhat different structure, we synthesized the 2 : 1 complex of Zn-TPP with *p*-phenylenediamine (**V**), and its structure was studied by X-ray analysis (Fig. 1, Table 2). In this complex, the ligand molecule is coordinated to two metalloporphyrin molecules; in addition, solvating chloroform molecule is present in the unit cell. Both zinc atoms deviate from the corresponding macrocycle planes by 0.300 Å, and the distances between the zinc atoms and nitrogen atoms of the ligand are equal to 2.266 Å. The macrocycles form dihedral angles of 24.54° with the benzene ring plane, and the amino groups of the ligand (∠HNH 107.7°) are antiparallel to

Table 1. Stability constants (*K*) of the molecular complexes of (tetraphenylporphyrinato)zinc(II) with anilines in chloroform at 25°C, shifts of the maxima of the *I*, *II*, and Soret bands (Δλ) in the electronic absorption spectra of (tetraphenylporphyrinato)zinc(II) upon complexation, substituent constants σ^+, and pK_a values of anilines in water at 25°C

Comp. no.	X	*K*, L/mo	σ^+ [9, 10]	pK_a [11–15]	Δλ, nm			$-\Delta H^0$, kJ/mol	ΔS^0, J mol^{-1} K^{-1}	$-\Delta G^{0,a}$, kJ/mol
					I	*II*	Soret			
Ii[b]	4-F	164±3	–0.073	4.65	17.2	14.4	9.4	13.47±0.05	–2.57±0.27	12.70
Ij[b]	4-Cl	138±3	0.114	3.98	16.2	13.7	9.4	13.66±0.6	–4.68±2	12.20
Ik[b]	4-Br	109±3	0.150	3.88	16.0	13.5	8.9	15.62±0.15	–13.23±0.3	11.62
Il[b]	4-I	124±4	0.135	3.79	14.8	13.0	8.8	14.24±0.6	–7.72±2	11.94
Im[b]	3-Cl	72±2	0.399	3.52	15.4	13.1	9.0	14.59±0.1	–13.35±0.26	10.59
In[b]	2-Cl	36±1	–	2.64	15.5	12.8	9.1	14.60±0.17	–19.51±0.5	8.87
Io	4-NO_2	12.4	1.27[c]	1.0	–	–	–	–	–	–
Ip	3-F	59±1	0.352	3.57	14.7	13.0	8.7	14.94±0.15	–16.1±0.6	10.1
Iq	3-Br	89±3	0.405	3.53	15.2	13.1	–	14.80±0.36	–12.0±0.7	11.12
Ir	2-F	41±1	–	3.20	16.0	13.5	9.3	15.02±0.3	–19.1±0.6	9.2
Is	2-Br	33.1±1.2	–	2.53	14.3	12.2	–	14.6±0.35	–20.1±1	8.66
It	2-I	31±1	–	2.55	16.3	14.0	8.9	14.67±0.69	–20.7±1.7	8.5
Iu	2,4-Cl_2	36±1	–	2.02	13.9	11.7	–	14.78±0.44	–20.0±0.7	8.82
Iv	2,5-Cl_2	29.8±1	–	1.53	13.8	11.4	–	14.4±0.41	–20.2±1.3	8.41
Iw	2,6-Cl_2	3.35±0.12	–	0.42	11.9	9.6	–	15.5±0.34	–40.4±1.3	2.99
Ix	2-Me-4-Cl	176±2	–	3.85	14.4	12.2	9.7	14.67±0.23	–5.89±0.4	12.80

[a] Calculated as $\Delta G^0 = -RT\ln K_{298}$. [b] The values of *K*, ΔH^0, and ΔS^0 were taken from [7]. [c] Substituent constant σ^-. Because of poor solubility of ligand **Io** in chloroform the Δλ value was not determined, and the *K* value was calculated by the approximate method [2]. Thermodynamic parameters were not calculated because of very weak temperature dependence of *K*.

each other, i.e., they appear in rigorously parallel planes at the opposite sides of the benzene ring of *p*-phenylenediamine. The porphyrin rings are coplanar to each other, and the distances between their planes and between the zinc atoms are 4.041 and 6.949 Å, respectively.

