

Nucleophilicity of Heteroaromatic *N*-Oxides in Coordination with Zn(II) Tetraphenylporphyrinate and in the Substitution Reactions

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Abstract—Linear correlations have been revealed between thermodynamic and kinetic parameters of the nucleophilic substitution and coordination reactions of zinc(II) tetraphenylporphyrinate with heteroaromatic *N*-oxides in different solvents. Complex formation of zinc(II) tetraphenylporphyrinate with *n*-donor ligands in chloroform can serve as model system in spectroscopy studies of nucleophilicity and basicity of the compounds capable of the *n*,*v* type complexes formation.

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This work extends the studies on correlation between the stability constants of zinc(II) tetraphenylporphyrinate complexes with various organic ligands and physicochemical parameters of the same ligands nucleophilic substitution reactions.

We have recently demonstrated [1, 2] that thermodynamic parameters of zinc(II) tetraphenylporphyrinate and zinc(II) protoporphyrinate dimethyl ester coordination with 3- and 4-substituted pyridines in chloroform linearly depend on the values of the bands shifts ($\Delta\lambda$) in electronic absorption spectra of these metal porphyrinates upon interaction with the pyridines as well as on pK_a of the ligands in water, and on the Hammett constants σ of the substituents. The linear correlation between changes of enthalpy and entropy of the complexes formation confirms that the process is “isoequilibrium” or “isothermodynamic”. Linear correlations have been found as well between thermodynamic and kinetic parameters of some nucleophilic substitution reactions of pyridines and complex formation reactions between zinc(II) tetraphenylporphyrinate and the pyridines.

Pyridines nucleophilicity is usually in line with reactivity of the corresponding pyridine *N*-oxides [3, 4]. In view of that, in this work we analyzed the kinetic and thermodynamic parameters of zinc(II) tetra-

phenylporphyrinate coordination with heteroaromatic pyridine-*N*-oxides (set **I**) and quinoline-*N*-oxides (set **II**) (Table 1). Taking into account the tabulated data, we will discuss some S_N reactions of the above-listed ligands and their non-oxidized analogs (sets **III** and **IV**). Noteworthy, *N*-oxides of 2,6-dimethyl-4-nitropyridine (pK_a –0.86 [5]), 2,6-dichloropyridine, and benzofuroxane (pK_a of the latter pair were not found in the available literature; in the case of 2-chloropyridine-*N*-oxide, pK_a was of –0.77 [6]) did not change the electron absorption spectrum of zinc(II) tetraphenylporphyrinate even when applied in the form of the saturated solutions in chloroform; that was evidently due to their extremely low nucleophilicity/basicity (see Scheme 1).

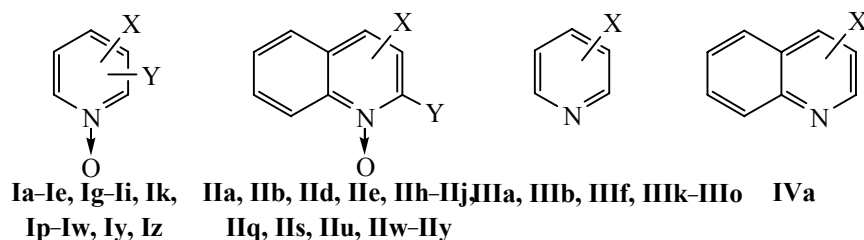
The measured stability constants K of zinc(II) tetraphenylporphyrinate complexes with heteroaromatic *N*-oxides in chloroform were, strictly speaking, the concentration ones. However, as the initial concentrations of the complex forming compounds were low (2×10^{-5} mol/L of zinc(II) tetraphenylporphyrinate and 10^{-4} – 10^{-2} mol/L of the ligands) and the ionic forms were absent in the solution, the experimentally determined values should have been fairly close to the thermodynamic stability constants.

Table 1. Stability constants (K), thermodynamic parameters of the complex formation (ΔG^0 , ΔH^0 , ΔS^0), shifts of I, II, and the Soret absorption bands ($\Delta\lambda$) upon the complex formation, σ and σ_{pyO} constants of the substituents, and basicity ($\text{p}K_{\text{a}}$) of the ligands in water at 25°C; see complexes description in the text

Ligand	K_{298}	$\text{p}K_{\text{a}}$ (25°C) [7–9]	σ [12]	σ_{pyO} [7]	$\Delta\lambda$ Cope	$\Delta\lambda_{\text{II}}$	$\Delta\lambda_{\text{I}}$	$-\Delta H^0$, kJ/mol	ΔS^0 , J mol ⁻¹ K ⁻¹	ΔG^0 , kJ/mol
Ie	2470±63	2.05	-0.268	-0.603	10.2	14.5	17.0	13.94±0.26	19.0±0.8	-19.35
Ib	1353±24	1.29	-0.17	-0.24	9.3	13.8	15.7	13.88±0.21	13.47±0.75	-17.85
Ig	1272±24	–	–	–	–	13.8	15.4	13.66±0.03	13.23±0.1	-17.70
Ia	816±35	0.79	0	0	8.8	13.3	15.0	13.43±0.39	10.6±0.6	-16.60
Ii	609±14	0.36	0.227	0.206	8.4	12.6	13.8	13.81±0.37	7.1±0.6	-15.88
Ih	134±2.5	-1.7	0.778	1.19	5.3	10.0	12.0	13.74±0.15	-5.71±0.4	-12.13
It	1650±27	1.43 [10]	(-0.21)	(-0.40)	–	14.1	16.3	13.90±0.31	15.16±0.8	-18.35
Ir	1311±30	1.25 [10]	(-0.12)	(-0.26)	–	13.6	15.8	13.83±0.25	13.23±0.7	-17.77
Ip	1142±25	1.10 [10]	(-0.06)	(-0.16)	–	13.4	15.6	13.81±0.22	12.47±0.4	-17.44
Iv	1040±25	1.05 [10]	(-0.03)	(-0.11)	–	13.0	15.2	13.77±0.44	11.7±0.8	-17.20
Ic	1030±11	1.08	-0.069	-0.139	9.1	13.5	15.8	13.82±0.31	11.4±0.65	-17.18
Ik	454±9	–	0.37	–	7.8	12.4	15.0	13.88±0.29	4.6±0.41	-15.15
Iz	185±6	-0.97	0.709 ^a	1.151 ^a	6.0	10.6	13.0	13.59±0.22	-2.1±0.2	-12.93
Iu	1495±29	–	–	–	–	14.1	16.1	13.83±0.28	14.22±0.9	-18.10
Is	1215±25	–	–	–	–	13.6	15.7	13.69±0.16	13.40±0.7	-17.59
Iq	1090±24	–	–	–	–	13.2	15.5	14.04±0.26	11.0±0.6	-17.32
IIe	5522±136	–	-0.268	-0.603	10.4	14.7	17.4	13.90±0.29	25.3±1.2	-21.34
IIb	3085±73	1.44	-0.17	-0.24	9.8	14.0	16.3	13.61±0.26	21.2±0.7	-19.90
IIa	2326±72	0.86	0	0	9.2	13.3	15.7	13.81±0.34	18.1±0.95	-19.20
IIj	2069±32	0.232	–	–	–	12.7	15.3	13.96±0.24	16.55±0.6	-18.91
IIi	1600±31	0.47	0.227	0.206	–	11.8	14.6	13.74±0.11	15.00±0.7	-18.27
IIh	267±9	-1.39	0.778	1.19	–	9.3	12.1	13.50±0.24	1.41±0.46	-13.86
Id	1237±32	1.02	–	–	9.0	13.3	15.9	11.91±0.03	19.2±0.45	-17.63
Iy	189±5	-0.967	–	–	5.8	10.4	12.9	11.85±0.29	5.40±0.4	-12.87
IIId	396±6	–	–	–	–	13.1	16.0	12.05±0.22	9.50 ±0.5	-14.81
IIx	344±7	–	–	–	–	12.6	14.7	12.18±0.24	7.90±0.5	-14.46
IIw	292±4	–	–	–	–	12.3	14.0	12.02±0.32	7.23±0.6	-14.06
IIy	67.2±1.6	–	–	–	–	9.6	12.3	11.80±0.11	-4.21±0.21	-10.42
IIu	429±6	–	–	–	–	15.4	16.9	12.03±0.15	10.0±0.6	-15.01
IIs	340±8	–	–	–	–	14.4	16.2	12.36±0.39	7.26±0.63	-14.43
IIq	251±6	–	–	–	–	14.0	15.9	12.15±0.34	5.90±0.41	-13.68
IIIa	3517±150	5.29	0	–	9.8	15.0	18.2	17.30±0.17	8.9±0.6	-20.2
IVa	114±3	4.81 [11]	0	–	8.5	14.7	16.3	14.58±0.14	-9.81±0.6	-11.73

