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Effect of Macrocycle Deformation and Electronic Effects of Substituents on the Stability of Zinc-5,15-di(*o*-nitrophenyl)octaalkylporphyrin Molecular Complexes

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Abstract—The process of intermolecular interaction of zinc-5,15-di(*o*-nitrophenyl)-octaalkylporphyrin with nitrogen-containing bases of various sturctures was studied using the method of absorption spectroscopy. A dependence of stability of axial zinc-porphyrin complex on electronic effects of nitro groups and basic properties of extra ligand is revealed. By quantum-chemical PM3 method geometric structure and energetic characteristics of optimized molecules of zinc-porphyrin and its axial complexes was calculated. The influence of conformational effects of the porphyrin ligands on the strength of σ-bond of zinc with nitrogen atom of the nitrogen base (Zn–N_L) was revealed. It was established that the formation of the Zn–N_L bond proceeded with the change in the type and degree of deformation of the macrocycle in the molecular complex. Correlations between the calculated values of energy of Zn–N_L bond and stability of the axial complexes were found.

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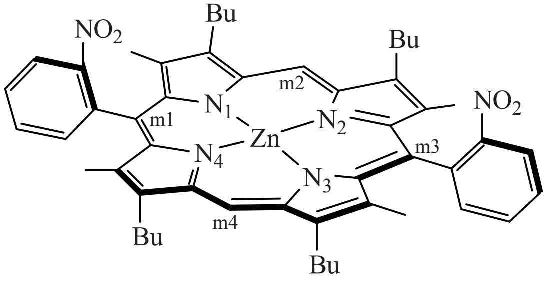
Among the methods of controlling the properties of porphyrins an important one is their modification by introduction of substituents of certain type (electron-releasing and withdrawing, hydrophilic, lipophilic, etc.) to the structure of the macrocycle. Besides the electronic factors, increased attention is paid now to the effect of deformational factor on the properties of metalloporphyrins, spectral and coordination characteristics first of all.

This work continues our systematic investigations of coordination properties of sterically hindered metalloporphyrins in reactions with organic bases (L). We studied effect of nitro groups and conformational effects of porphyrin macrocycle on the properties of zinc-5,15-di(*o*-nitrophenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin [ZnP(I)] in the reaction of axial binding with imidazole (Im), 2-methylimidazole (2-MeIm), 2-methylbenzimidazole (2-MeBzI), pyridine (Py), quinoline (Hi), 3, 5-dimethylpyrazole (DMP), dimethylformamide (DMF), pyridazine (Prd), pyrimidine (Prm), and pyrazine (Prz). The study was carried out using the spectrophotometric titration [1] and computer simulation [2–4] allowing prediction of the process course and character, the estimation of the structure, and state of reagents and reaction products.



ZnP(I)

The axial binding of zinc-porphyrin with an organic base in benzene at 298K leads to the formation of a complex with composition $(L)_nZnP(I)$. The reaction proceeds almost instantly and leads to the shift of absorption bands (B, Q_1 and Q_2) in electron absorption spectrum of the metalloporphyrin (EAS) and to the change in their intensity (Fig. 1). Such variations in the