If a substituent at the nitrogen atom strongly affects steric environment of the ligand reaction center, the coordination process in solution cannot be described properly by Hammett type equations; in this case, steric constants should be used (e.g., modified Taft equation). Because of steric hindrances, *N*,*N*-diethylaniline even at a Zn-TPP-to-ligand concentration ratio of 1 : 150000 did not ensure complete binding of Zn-TPP, and we were unable to determine the molar absorption coefficient (ε) of the complex and hence the *K* value. Therefore, the stability constant (*K* = 2.5) of the complex of Zn-TPP with *N*,*N*-diethylaniline, as well as with 4-nitroaniline, was determined by the approximate method [2].

The thermodynamic parameters of complex formation were determined from the experimental stability constants of the Zn-TPP complexes with anilines at different temperatures (273–313 K; Table 1). Attention should be given to fairly similar values of ΔH^0 [except for 4-haloanilines **Ii**–**Il** and 2,6-dichloroaniline (**IIw**)], $\Delta H^0_{av} = -14.7\pm0.1$ kJ/mol (*n* = 20; cf. [7]), i.e., coordination of these 20 anilines (including 3- and 2-halo derivatives) with Zn-TPP is an isoenthalpic process.

Analogous pattern (with some peculiarities) was observed previously [17, 18] for the complexation of Zn-TPP with heteroaromatic *N*-oxides, such as pyridine *N*-oxides containing substituents in positions