^a $\Sigma\sigma$ and $\Sigma\sigma_{\text{pyO}}$, respectively.

Scheme 1.



Y = H, X = H (**a**), 4-Me (**b**), 3-Me (**c**), 2-Me (**d**), 4-MeO (**e**), 4-NMe₂ (**f**), 4-N₃ (**g**), 4-NO₂ (**h**), 4-Cl (**i**), 4-Br (**j**), 3-COOEt (**k**), 4-CONHNH₂ (**m**), 3-CONH₂ (**n**), 4-CN (**o**), 4-(C₆H₅CH=CH) (**p**), 2-(C₆H₅CH=CH) (**q**), 4-(4-MeOC₆H₄CH=CH) (**r**), 2-(4-MeOC₆H₄CH=CH) (**s**), 4-(4-NMe₂C₆H₄CH=CH) (**t**), 2-(4-NMe₂C₆H₄CH=CH) (**u**), 4-(4-ClC₆H₄CH=CH) (**v**); Y = 2-Me, X = 4-Cl (**w**), 4-Br (**x**), 4-NO₂ (**y**); Y = 3-Me, X = 4-NO₂ (**z**).

Similarly to the case of pyridines [1, 2], the steric factor being of minor significance, the logarithms of stability constant of zinc(II) tetraphenylporphyrinate complex with pyridine-*N*-oxides and quinoline *N*-oxides (**IIIa** > **IIa** > **Ia** > aniline > **IVa**) in chloroform

were linearly correlated with p*K*_a of the respective ligand in water, with the Hammett constant σ of the respective substituent, and with the bands shift ($\Delta\lambda$) of the electron absorption spectra (Table 1 and Fig. 1).

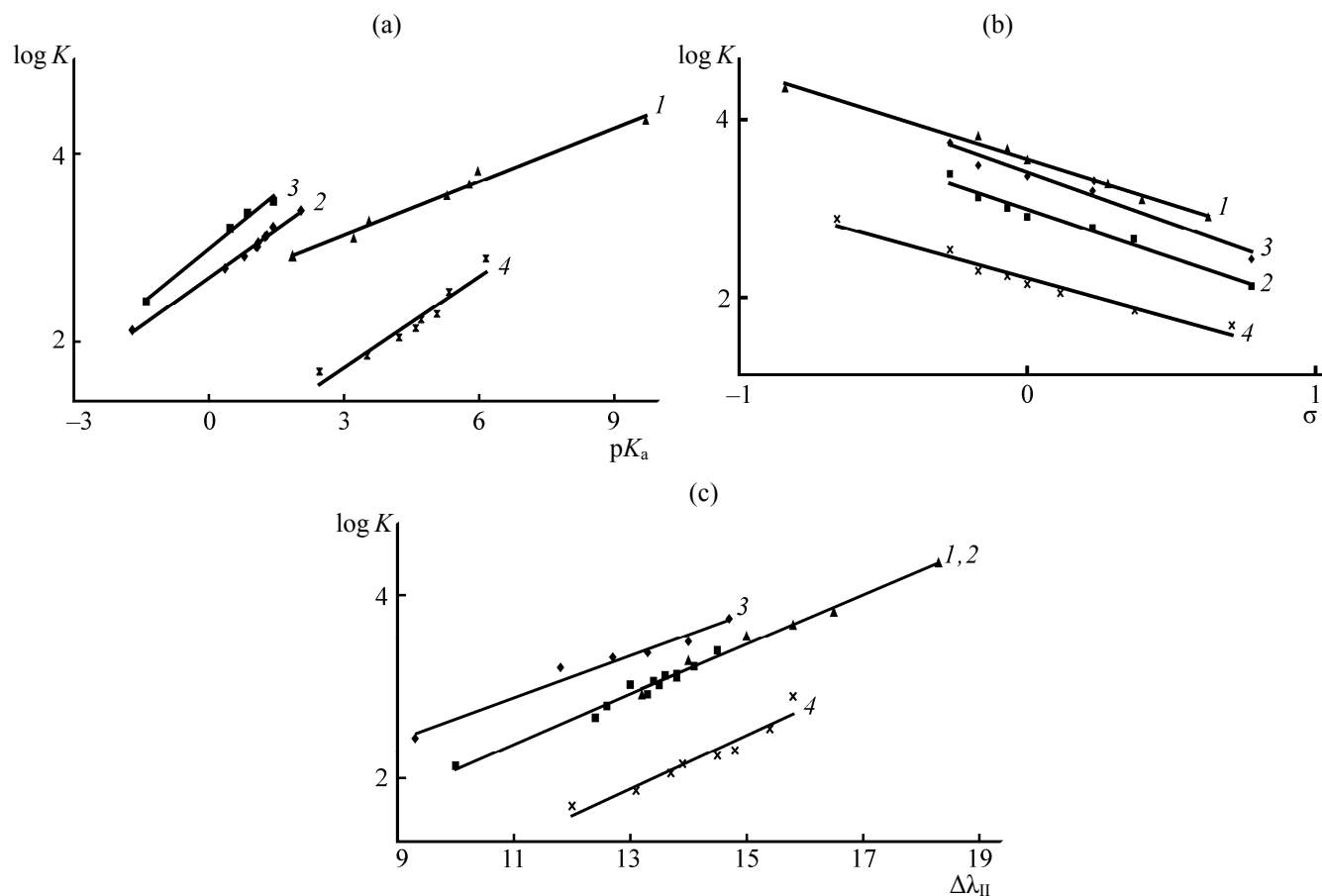


Fig. 1. Stability of the complexes of zinc(II) tetraphenylporphyrinate with 3- and 4-substituted pyridines [1] (**1**, triangles), pyridine-*N*-oxides (**2**, diamonds), quinoline-*N*-oxides (**3**, squares), and anilines [13, 14] (**4**, crosses) in chloroform at 298 K as functions of (a) p*K*_a of the ligands in water, (b) the Hammett constant, and (c) absorption band II shift upon complexation.