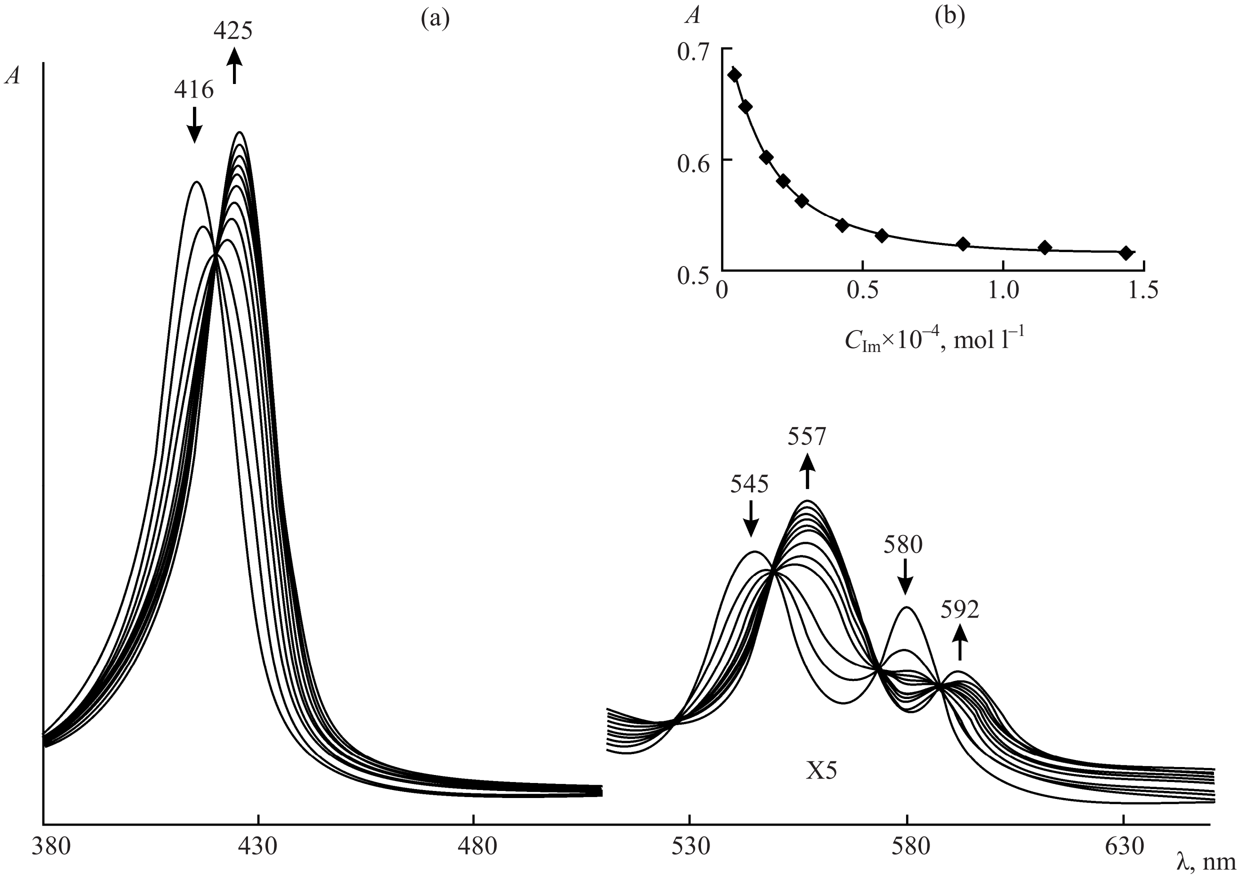


Fig. 1. (a) Changes in electron absorption spectra of ZnP(I) at the reaction with imidazole: (*1*) ZnP without imidazole (c_{ZnP} = 3.9×10^{-6} mol l^{-1}); (*2–11*) ZnP with imidazole at varied concentration (c_{ZnP} = 3.9×10^{-6} mol l^{-1}; c_{Im} =5.7×0^{-6}–1.4×10^{-4} mol l^{-1}); (*12*) ZnP with imidazole excess (2.8×10^{-3} mol l^{-1}) in benzene; (b) The corresponding titration curve at Δλ = 413 nm.

spectrum of the complex allow the application of spectral methods to the evaluation of the qualitative and quantitative characteristics of the process of intermolecular interaction.

The composition of the formed zinc complex was estimated from the linear plot log [$(A_p - A_0)/(A_\infty - A_p)$] on log c_L [1] (Fig. 2). The slope (tan α) of these strait lines for compounds $(L)_n$ZnP(I), where L = Im, 2-MeIm, 2-MeBzIm, Py, DMP, Hi, Prd, Prm and DMF falls in the range 0.9–1.1, that is, equals unity within the experimental error (n = 1). For the complex with pyrazine, tgα equals 1.45 (n = 1.5). Thus, the structure of the molecular complexes corresponds to the types (L)ZnP and $(L)_3(ZnP)_2$. The structure $(Prz)_3[ZnP(I)]_2$ becomes possible owing to the relatively low basicity of the porphyrin ligand (due to the electronic effect of nitro groups and a weak deformation of the macrocycle) and to the presence of two reaction centers in the nitrogen-containing base with an appropriate orientation for the axial binding.

The comparison of the obtained quantitative characteristics of the reaction of zinc-porphyrin axial binding with organic bases (Table 1) allows to reveal the following sequence of stability of molecular complexes: (Im)ZnP(I) > (2-MeIm)ZnP(I) > (Py)ZnP(I) > (DMP)ZnP(I) > (DMF)ZnP(I). The trend obtained is caused by the decrease in basic properties of axial ligand in going from imidazole to dimethylformamide. The basicity is indicated by the values of pK_{BH+} [5]. The decrease in stability (K_{stab}) of axial complexes (Hi) ZnP(I) and (2-MeBzIm)ZnP(I) as compared with (Py) ZnP(I), (DMP)ZnP(I) and the similarity of the values of constants for (2-MeIm)ZnP(I) and (Py)ZnP(I) (Table 1) results from the fact that the formation of Zn–L bond leads to the appearance of steric hindrances due to the bulky structure of 2-methylimidazole, quinoline and 2-methylbenzimidazole.