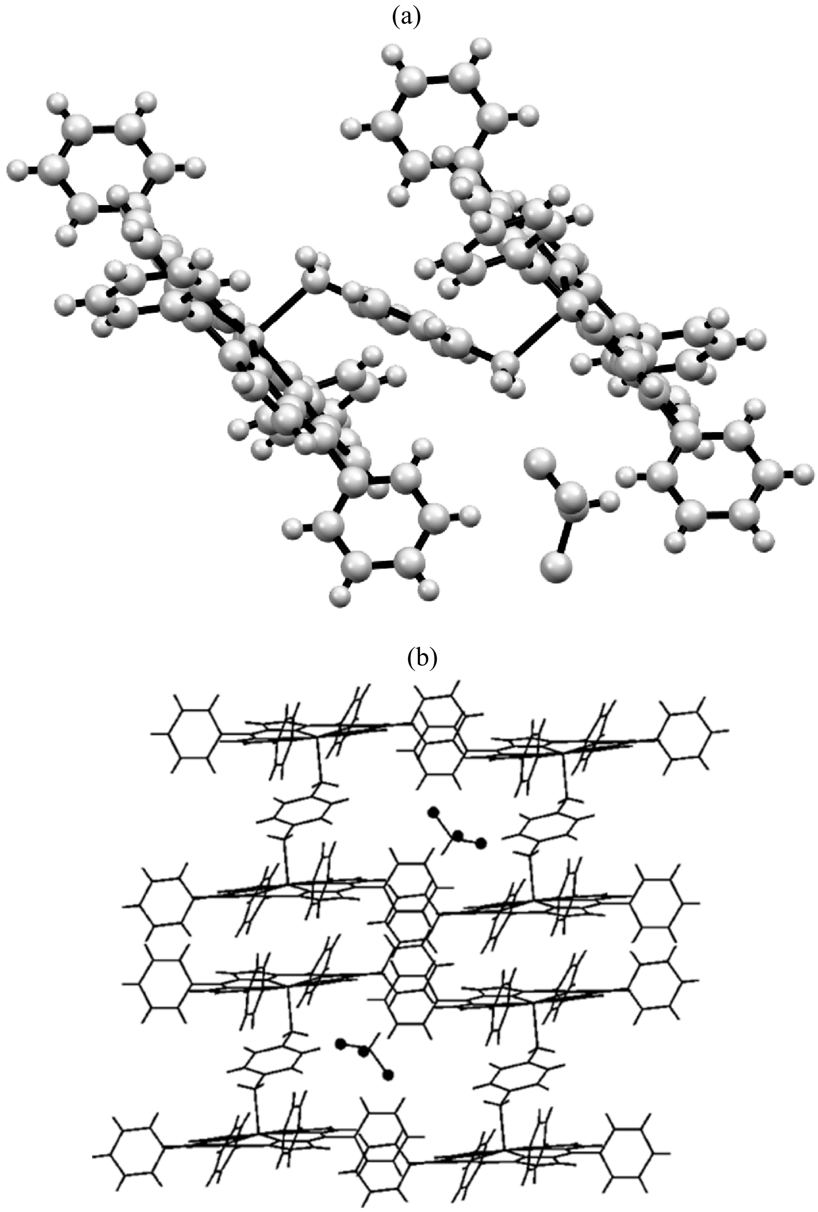


Fig. 1. (a) Structure of the molecule and (b) crystal packing of complex **V** formed by Zn-TPP with *p*-phenylenediamine (2 : 1) according to the X-ray diffraction. The crystal structure includes solvation chloroform molecules.

3 and 4 and styryl substituents in position 2,4-substituted quinoline *N*-oxides ($\Delta H^0_{\text{av}} = -13.8\pm0.2$ kJ/mol), and 2-methylpyridine, 2-methylquinoline, and 2-styrylquinoline *N*-oxides ($\Delta H^0_{\text{av}} = -12.0\pm0.2$ kJ/mol). Unlike the above ligands, pyridines conformed to a linear relation between ΔH^0 and ligand basicity, and the $\Delta H/\Delta S$ ratio was constant.

In the series of 3- and 4-substituted anilines with primary amino group [7], the ΔS^0 value changes from positive (5.86 J mol^{-1} K^{-1} for most basic *p*-phenylenediamine, pK_a 6.08) to negative (–17.3 J mol^{-1} K^{-1} for least basic 3-nitroaniline, pK_a 2.46). In the series of 2-haloanilines **In** and **Ir**–**Iw**, the ΔS^0 value changes even more strongly (Table 1), from –19.5 for 2-chloroaniline to –40.4 J mol^{-1} K^{-1} for 2,6-dichloroaniline. Presumably, this is related not only to increased steric hindrances to coordination but also to electron-withdrawing properties of substituents. The ΔS^0 value for 4-chloro-2-methylaniline (**Ix**), –5.9 J mol^{-1} K^{-1}, is higher than that for 2-chloroaniline and comparable with the ΔS^0 value for 4-chloroaniline (–4.7 J mol^{-1} K^{-1}).

Insofar as 4-chloro-2-methylaniline (**Ix**) differs from 2,4-dichloroaniline (**Iu**) by the presence of a larger (than chlorine atom) methyl group, the factor responsible for the higher ΔS^0 value is likely to be electron-donor properties of methyl group.

Anilines constituting the isoenthalpic series, including *ortho*-substituted ligands, are characterized by ΔS^0 values linearly related to $\log K$ ($\Delta S^0 = 19.5\log K - 50.1$; $r = 0.998$; $n = 21$). Thus, despite the fact that the mere possibility of coordination is enthalpy controlled (major contribution to ΔG^0), the selectivity of the complex formation, i.e., the dependence of the relative K value on the aniline structure, is determined by change of the entropy. The ΔS^0 values for the complexation of pyridines as well as pyridine and quinoline *N*-oxides [18] are linearly related to the ligand basicity and take considerably higher positive values (–27 to 54 and –5.7 to 25 J mol^{-1} K^{-1}, respectively). This may be due to greater steric hindrances to coordination with anilines where the amino nitrogen atom bears two hydrogen atoms.

Decrease of ΔS^0 for coordination with primary anilines **Ia**–**Ix** as the electron-donor power of the substituent in the benzene ring decreases (increase of electron-acceptor properties) may be related to some extent (in contrast to pyridines) to gradual increase in the *p*-character of the nitrogen lone electron pair orbital as a result of electron density displacement toward the benzene ring ($sp^3 \rightarrow sp^2$ rehybridization). This should be accompanied by change of the steric environment of the reaction center (the ligand molecule becomes more planar), and the formation of N→Zn dative bond requires greater structural reorganization to ensure the reverse process, $sp^2 \rightarrow sp^3$ rehybridization. Analysis of the Cambridge Structural Database (CSD) showed that the hybridization of the amino nitrogen atom in anilines in crystal depends on the electronic properties of substituents in the benzene ring: electron-withdrawing substituents favor sp^2 hybridization, and electron-donating, sp^3 [6].