The $\log K - pK_a$ and $\log K - \sigma$ data were described with different linear equations within the sets of pyridines, pyridine-*N*-oxides, and quinoline-*N*-oxides (lines 1–3 in Figs. 1a and 1b). However, the $\log K - \Delta\lambda$ dependences coincided in the cases of pyridines and pyridine-*N*-oxides (sets 1 and 2 in Fig. 1c); for example, in the case of band II, $\log K = 0.272\Delta\lambda_{II} - 0.623$, $n = 18$, $r = 0.992$). In the cases of all the datasets, except for $\log K - pK_a$ data for pyridines, the lines slopes were close in the cases of ligands of different classes.

The higher activity in the nucleophilic substitution reactions (“supernucleophilicity”) of pyridine-*N*-oxides as compared to pyridines of close basicity is usually explained by better steric availability of the N→O group oxygen atom [3, 4] as compared to that of nitrogen atom in pyridines. However, the basicity of pyridines in water was much more sensitive ($pK_a^{py} = -5.33\sigma + 5.23$) to the nature of heteroaromatic ring substituents than that of pyridine-*N*-oxides ($pK_a^{pyO} = -3.35\sigma + 0.93$); hence, the above-mentioned trend might be due to difference in hydration of the bases and their protonated forms [1]. Therefore, in order to correctly compare the complex formation ability of pyridines and the corresponding *N*-oxides, the zinc(II) tetraphenylporphyrinate complexes stability should have been measured in the same medium (chloroform was chosen in this work due to availability of experimental data). Unfortunately, the found pK_a values of the studied compounds in chloroform were scarce; therefore, we used the available data on basicity in acetonitrile, another aprotic solvent. Analysis of the data in the $\log K - pK_a(\text{MeCN})$ coordinates revealed that [in contrast to the $\log K - pK_a(\text{H}_2\text{O})$ plots] the pyridine complexes with zinc(II) tetraphenylporphyrinate were more stable than those of pyridine-*N*-oxides of the same basicity, the exceptions being only the ligands containing very strong electron-donating substituents (for instance, 4-dimethylaminopyridine, $\sigma = -0.84$). To conclude, the term “supernucleophilicity” should not be used to discuss the complex formation of pyridine-*N*-oxides with zinc(II) tetraphenylporphyrinate. Moreover, the substituents in the aromatic rings being the same, the stability constants in the case of pyridine derivatives were always higher than those in the cases of pyridine-*N*-oxides.

The fitting lines 2–4 in Figs. 1a–1c were almost parallel. That fact could point at the similar mechanisms of coordination and protonation of heteroaromatic *N*-oxides and anilines, therefore, similarity in

the mechanism of their nucleophilic substitution reactions S_N could be assumed. At close basicity, the somewhat higher nucleophilicity of quinoline-*N*-oxides ($\log K = 0.387pK_a + 2.68$, $n = 4$, $r = 0.997$) as compared to that of pyridine-*N*-oxides ($\log K = 0.339pK_a + 2.68$, $n = 10$, $r = 0.991$) and of pyridines ($\log K = 0.189pK_a + 2.57$, $n = 7$, $r = 0.991$; in the case of quinoline, the data point was much lower than the fitting lines 1–3 in Fig. 1a) was seemingly due to special features of the above-mentioned heterocycles dynamic polarization upon interaction with acceptors of various Pearson hardness [15] in the protic and aprotic solvents (H^+ in water and zinc(II) tetraphenylporphyrinate in chloroform).

The slopes of the $\log K - \sigma$ fitting lines (Fig. 1b) were not significantly different between the sets of pyridines ($\log K = -1.01\sigma + 3.56$, $n = 7$, $r = 0.994$), pyridine-*N*-oxides ($\log K = -1.09\sigma + 2.99$, $n = 7$, $r = 0.98$), quinoline-*N*-oxides ($\log K = -1.15\sigma + 3.14$, $n = 6$, $r = 0.98$), and anilines ($\log K = -0.85\sigma + 2.32$, $n = 14$, $r = 0.97$). As σ values depended exclusively on the nature of aromatic rings substituents, it was concluded that their coordination to zinc(II) tetraphenylporphyrinate in chloroform was not very sensitive to the (O,N) donor center type and to the aromatic system of the ligand.

Analysis of correlation of the complexes stability and their spectral properties ($\log K - \Delta\lambda$ data, the both parameters were determined in chloroform medium) revealed that behavior of 3- and 4-substituted pyridines and pyridine-*N*-oxides could be fitted with the same equation ($\log K = 0.272\Delta\lambda_{II} - 0.623$, $n = 19$, $r = 0.992$). Evidently, in the cases of those ligands, the steric effects on the complex formation and solvation in the low-polar solvent were similar, and the electronic spectra changes resulting from zinc(II) tetraphenylporphyrinate coordination were affected exclusively by the electron-donating properties of heteroatoms (oxygen or nitrogen) depending in turn on their polarizability and electronegativity as well as on the electronic effects of the substituents. In the case of quinolines and quinoline-*N*-oxides, the surrounding of nitrogen and oxygen atoms were much different, and the $\log K - \Delta\lambda$ data were therefore fitted with other equations (Fig. 1c).