In the case of reactions with dibasic compounds the stability of (Prm)ZnP(I) complex is higher than that of (Prd)ZnP(I) (Table 1). We believe that in going from

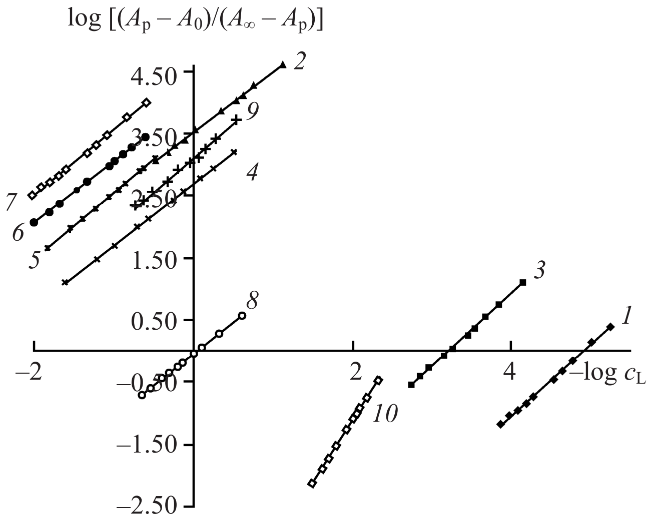


Fig. 2. Plot log [(A_p – A_0)/(A_∞ – A_p)] vs. log c_L for the intermolecular interaction between ZnP and (*1*) Im, (*2*) 2-MeIm, (*3*) 2-MeBzI, (*4*) Py, (*5*) Hi, (*6*) DMP, (*7*) DMF, (*8*) Prd, (*9*) Prm, and (*10*) Prz. A_0, A_p, A_∞ are optical density of solutions at the operating wavelength of metalloporphyrin, equilibrium mixture at certain ligand concentration, and of ligand, respectively.

the water phase into the organic solvent many nitrogen-containing bases can change the basicity index. As known, the regularities in the change of p$K_{\text{BH+}}$ in inert organic solvents are similar to those in the gas phase [6]. Therefore we calculated using PM3 method [7] the proton affinity (E_{prot}) in gas phase for all the studied bases (Table 1). Finally we found that E_{prot} of pyridazine is slightly below that of pyrimidine and pyrazine.

The orientation of the second nitrogen atom in (Prd)ZnP(I) complex also contributes to the decrease in the complex stability. The closeness of the second nitrogen atom (in the *ortho* position) to the reaction center leads to the effect of its repulsion and hence of repulsion of the whole molecule of the base by the nearest intracyclic nitrogen atoms of metalloporphyrin.

The absence of molecular complex with pyrazine in the stability series is due to another type of structure of $(\text{Prz})_3(\text{ZnP(I)})_2$. It is important to note that to the existence of this structure contributes energetically also the profitable proton affinity of pyrazine at the double protonaton (at the second nitrogen atom). The corresponding value of E_{prot} is higher than in pyridazine and pyrimidine by 22.63 and 3 kcal mol^{-1}, respectively.

The proton affinity of basic nitrogen-containing compounds suffers practically no change at the transfer from water to gas phase. Bulky molecules form an exclusion: their proton affinity is slightly higherin gas than in water (Table 1). With accounting for the calculated characteristics of the nitrogen-containing bases the above sequence of stability is transformed into the following sequence: (Im)ZnP(I) > (Py)ZnP(I) > (DMP)ZnP(I) > (Prm)ZnP(I) > (Prd)ZnP(I) > (DMF) ZnP(I).

Using the data of Table 1 we found the following correlations between log $K_{\text{stab.}}$ and p$K_{\text{BH+}}$, and between log K_{stab} and E_{prot}:log $K_{\text{stab}} = 2.4376e(_{0.1023\text{p}K_{\text{BH+}}})$ (correlation coefficient $r = 0.98$) and log $K_{\text{stab}} = 0.1054e(0.0227E_{\text{prot}})$ ($r = 0.99$) (Figs. 3 and 4). Also,

Table 1. Thermodynamic characteristics of molecurar complexes ZnP(I)