Particular attention should be given to the behavior of 4-haloanilines **Ii**–**Il**; in the complexation of Zn-TPP with 4-haloanilines **Ii**–**Il** the ΔH^0 value varies from –13.47 to –15.62 kJ/mol. Figure 2 shows that ligands **Ii**–**Il** do not fit the relations between ΔS^0, on the one hand, and substituent constants σ^+ and $\log K$ (ΔG^0), on the other, which are observed for the other primary anilines. Interestingly, the points for 3-haloanilines **Im**, **Ip**, and **Iq**, also deviate, though to a lesser extent, from the straight line $\Delta S^0 = -11.56\sigma^+ - 9.15$, whereas ΔH^0 remains almost constant. However, the behavior of 2-haloanilines **In** and **Ir**–**It** conforms well to the linear relation ΔS^0—$\log K$.

Table 2. Bond lengths (*d*) and bond angles (ω) in the molecule of 2 : 1 Zn-TPP complex with *p*-phenylenediamine (**V**)

Bond	*d*, Å	Angle	ω, deg
Zn^1–N^1	2.050(7)	$N^{1B}C^{1B}C^{2B}$	116.8(4)
Zn^1–N^2	2.066 (6)	$N^{1B}C^{1B}C^{3B}$	118.2(4)
Zn^1–N^3	2.053 (7)	$N^{1B}Zn^1N^1$	97.6(2)
Zn^1–N^4	2.050 (6)	$N^{1B}Zn^1N^2$	97.2(2)
Zn^1–N^{1B}	2.266 (3)	$N^{1B}Zn^1N^3$	95.3(2)
N^{1B}–C^{1B}	1.430 (6)	$N^{1B}Zn^1N^4$	97.8(2)
		$H^{1B1}N^{1B}H^{1B2}$	107.7(4)

It should be emphasized that, in accordance with Fig. 3, the relation ΔS^0—$\log K$ (ΔG^0) is general for the coordination of all primary anilines (except for 4-halo derivatives **Ii**–**Il**), including those containing a substituent in the *ortho* position of the benzene ring (2-F, 2-Cl, 2-Br, 2-I, 2,4-Cl_2, 2,5-Cl_2, 2,6-Cl_2) or at the amino nitrogen atom (NMe, NEt, NMe_2).

We also tried to elucidate how introduction of acetylenic substituents (propargyl groups) into the amino group will affect the complexation of anilines with Zn-TPP. *N*-Mono- and *N*,*N*-dipropargylanilines **II**–**IV** were synthesized via reaction of the corresponding anilines with propargyl bromide according to the procedure described in [19, 20]. 4-Fluoro- and 4-iodo-*N*-propargylanilines **IIi** and **IIl** were synthesized by us for the first time, and their purity was confirmed by TLC, HPLC, and elemental analysis. IR spectra of **IIi** and **IIl** contained absorption bands assigned to stretching vibrations of triple C≡C bond (2103–2115 cm^{-1}) and the acetylenic ≡C–H bond (3279–3310 cm^{-1}). Anilines **IIi** and **IIl** contained a doublet at δ 3.9 ppm (2H) assigned to the NCH_2 methylene protons and a triplet at δ 2.2 ppm (1H) corresponding to the terminal acetylenic proton in ^{1}H NMR spectra.

We found that there are linear relations between the logarithms of the stability constants ($\log K$) of Zn-TPP complexes with *N*-propargylanilines **II** (Table 3) and other parameters characterizing the coordination process (Fig. 3); i.e., introduction of a $CH_2C{\equiv}CH$ group into the amino group is accompanied by