Conclusions on evaluation of the steric effects on the zinc(II) tetraphenylporphyrinate complex formation with heteroaromatic *N*-oxides were as follows. Contrary to the pyridines case [16], location of methyl

substituent in pyridine-*N*-oxide slightly influenced the complexes stability constant (pyridine-*N*-oxide, $K = 816$ L/mol; 2-methylpyridine-*N*-oxide, $K = 1237$ L/mol; 4-methylpyridine-*N*-oxide, $K = 1353$ L/mol, and 3-methylpyridine-*N*-oxide, $K = 1030$ L/mol). Hence, the hyperconjugation effect of Me group in the positions 2 and 4 (in the case of 3-substituted ligand that effect was absent) affected the nucleophilicity of ligands more than its inductive and steric effects. Besides, in the cases of all the studied 2-, 3-, and 4-substituted pyridine-*N*-oxides (including styryl derivatives and 3-methyl-4-nitropyridine-*N*-oxide), the general equations ($\log K = 0.268\Delta\lambda_{II} - 0.556$, $n = 18$, $r = 0.99$ and $\log K = 0.358pK_a + 2.66$, $n = 13$, $r = 0.994$) were held satisfactorily. Position of methyl group in the substituted quinoline-*N*-oxides affected more the studied coordination process. In particular, the complex stability constant was of $K = 2326$ L/mol in the case of parent quinoline-*N*-oxide; that in the case of 4-methylquinoline-*N*-oxide ($K = 3085$ L/mol) was higher and that in the case of 2-methylquinoline-*N*-oxide ($K = 396$ L/mol) was much lower. Evidently, in the latter case, steric hindrance was extremely significant due to combined spatial influence of 2-Me and 8-H. Behavior of quinoline-*N*-oxides bearing 2-styryl substituents was somewhat special. Their coordination with zinc(II) tetraphenylporphyrinate was characterized by significantly lower stability constants, but it caused much stronger spectral changes ($\Delta\lambda$ of chloroform solutions) than that of 2- and 4-styrylpyridine-*N*-oxides. Hence, on the contrary to the pyridine-*N*-oxides case (line 2 in Fig. 2), the data corresponding to quinoline-*N*-oxides was fitted by three different lines 1, 3, and 4 (Fig. 2). That was probably due to special features of steric interaction of hydrogen atom, methyl and styryl groups in the position 2 of quinoline ring with the zinc(II) tetraphenylporphyrinate macrocycle in the course of the complex formation.

Probably, the measured stability constants of pyridine-*N*-oxides and quinoline-*N*-oxides complexes with zinc(II) tetraphenylporphyrinate corresponded to the n, ν type 1 : 1 molecular complexes with the dative O–Zn bond. In particular, the linear correlation between pK_a in water and $\log K$ in chloroform (Table 1, Fig. 1a) along with the X-ray diffraction data for the isoquinoline-*N*-oxide complex with zinc(II) tetraphenylporphyrinate [9] confirmed that protonation and coordination of ligands **I** and **II** with metal porphyrinates proceeded via the same center, the N→O group oxygen atom.

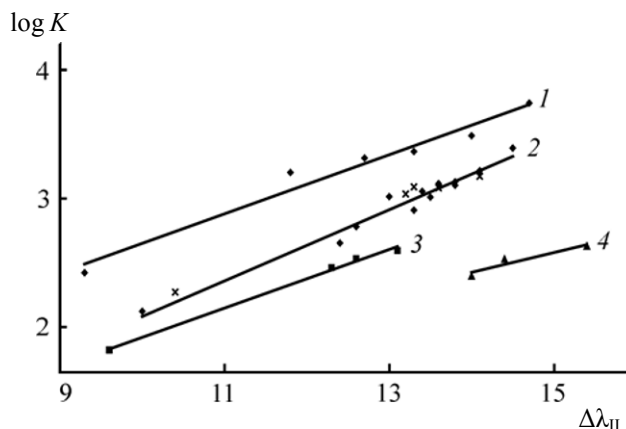


Fig. 2. Stability of the complexes of zinc(II) tetraphenylporphyrinate with 4-substituted quinoline-*N*-oxides (1), 2-, 3-, and 4-substituted pyridine-*N*-oxides (2), 4-substituted 2-methylquinoline-*N*-oxides (3), and 2-styryl-substituted quinoline-*N*-oxides (4) in chloroform at 298 K as function of the absorption band II shift upon complex formation. The symbols shape corresponds to that in Fig. 1.

Furthermore, we studied the structure of zinc(II) tetraphenylporphyrinate complex with 4-chloroquinoline-*N*-oxide by X-ray diffraction (Fig. 3). Data in Table 2 confirm that it was the axial 1 : 1 molecular complex.

The dsp^2 Zn atom was located in the porphyrin cycle plane the molecule of zinc(II) tetraphenylporphyrinate. In the course of 1 : 1 axial complex formation, the Zn hybridization was changed to sp^3d^2 [9]. The four hybrid orbitals were located in the porphyrin cycle plane, and the other two orbitals (the free and the ligand-binding) were normal to it.

In the complex of zinc(II) tetraphenylporphyrinate with 4-chloroquinoline-*N*-oxide, the coordination number of zinc equaled five, with tetragonal pyramid as coordination polyhedron (Fig. 3a). Zinc atom was off the base plane (determined by the porphyrin nitrogen atoms) by 0.28 Å and was located at 2.13 Å from oxygen atom. That was typical of such zinc coordination; for example, in the zinc(II) tetraphenylporphyrinate complex with 3-nitroaniline (Cambridge Structural Database reference code HAMLAI [17]) the off-plane distance was of 0.25 Å. The L_2 ligand (4-chloroquinoline-*N*-oxide) was disordered in such a way (Fig. 3b) that L_2 atoms of the both positions were located practically in the same plane (average deviation from the mean plane passing through all the non-hydrogen atoms of L_2 was of 0.03 Å, the largest deviation being of 0.12 Å). The angle between the planes of porphyrin and the ligands was of 26.58°.

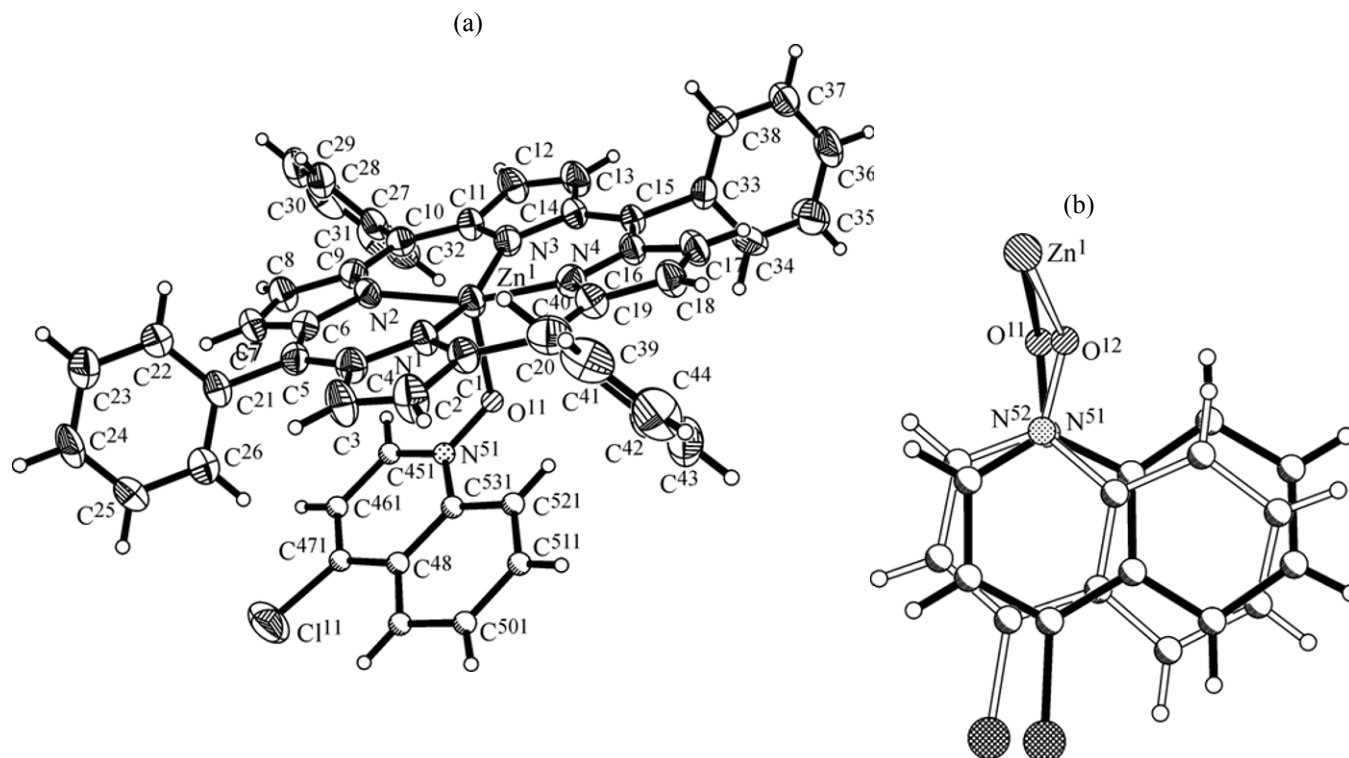


Fig. 3. (a) Structure of the 1 : 1 molecular complex of zinc(II) tetraphenylporphyrinate with 4-chloroquinoline-*N*-oxide **I** (one of the positions of disordered ligand L_2 is shown) and (b) scheme the disordering.

We failed to find any compounds containing the L_2 ligand in the Cambridge Structural Database [17] (version 5.32, August 2011). The geometry parameters were close to those of $[\text{Zn}(\text{2-methylquinoline-1-oxide})_2\text{Cl}_2]$; in particular, the $\text{N}\rightarrow\text{O}$ bond length coincided with the data reported on the of n,v type molecular complexes formed by heteroaromatic *N*-oxides [18].

Geometry of zinc(II) tetraphenylporphyrinate complex with 4-chloroquinoline-*N*-oxide most likely corresponded to the sp^3 hybridization state of oxygen because the angle between the plane of heterocycle and the plane of the NOZn fragment ruled out the conjugation of oxygen atom with heterocyclic ring as well as with the metal ion.

Using the above-derived linear equations of $\log K = f(\sigma^{\text{PyO}})$, we calculated the σ constants of styryl substituents (Table 1, in parentheses). From the result it followed that upon coordination of zinc(II) tetraphenylporphyrinate with the **Ip**, **Ir**, **It**, and **Iv** ligands, the electronic effects of NMe_2 and OMe groups in *p*-position of benzene rings were weakened by the $-\text{CH}=\text{CHPh}$ conjugated system. Hence, the σ_p values of $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}=\text{CH}$ and $p\text{-MeOC}_6\text{H}_4\text{CH}=\text{CH}$ were of -0.21 and -0.12 , respectively. The chlorine atom of the

styryl fragment (evidently being weaker electron acceptor than the $\text{N}\rightarrow\text{O}$ group and being conjugated with the latter) became the electron-donating group as well, due to its $+M$ -effect ($\sigma_{\text{PyO}} -0.11$). However, its effect was weaker than that of unsubstituted styryl group ($\sigma_{\text{PyO}} -0.16$).

As the structure of zinc(II) tetraphenylporphyrinate complexes with heteroaromatic *N*-oxides was similar to that of the S_N reactions transition states [5] (the *N*-oxides acting as nucleophile), we evaluated the correlation between the parameters characterizing those processes. Examples of linear correlations between rate constants of five nucleophilic substitution reactions $\log k$ in acetonitrile and dichloromethane with $\log K$ and $\Delta\lambda$ of the corresponding zinc(II) tetraphenylporphyrinate complexes with 3- and 4-substituted pyridine-*N*-oxides are collected in Table 3.

Hence, the rate constant of nucleophilic substitution reactions in different organic solvents could be calculated from the K and $\Delta\lambda$ values using the nucleophilicity/basicity scale offered in [16]; reverse calculation was possible as well. Importantly, similar trends were revealed in the cases of 2-, 3-, and 4-methylpyridine-*N*-oxides coordination with zinc(II)

tetraphenylporphyrinate as well as in the cases of their S_N reactions [24]. Therefore, we concluded that the steric effects of methyl group were insignificant. However, that was not the case of styryl derivatives [23]. Stability of zinc(II) tetraphenylporphyrinate complexes with compounds **It** and **Iu** was almost equal, but the corresponding equilibrium constants of acyl group transfer [Table 3, reaction (5)] differed by almost an order of magnitude. Evidently, that was due to more strict steric demands for formation of pentacoordinated S_N reactions transition state than those in the case of 1 : 1 n,v complex with planar molecule of metal porphyrin.

It was natural to expect the linear correlation between thermodynamic parameters of the studied nucleophilic reactions and complex formation. We calculated thermodynamic parameters of their formation from the measured values of stability constants of zinc(II) tetraphenylporphyrinate complexes with heteroaromatic *N*-oxides at different temperatures (273–313 K) (Table 1).

ΔH^0 values in all the cases were negative. In the cases of 3- and 4-substituted pyridine-*N*-oxides, 2-styryl substituted pyridine-*N*-oxides, and 4-substituted quinoline-*N*-oxides, the values were close (–13.50 to –14.04 kJ/mol, $\Delta H^0_{\text{average}} = -13.78 \pm 0.15$ kJ/mol, $n = 22$, series A). In the cases of *N*-oxides of 2-methylpyridine, 2-methylquinoline, and 2-styrylquinoline, ΔH^0 values were close as well, however, the average value was different (–11.80 to –12.36 kJ/mol, $\Delta H^0_{\text{average}} = -12.04 \pm 0.18$ kJ/mol, $n = 9$, series B). Hence, within the both series of heteroaromatic *N*-oxides (similarly to 3- and 4-substituted anilines with $\Delta H^0_{\text{average}}$ of –14.6 $\pm$ 0.14 kJ/mol [1]) the coordination with zinc(II) tetraphenylporphyrinate was isoenthalpic. Noteworthy, in the case of pyridines, ΔH^0 values were variable and linear with the ligand basicity [1].