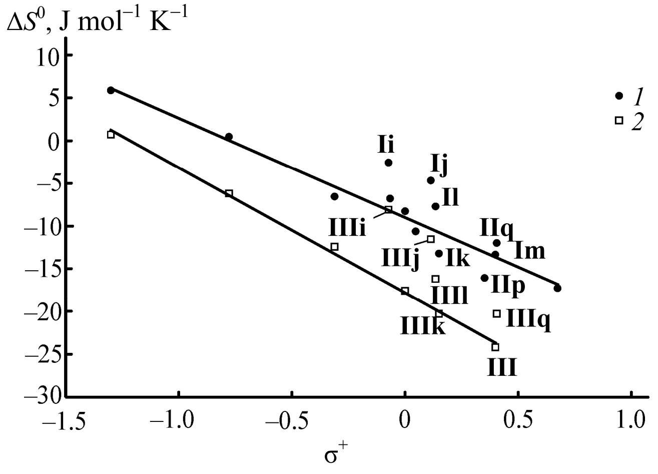


Fig. 2. Plots of ΔS^0 for the complex formation of (*1*) primary anilines **I** and (*2*) *N*-propargylanilines **II** with (tetraphenylporphyrinato)zinc(II) vs. substituent constants σ^+ in chloroform at 25°C.

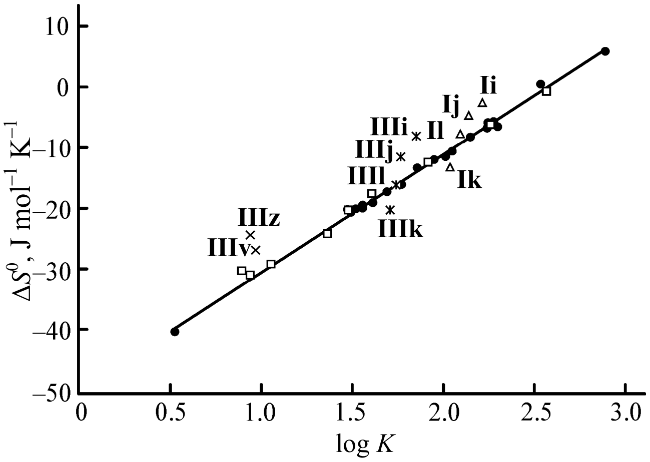


Fig. 3. Plots of ΔS^0 for the complex formation of anilines **I** and **II** with Zn-TPP versus log*K* in chloroform at 25°C.

proportional change of log*K*, including log*K* of 4-halo derivatives.

$$\log K = 1.20 \log K_{\text{II}} - 0.858;\ n = 10,\ r = 0.985;$$

$$\Delta S^0 = 1.12\Delta S^0_{\text{II}} - 6.71;\ n = 10,\ r = 0.98;$$

$$\Delta\lambda^{\text{II}} = 1.115\ \Delta\ \lambda^{\text{II}}_{\text{II}} + 1.006;\ n = 10,\ r = 0.97.$$

Noteworthily, unlike general linear dependence ΔS^0—log*K* covering most ligands **I** and **II** (Fig. 3), the complexation with Zn-TPP in the coordinates ΔS^0—σ^+ is described by two straight lines from which not only 4- but also 3-halo derivatives deviate (Fig. 2). The data for 2,5-dichloro-*N*-propargyl- and *N*-methyl-*N*-propergylanilines **IIz** and **IIv** do not fit the above relations because of very strong steric shielding of the nitrogen atom.

The complexation of Zn-TPP with monoacetylenic secondary anilines **II** (except for 4-halo derivatives) and *N*,*N*′-dipropargyl-*p*-phenylenediamine is an isoenthalpic process (ΔH^0_{av} = –14.6 kJ/mol). The ΔH^0_{av} value for anilines having no propargyl substituent on the nitrogen atom is equal to –14.7 kJ/mol; i.e., introduction of one propargyl group, as well as of methyl group (ΔH^0 = –14.8 kJ/mol for *N*-methylaniline) almost does not affect variation of the enthalpy. The low stability [7] of the complex of Zn-TPP with *N*-propargylaniline compared to *N*-methylaniline (*K* = 40.5 and 103 L/mol, respectively) is determined by electron-withdrawing properties of the triple bond, which is reflected in the ΔS^0 values (–17.6 and –11.5 J mol^{-1} K^{-1}, respectively).