ΔS^0 as well as ΔG^0 values of formation of zinc(II) tetraphenylporphyrinate complexes with *N*-oxides of 3- and 4-substituted pyridines ($\Delta S^0 = 6.67pK_a + 4.96$, $n = 11$, $r = 0.998$) and quinolines ($\Delta S^0 = 7.12pK_a + 11.47$, $n = 4$, $r = 0.999$) in chloroform (Fig. 4) were proportional to the ligands basicity and Hammett constants σ . Thus, despite enthalpy control of coordination process (ΔS^0 gave the major contribution to ΔG^0), the selectivity of complexes formation (dependence of K value on the *N*-oxides structure similarly to the case of anilines [13]) was determined by the entropy effects. In the case of zinc(II)

Table 2. Selected geometry parameters of complex **I** (bond lengths, Å and bond angles, deg)^a

Bond	<i>d</i> , Å	<i>n</i> = 1	<i>n</i> = 2
Zn ¹ –N ³	2.049(4)		
Zn ¹ –N ⁴	2.057(4)		
Zn ¹ –N ¹	2.066(3)		
Zn ¹ –N ²	2.075(4)		
Zn ¹ –O ¹ⁿ		2.126(11)	2.130(7)
O ¹ –N ⁵ⁿ		1.332(9)	1.356(10)
Cl ¹ⁿ –C ⁴⁷ⁿ		1.737(8)	1.741(10)
N ⁵ⁿ –C ⁴⁵ⁿ		1.336(10)	1.324(11)
N ⁵ⁿ –C ⁵³ⁿ		1.381(10)	1.400(11)
C ⁴⁵ⁿ –C ⁴⁶ⁿ		1.412(11)	1.419(14)
C ⁴⁶ⁿ –C ⁴⁷ⁿ		1.352(13)	1.355(15)
C ⁴⁷ⁿ –C ⁴⁸ⁿ		1.407(13)	1.388(16)
C ⁴⁸ⁿ –C ⁴⁹ⁿ		1.373(11)	1.363(15)
C ⁴⁸ⁿ –C ⁵³ⁿ		1.418(11)	1.419(14)
C ⁴⁹ⁿ –C ⁵⁰ⁿ		1.456(13)	1.483(17)
C ⁵⁰ⁿ –C ⁵¹ⁿ		1.397(13)	1.371(17)
C ⁵¹ⁿ –C ⁵²ⁿ		1.384(10)	1.401(14)
C ⁵²ⁿ –C ⁵³ⁿ		1.385(12)	1.383(14)

^a Bond angles, ω: O¹²Zn¹O¹¹ 10.2(4), $n = 1$; N⁵ⁿO¹ⁿZn¹ 113.5(11), $n = 1$; 116.7(11), $n = 2$.

tetraphenylporphyrinate coordination with pyridines [1, 2], ΔS^0 was linear with the ligand basicity (and with ΔH^0) as well, but the values were more variable (–27 to +54 J mol^{–1} K^{–1}).

The ΔS^0 decrease with the decreasing of electron-donating ability of the heteroaromatic *N*-oxide ligands (similarly to the case of primary anilines [14]) could be at least partially due to the gradual increase of *p*-character of the lone-electron pair of nitrogen atom with shifting the electron density towards benzene ring (and, therefore, the change of sp^3 hybridization into sp^2 one).

As expected, the stability constants of zinc(II) tetraphenylporphyrinate complexes increased with decreasing temperature. The plots of ΔG as function of T (Fig. 5) revealed that at approximately 40 K the complexes stability should have become independent

Table 3. Nucleophilic substitution reactions with $\lg k$ values linearly ($r = 0.97\text{--}0.999$) correlated with $\lg K$ and $\Delta\lambda$ of complex formation; see detailed description in the text

Reaction no.	Reaction	Conditions
1	$R^1C_5H_4N \rightarrow O + R^2X \rightarrow R^1C_5H_4NOR^2X$ $R^1 = H, 4\text{-Me}, 4\text{-MeO}; R^2 = Me, Et, PhCH_2; X = I, Br$	Acetonitrile, 25°C [19]
2	$R^1C_5H_4N \rightarrow O + R^2X \rightarrow R^1C_5H_4NOR^2X$ $R^1 = H, 4\text{-Cl}, 4\text{-Me}, 4\text{-MeO}; R^2 = Me, Et, i\text{-Pr}; X = I, Br$	Acetonitrile, 25°C [20]
3	$R^1C_5H_4N-OAc + R^2C_5H_4N \rightarrow O \rightarrow R^1C_5H_4N \rightarrow O + R^2C_5H_4N-OAc$ $R^1, R^2 = H, 4\text{-Cl}, 4\text{-Me}, 4\text{-MeO}$	Acetonitrile, дихлорметан, 25°C [21, 22]
4	$Me_2NCO(R^1C_5H_4N \rightarrow O)^+BPh_4^- + R^2C_5H_4N \rightarrow O \rightleftharpoons Me_2NCO(R^2C_5H_4N \rightarrow O)^+BPh_4^- + R^1C_5H_4N \rightarrow O$ $R^1, R^2 = H, 4\text{-Me}, 4\text{-MeO}, 3\text{-Me}, 4\text{-NC}_4H_8O, 4\text{-(4-Me}_2NC_6H_4CH=CH)$	Acetonitrile, 25°C [10]
5	$AcCl + RC_5H_4N \rightarrow O \rightleftharpoons RC_5H_4N^+-OAc + Cl^-$ $BzCl + RC_5H_4N \rightarrow O \rightleftharpoons RC_5H_4N^+OBz + Cl^-$ $R = H, 4\text{-Cl}, 4\text{-Me}, 4\text{-MeO}, 4\text{-(4-NMe}_2C_6H_4CH=CH), 4\text{-Me}_2N,$ $2\text{-(4-Me}_2NC_6H_4CH=CH), 4\text{-C}_6H_4CH=CH, 2\text{-Me}, 4\text{-NC}_4H_8O$	Acetonitrile, Dichloromethane, 15–35°C [23–25]

of the ligand structure (ΔG being of -13.78 and -12.04 kJ/mol in the cases of ligands series A and B, respectively), provided that the trends revealed in the case of solutions were still operative. Similar conclusions followed from the analysis of corresponding data in the cases of aniline [14] and pyridine [1] ligands; in the latter case the critical temperature was of at 196 K.

The slopes of ΔG plots as function of T with various Hammett constants suggested that at certain $\Sigma\sigma$

value ($\Sigma\sigma$ of $0.7\text{--}0.8$ in the case of series A) ΔG of the process should be temperature-independent; indeed, that was observed in the case of 4-nitroquinoline-*N*-oxide ($\sigma = 0.778$) (Fig. 5).

According to the X-ray diffraction data collected on crystals [26], zinc(II) tetraphenylporphyrinate complexes with heteroaromatic *N*-oxides and anilines were of molecular 1 : 1 *n,v*-type with the angle between metal porphyrin plane and the ligand aromatic ring of $24^\circ\text{--}34^\circ$. In the similar complexes, pyridines were oriented almost perpendicularly (with the angle of $80^\circ\text{--}89^\circ$) to the porphyrin plane. Seemingly, those structural differences caused the different in thermodynamics and kinetics of pyridines coordination to zinc(II) tetraphenylporphyrinate as compared with that of anilines and heteroaromatic *N*-oxides.