Due to very strong steric effect, the ΔH^0 values for *N*-methyl-*N*-propargyl- and *N*,*N*-dipropargylanilines are considerably higher (–12.7 and –13.0 kJ/mol, respectively), whereas introduction of the second chlorine atom into the 5-position of 2-chloro-*N*-propargylaniline (ΔH^0 = –14.7 kJ/mol; the same value was found for 2-chloro- and 2,4- and 2,5-dichloroanilines) induces slightly smaller variation of ΔH^0 (–13.6 kJ/mol). As might be expected, the coordination of *N*,*N*′-dipropargyl-*p*-phenylenediamine and *N*-propargylaniline to Zn-TPP is characterized by the same ΔH^0 value, but the stability constant of the complex formed from the former is slightly higher.

The stability of the Zn-TPP complexes with anilines expectedly decreases upon introduction of one and then two propargyl groups into the amino group. If there are two *N*-propargyl substituents in molecules of 4-haloanilines, the latter lose their unique thermodynamic (ΔH^0 for 4-chloro- and 4-bromo-*N*,*N*-dipropargylanilines becomes equal to that found for other anilines **I** and **II**; Tables 3, 4) and kinetic properties ($K_{4\text{-Br}} > K_{4\text{-Cl}}$). Moreover, unlike *N*-propargyl- and *N*-unsubstituted 4-haloanilines, *N*,*N*-dipropargylanilines fit the general relation $\Delta S^0 = 18.7\log K - 48.2$; $n = 34$, $r = 0.995$ (ligands **Ia**–**Ic**, **Ie**–**Ih**, **Im**, **In**, **Ip**–**Ix**; **IIa**, **IIc**, **IIf**, **IIg**, **IIm**, **IIn**, **IIq**, **IIs**, **IIv**, **IIy**; **IIIa**, **IIIc**, **IIIf**, **IIIj**, **IIIk**; **IV**). Here, an important factor is variation of ΔS^0: introduction of one *N*-propargyl group into the molecules of 4-chloro- and 4-bromoanilines and of two *N*-propargyl groups into the molecule of the latter reduces the ΔS^0 value by

Table 3. Stability constants (*K*) of the complexes of (tetraphenylporphyrinato)zinc(II) with *N*-propargylanilines in chloroform at 25°C, shifts of the maxima of the *I*, *II*, and Soret bands (Δλ) in the electronic absorption spectra of (tetraphenylporphyrinato)zinc(II) upon complexation, and substituent constants σ^+

X	*K*, L/mol	σ^+ [20, 21]	Δλ, nm			$-\Delta H^0$, kJ/mol	ΔS^0, J mol^{-1} K^{-1}
			I	*II*	Soret		
4-NH_2	369±12	–1.3	15.6	13.1	–	14.86±0.41	0.71±1
4-OMe	182±3	–0.778	15.0	12.7	–	14.75±0.3	–6.2±0.8
4-Me	82.5±1.7	–0.311	14.7	12.4	–	14.67±0.26	–12.43±0.5
H	40.5±1.5	0	13.0	12.1	7.9	14.52±0.29	–17.6±1
3-Cl	23.1±0.3	0.399	12.4	10.7	6.9	15.01±0.5	–24.2±1.7
3-Br	30±1	0.405	13.1	10.9	–	14.56±0.34	–20.3±1.2
2-Cl	11.3±0.2	–	13.4	10.5	–	14.74±0.22	–29.2±0.7
2-Br	7.8±0.4	–	13.2	10.3	–	14.2±0.56	–30.3±2.4
4-F	71±2	–0.073	13.3	11.7	–	12.96±0.35	–8.1±0.7
4-Cl	58.3±0.5	0.114	12.9	11.4	7.8	13.54±0.11	–11.54±0.6
4-Br	51±1	0.150	13.8	11.3	7.4	15.72±0.29	–20.3±1.2
4-I	55±1	0.135	12.8	11.4	–	14.74±0.5	–16.2±1.3
2,5-Cl_2	9.3±0.2	–	11.8	9.3	–	13.58±0.35	–26.9±1.6
IIy	8.7 ± 0.3	–	11.3	9.4	–	14.72±0.27	–31±1
IIz	8.7±0.2	–	9.8	8.9	–	12.66±0.17	–24.4±0.9
IV	44.5±1	–	13.9	12.4	–	14.6±0.35	–17.3±1.5

half, whereas in going from 4-chloro- *N*-propargylaniline (**IIj**) to *N*,*N*-dipropargyl derivative **IIIj** the ΔS^0 value decreases fivefold. Furthermore, introduction of one *N*-propargyl group does not change ΔH^0, whereas introduction of the second *N*-propargyl substituent reduces ΔH^0 for the 4-chloro derivative and increases ΔH^0 for the 4-bromo analog.

In summary, we have revealed isoenthalpic coordination of (tetraphenylporphyrinato)zinc(II) with *N*-unsubstituted and *N*-mono- and *N*,*N*-dipropargyl-substituted anilines both within each series and for all series on the whole. A probable reason is solvation. For example, *p*-anisidine is a stronger base and is better solvated than aniline, so that it should form a stronger coordination bond with zinc (gain in ΔH); however, its desolvation should lead to loss in ΔH but gain in ΔS. In our further studies we plan to elucidate factors responsible for isoenthalpic coordination and specific thermodynamic behavior of anilines containing halogen atoms in the *para* position of the benzene ring.

EXPERIMENTAL

Aniline and its acetylenic derivatives were purified as described in [13]; their physical constants coincided with reference data. The electronic absorption spectra were recorded with the SF 2000-02 spectrophotometer. The stability constants of the complexes of Zn-TPP with anilines in chloroform were determined according to the procedure reported in [7]. The IR spectra were measured in the range from 4000 to 600 cm^{-1} using the Shimadzu IR Prestige-21 and Perkin Elmer Paragon 1000 FTIR instruments. The ^{1}H NMR spectra of the solutions in $CDCl_3$ were recorded at room temperature using the Bruker WM 400 spectrometer with TMS as internal reference. The high-resolution mass spectra (electrospray ionization) were obtained with the Bruker micrOTOF 10223 mass spectrometer.

The thermodynamic parameters for the complex formation were determined graphically using Eq. (2) (first Ulich's approximation) [21] on the assumption

Table 4. Stability constants (K) of the molecular complexes of (tetraphenylporphyrinato)zinc(II) with *N*,*N*-dipropargylanilines in chloroform at 25°C, shifts of the maxima of the *I*, *II*, and Soret bands ($\Delta\lambda$) in the electronic absorption spectra of (tetraphenylporphyrinato)zinc(II) upon complexation, and substituent constants σ^+

Comp. no.	X	K, L/mol	σ^+ [20, 21]	$-\Delta H^0$, kJ/mol	ΔS^0, J mol^{-1} K^{-1}
IIIa	H	4.58±0.25	0.000	12.98±0.46	–30.7±2.1
IIIc	4-Me	6.5±0.6	–0.311	14.65±0.54	–33.6±2.5
IIIf	4-OMe	11.3±0.45	–0.778	14.38±0.44	–26±2
IIIj	4-Cl	0.42±0.04	0.114	15.04±0.44	–57.0±3
IIIk	4-Br	2.46±0.06	0.150	14.79±0.41	–42.3±2

Table 5. Crystallographic parameters of 2:1 Zn-TPP complex with *p*-phenylenediamine (**V**)

Parameter	Value
Formula	$C_{94}H_{64}N_{10}Zn_2 \cdot 2CHCl_3$
Molecular weight	1703.07
Crystal dimensions, mm	0.1 × 0.05 × 0.05
Temperature, K	296
Crystal system	Triclinic
Space group	*P*-1
a, Å	11.0736(2)
b, Å	12.8474(3)
c, Å	15.3130(4)
α, deg	78.459(2)
β, deg	77.381(2)
γ, deg	77.467(2)
V, Å^3	2048.43
Z	1
d_{calc}, g/cm^3	1.381
μ	2.950
θ, deg	3.0–65.4
h, k, l	–13.10, –15.15, –17.14
Total number of reflections	7171
Number of independent reflections	6551
Number of reflections with [$I > 2\sigma(I)$]	3699
Number of variables	421
$R(F^2)$	0.10
$R_w(F^2)$	0.27
Goodness of fit	1.128
$\Delta\rho_{max}/\Delta\rho_{min}$, $\bar{e}$/Å^3	1.67/–1.17