To conclude, heteroaromatic *N*-oxides behavior in the S_N reactions as well as in the coordination processes (in particular, the linear correlations between $\log K$, $\log k$, pK_a , and σ constants) was quite similar to that of the non-oxidized analogs. However, thermodynamics of Zn(II) tetraphenylporphyrinate complexes formation revealed some differences between the ligands. In the cases of pyridines, the process was isoequilibrium, whereas in the cases of pyridine-*N*-oxides and quinoline-*N*-oxides it was isenthalpic (similarly to the cases of anilines). The latter group of ligands could be divided into two series according to the ΔH values. Series A included 3- and 4-substituted

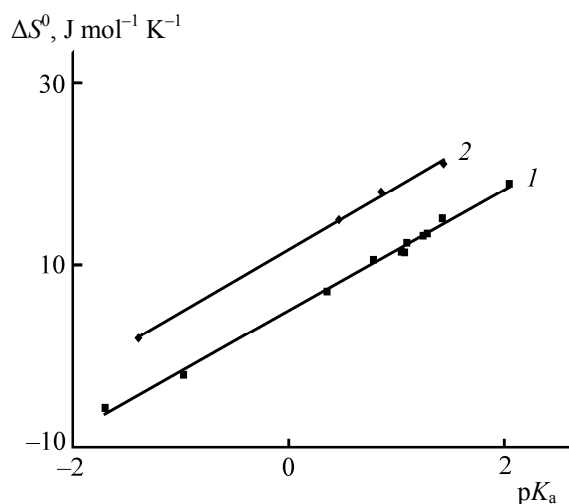


Fig. 4. ΔS^0 of formation of the complex between zinc(II) tetraphenylporphyrinate and 3- or 4-substituted pyridine-*N*-oxides (1) and quinoline-*N*-oxides (2) in chloroform as function of pK_a of the ligands in water at 25°C.

ligands and pyridine-*N*-oxides containing 2-styryl substituents. Series B consisted of 2-methyl-substituted ligands and quinoline-*N*-oxides containing 2-styryl substituents.

The special features of the second series was seemingly due to different steric hindrances in the cases of 2-styrylpyridine *N*-oxides (planar molecules) and 2-methyl derivatives (with sp^3 carbon atom) and 2-styrylquinoline-*N*-oxides (with 8-H and 2-styryl substituents preventing the location of two sp^2 oxygen orbitals in the heterocycle plane).

When planning the research, we expected that analysis of thermodynamic parameters of nucleophilic substitution reactions of heteroaromatic *N*-oxides would explain the difference in thermodynamic behavior of pyridine-*N*-oxide and heteroaromatic *N*-oxides. However, the scarce data on pyridine-*N*-oxides [20–25] (for quinoline-*N*-oxides, no data was found) revealed that in all the cases the linear correlations between $\Delta H^\#$ and $\Delta S^\#$ or between $\Delta G^\#$ and $\Delta S^\#$ were fulfilled, meaning that the reactions were isokinetic.

We expect that the evaluation of limits of analogies between complex formation and chemical reactions of the same organic compounds will clarify the underlying mechanisms.

EXPERIMENTAL

Pyridine-*N*-oxides and quinoline *N*-oxides [9, 27, 28] and styryl derivatives [29–31] were prepared as described in the above-cited works, the products physical constants agreed with the reference data.

Electron absorption spectra were recorded SF 2000–02 spectrophotometer. Stability constants of zinc(II) tetraphenylporphyrinate complexes with pyridine-*N*-oxides in chloroform (previously estimated from KFK-3 photocalorimeter data [32]) were evaluated with higher accuracy and processed according to [1]. Thermodynamic constants of complex formation were determined graphically using the equation below (as the first approximation, in the narrow temperature range of 273–313 K the ΔH and ΔS values were considered constant [33]).

$$\ln K_T = -\Delta H_{298}^0/RT + \Delta S_{298}^0/R.$$

Synthesis of $[\text{ZnL}_1\text{L}_2]$, L_1 : 5,10,15,20-tetraphenylporphyrin, L_2 : 4-chloroquinoline-*N*-oxide (I**).** Acetone solutions of zinc(II) tetraphenylporphyrinate (5×10^{-5} mol/L) and 4-chloroquinoline-*N*-oxide (5.5×10^{-5} mol/L), saturated at boiling point, were mixed,

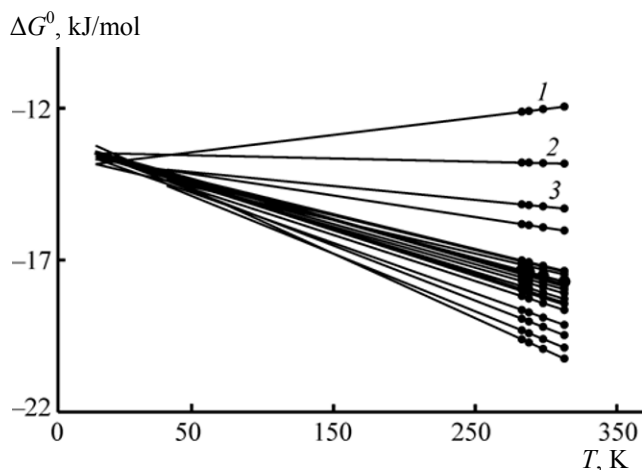


Fig. 5. ΔG of formation of the complex between zinc(II) tetraphenylporphyrinate and pyridine-*N*-oxides or quinoline-*N*-oxides in chloroform as function of temperature. (1) 4-NPyO, (2) 4-NQO, and (3) 3-COOEtPyO.

and the formed precipitate was centrifuged off, washed with acetone (3×2 mL), and dried in air.

X-ray diffraction data on compound **I** ($\text{C}_{53}\text{H}_{34}\text{ClN}_5\text{OZn}$, $M = 857.67$) was collected with Bruker APEX2 diffractometer [34] (Mo- $K\alpha$ radiation, graphite monochromator, $\phi\chi$ and ω scanning, room temperature). Red crystal of $0.15 \times 0.09 \times 0.04$ mm. Triclinic, P-1 space group, $a = 10.3815(10)$ Å, $b = 13.0004(12)$ Å, $c = 15.8764(15)$ Å, $\alpha = 104.196(2)^\circ$, $\beta = 95.096(2)^\circ$, $\gamma = 101.090(2)^\circ$, $Z = 2$, $V = 2017.6(3)$ Å³, $d_{\text{calc}} = 1.412$ g/cm³, $\mu = 0.724$ mm⁻¹, $F(000) = 884$, $2\theta_{\text{max}} = 50^\circ$, $-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$; 16756 reflections were collected in total, 7111 of them being independent ($R_{\text{int}} = 0.0768$), 3822 independent reflections with $I > 2\sigma(I)$ were registered. Absorption was accounted for semiempirically according to the equivalents (SADABS software [35]).