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

$$\ln K_T = -\Delta H^0_{298}/RT + \Delta S^0_{298}/R. \quad (2)$$

4-Fluoro-*N*-(prop-2-yn-1-yl)aniline (IIi). A solution of 8 g (5 mL) of propargyl bromide in 5 mL of methanol was added dropwise under vigorous stirring to a mixture of 11.7 g (10 mL, 0.1 mol) of 4-fluoroaniline in 50 mL of methanol and 10.9 g (0.133 mol) of calcined sodium acetate, and the mixture was left to stand for 4 days at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in water, the product was extracted into benzene, the solvent was removed, and the residue was distilled under reduced pressure. Yield 79%, bp 74–76°C (1 mm). IR spectrum (film), ν, cm^{-1}: 3402 s, 3294 v.s, 3061 m, 3041 m, 2840 m.br, 2114 w, 1854 m, 1613 s, 1500 v.s, 1437 m, 1349 s, 1212 v.s, 1158 m, 1109 m, 1078 m, 1009 m, 981 m, 943 m, 909 s, 823 v.s, 778 w, 654 s. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 2.25 t (1H, C≡CH, J = 2.4 Hz), 3.74 br.s (1H, NH), 3.93 d (2H, $CH_2C{\equiv}C$, J = 2.3 Hz), 6.63–6.69 m and 6.94–6.98 m (2H each, C_6H_4). Mass spectrum: m/z 150.0721 $[M + H]^+$. Found, %: C 72.57; H 5.28; N 9.27. C_9H_8NF. Calculated, %: C 72.41; H 5.36; N 9.39.

4-Iodo-*N*-(prop-2-yn-1-yl)aniline (IIl). Propargyl bromide, 1.2 g (0.8 mL, 0.01 mol), was added dropwise to a solution of 3 g (0.0137 mol) of 4-iodoaniline in 5 mL of methanol, and the mixture was left to stand for 4 days at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in water, the solution was extracted with benzene, the extract was washed with water and applied to a column charged with alumina, and the column was eluted with heptane. Yield 1.5 g (75%), bp 112–118°C (1 mm), mp 34–35°C. IR spectrum (film), ν, cm^{-1}: 3389 s, 3279 v.s, 3062 m, 3025 m, 2836 m, 2112 m, 1869 w, 1590 v.s, 1481 v.s, 1435 m, 1395 m, 1251 m, 1183 m, 1123 s, 1078 m, 1058 s, 996 s, 947 m, 912 s, 813 v.s, 660 v.s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 t (1H, C≡CH, J = 2.4 Hz), 3.90 m (3H, $CH_2C≡C$, NH), 6.48 d and 7.52 d (2H each, C_6H_4, J = 8.8 Hz). Mass spectrum: m/z 257.9783 $[M + H]^+$. Found, %: C 42.16; H 3.21; N 5.48. C_9H_8NI. Calculated, %: C 42.05; H 3.13; N 5.45.

Complex of (tetraphenylporphyrinato)zinc(II) with *p*-phenylenediamine (V). Saturated solutions of Zn-TPP (1.47×10^{-5} mol, 10 mg in 10 mL) and *p*-phenylenediamine (1.55×10^{-5} mol) in chloroform were mixed together, and the mixture was left to stand in the dark at room temperature on exposure to air. The crystals were filtered off and dried in air.

X-Ray analysis of complex V. The X-ray diffraction data for a single crystal of **V** were acquired using the STOE StadiVari PILATUS 100K diffractometer [CuK_α irradiation generated by GeniX^{3D} Cu HF with a microfocus X-ray tube and a Xenocs FOX3D HF multilayer thin-film ellipsoid monochromator (France)]. The data were collected and processed, and the unit cell parameters were determined and refined, using STOE X-Area software package. The principal crystallographic parameters are given in Table 5. The structural data for compound **V** were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 912710). The structure was solved by the direct method using SHELXS-97 [22]. The positions and thermal parameters of non-hydrogen atoms were refined in full-matrix anisotropic approximation. The positions of hydrogen atoms were calculated and refined in isotropic approximation according to the *rider* model. Graphical images of the molecule in crystal were plotted using DIAMOND [23].

The X-ray diffraction study was performed with the aid of the equipment of the Moscow State University in terms of the Collaboration Agreement between the Faculty of Chemistry of the Lomonosov Moscow State University and the Faculty of Ecology and Biology of the Petrozavodsk State University.

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