The structure was solved by combination of direct method and the differential Fourier syntheses (all calculations were carried out in SHELXS-97 and SHELXL-97 programs [36]). The L_2 ligand was disordered between two positions in the 3 : 2 ratio. The population value was refined in the course of isotropic refining of structure with fixed thermal parameters of L_2 atoms and was left constant in further refinement. Hydrogen atoms of ligands were located from geometry considerations. The structure was refined by means of full-matrix mean squares method (F^2) in the anisotropic-isotropic (O, N, and C atoms of the disordered L_2 ligand) approximation accounting for hydrogen atom in *rider* model with thermal parameters

20% higher than the equivalent thermal parameters of the adjacent carbon atoms. In the course of refinement, the SAME card of SHELXL-97 program was used for the ligand L₂. Refining results (548 parameters, 43 limitations on the bond lengths) were as follows: $R_1 = 0.0566$, $wR_2 = 0.1071$ over the reflections with $I > 2\sigma(I)$; $R_1 = 0.1296$, $wR_2 = 0.1351$ over all reflections, $GOF = 0.957$, maximum and minimum peaks in the zero Fourier synthesis 0.404 and $-0.410 \text{ e}/\text{\AA}^3$. Structure data were deposited in a Cambridge bank of structure data, CCDC 846681.

REFERENCES

- Andreev, V.P., Vapirov, V.V., Nizhnik, Ya.P., Tunina, S.G., and Sobolev, P.S., *Russ. J. Org. Chem.*, 2010, vol. 46, no. 10, p. 1563.
- Andreev, V.P., Sobolev, P.S., Larkina, E.A., and Tkachevskaya, E.P., *Chem. Heterocycl. Comp.*, 2012, vol. 48, no. 3, p. 497.
- Litvinenko, L.M. and Oleinik, N.M., *Mekhanizmy deistviya organicheskikh katalizatorov. Osnovnoi i nukleofil'nyi kataliz* (Mechanisms of Action of Organic Catalysts. Basic and Nucleophilic Catalysis), Kiev: Naukova Dumka, 1984.
- Andreev, V.P., *Russ. J. Org. Chem.*, 2009, vol. 45, no. 7, p. 1061.
- Andreev, V.P., *Chem. Heterocycl. Comp.*, 2010, vol. 46, no. 2, p. 184.
- Johnson, C.D., Katritzky, A.R., Ridjewell, B.D., and Shakir, N., *Tetrahedron*, 1965, no. 21, p. 1055.
- Garvey, R.G., Nelson, J.N., and Ragsdale, R.O., *Coord. Chem. Rev.*, 1968, no. 3, p. 375.
- Dega-Szafran, Z., Grundwald-Wyspianska, M., Kania, A., Kosturkiewicz, Z., Tykarska, E., and Szafran, M., *J. Mol. Struct.*, 1995, no. 356, p. 169.
- Andreev, V.P., *Doctoral (Chem.) Dissertation*, Moscow, 2007.
- Shreder, G., Rybachenko, V.I., Chotyi, K.Yu., Kovalenko, V.V., Grebenyuk, L.V., Lenska, B., Eitner, K., *Russ. J. Gen. Chem.*, 2003, vol. 73, no. 3, p. 455.
- Budu, G.V. and Thoryak, A.N., *Zh. Neorg. Khim.*, 1980, vol. 25, no. 4, p. 1006.
- Becker, H.G.O., *Introduction to Electronic Theory of Organic Reactions*, Berlin: Deutscher Verlag der Wissenschaften, 1974.
- Andreev, V.P. and Sobolev, P.S., *Russ. J. Bioorg. Chem.*, 2012, vol. 38, no. 2, p. 211.
- Andreev, V.P., Sobolev, P.S., and Zaitsev, D.O., *Russ. J. Org. Chem.*, 2012, vol. 48, no. 6, p. 772.
- Dneprovskii, A.S. and Temnikova, T.I., *Teoreticheskie osnovy organicheskoi khimii* (Theoretical Basis of Organic Chemistry), Leningrad: Khimiya, 1991.
- Andreev, V.P., Nizhnik, Ya. P., and Lebedeva, N.Sh., *Russ. J. Org. Chem.*, 2008, vol. 44, no. 6, p. 906.
- Allen, F.H., *Acta Cryst. (B)*, 2002, vol. 58, p. 380.
- Andreev, V.P., Vapirov, V.V., Nizhnik, Ya.P., Ale-shina, L.A., and Semenova, T.A., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 5, p. 973.
- Popov, A.F., Matveev, A.A., Koblik, I.V., Savelova, V.A., and Matvienko, V.N., *Zh. Org. Khim.*, 1996, vol. 32, no. 4, p. 609.
- Matveev, A.A., Koblik, I.V., Popov, A.F., Savelova, V.A., and Matvienko, V.N., *Russ. J. Org. Chem.*, 1998, vol. 34, no. 2, p. 271.
- Rybachenko, V.I., Chotyi, K.Yu., Kovalenko, V.V., and Shreder, G., *Russ. J. Gen. Chem.*, 2001, vol. 71, no. 5, p. 6786.
- Rybachenko, V.I., Chotyi, K.Yu., Kovalenko, V.V., and Shreder, G., *Russ. J. Phys. Chem., A*, 2003, vol. 77, no. 10, p. 1695.
- Rybachenko, V.I., Shreder, G., Chotyi, K.Yu., Lenska, B., and Red'ko, A.N., *Russ. J. Org. Chem.*, 2004, vol. 40, no. 3, p. 412.
- Rybachenko, V.I., Shreder, G., Chotyi, K.Yu., Kovalenko, V.V., Red'ko, A.N., and Lenska, B., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 6, p. 1241.
- Rybachenko, V.I., Shreder, G., Chotyi, K.Yu., Lenska, B., Red'ko, A.N., and Kovalenko, V.V., *Russ. J. Org. Chem.*, 2005, vol. 41, no. 5, p. 774.
- Andreev, V.P., Sobolev, P.S., Zaitsev, D.O., Remizova, L.A., and Tunina, S.G., *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 6, p. 1157.
- Ochiai, E., *Aromatic Amine Oxides*, Amsterdam: Elsevier, 1967, p. 444.
- Andreev, V.P., Kalistratova, E.G., and Ryzhakov, A.V., *Chem. Heterocycl. Comp.*, 1996, vol. 32, no. 4, p. 449.
- Andreev, V.P., Ryzhakov, A.V., and Tekanova, S.G., *Chem. Heterocycl. Comp.*, 1995, vol. 31, no. 4, p. 453.
- Brink, C.v.d.M. and de Jager, P.J., *Tydskr. Natuurwet*, 1963, no. 3, p. 74.
- http://www.patika.ru/Poisk_po_nomeru_FIPS.html.
- Andreev, V.P., Nizhnik, Ya.P., Bezruchko, D.G., and Morozov, A.K., *Russ. J. Gen. Chem.*, 2005, vol. 75, no. 8, p. 1309.
- Fisicheskaya khimiya* (Physical Chemistry), Nikol'skii, B.P., Ed., Leningrad: Khimiya, 1987.
- Bruker APEX2 and SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
- Sheldrick G.M., *SADABS*, University of Gottingen, Germany, 1997.
- Sheldrick G.M., *Acta Cryst. (A)*, 2008, vol. 64, p. 112.