Complex	K_{stab}(298 K)×10^{-3}, mol^{-1} l	p$K_{\text{BH+}}$ [5]	$-E_{\text{prot of base}}$, kcal mol^{-1}	$-E_{\text{b M–NL}}$, kcal mol^{-1}	$\Delta\lambda_{\max\,(\text{Q1, Q2})}$, nm
(Im)ZnP	109.00±11.70	6.65	169.36	23.56	12
(2-MeBzIm)ZnP	1.57±0.25	6.19	175.21	12.09	10
(2-MeIm)ZnP	18.60±8.14	5.89	173.06	18.61	11
(Py)ZnP	13.60±1.16	5.29	162.79	18.25	10
(Hi)ZnP	3.66±0.55	4.94	168.72	12.42	9
(DMP)ZnP	5.89±0.80	4.27	157.60	15.97	9
(DMF)ZnP	0.50±0.08	0.92	142.92	4.18	6
(Prd)ZnP	1.31±0.22	2.33	148.49	11.91	8
(Prm)ZnP	4.15±0.36	1.3	155.54	15.03	9
$(\text{Prz})_3(\text{ZnP})_2$	2.41±0.45	0.6	151.77	3.76	8
1 macrocycle				0.17	
2 macrocycle				3.43	
				0.68	

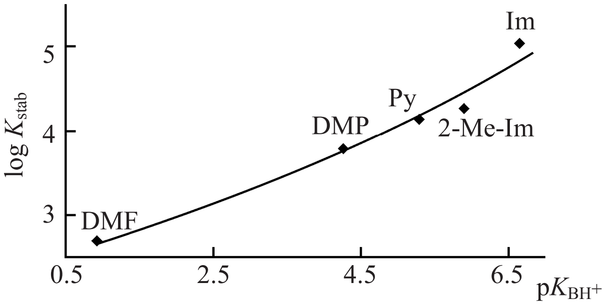


Fig. 3. Plot of the complex (L)ZnP(I) stability vs K_{BH+} of organic base.

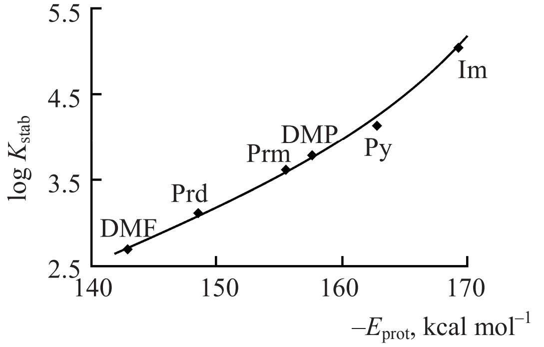


Fig. 4. Plot of stability of (L)ZnP(I) complex vs. the E_{prot} of organic bases calculated by PM3 quantum-chemical method.

there is a dependence between the stability of the molecular complex and the value of shift ($\Delta\lambda_{max}$) of the maxima of the main absorption bands (Q_1 and Q_2) in the respective electronic spectrum (Fig. 5). This dependence is also of symbatic character, and is described by the equation log $K_{stab} = 1.5032e(0.0994\Delta\lambda)$ ($r = 0.98$). This dependence can be used for qualitative estimation of stability of the complexes.

Note that unlike the earlier studied *meso*-diphenyl-substituted zinc-porphyrins {Zn-5,15-di(*p*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin [ZnP(II)], "overlapped" Zn-5,15-[2,5-bis(2'-phenyleneoxymethylene)-1,4-dimethoxybenzene]-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin {ZnP(III))} [8–10] the shape of the plots obtained for the molecular complexes ZnP(I) is close to linear. In our opinion this is connected with a low steric strain in the ZnP(I) macrocycle.

Comparing the values of $K_{stab.}$ for compounds (L) ZnP(II), (L)ZnP(III) and (L)Zn-5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin ((L)ZnP(IV)) studied in [8–10] and of the molecular complexes ZnP(I) (Table 1) we can note a significant higher stability of the latter. This is caused by the presence of electron-acceptor substituents in *o*-positions and a low degree of deformation of ZnP(I) macrocycle leading to higher positive charge on the zinc atom. Eventually this results in a higher ability of the metalloporphyrin to coordinating a base with the formation of stronger metal–axial ligand σ-bond (Zn–N_L).

Proceeding from the calculated characteristics obtained by quantum-chemical PM3 method we noted the effect of steric screwing of the ZnP(I) macrocycle on its structure and its properties in the reaction of axial binding with organic bases.

Analysis of the results of calculation shows that the molecule of ZnP(I) is not planar: it has deformation of a saddle type (Table 2, Figs. 6, 7). Phenyl substituents are tilted toward the *XY* plane containing N_4 coordination center at the angle 86°–88°. The butyl substituents in the macrocycle are oriented alternatively up and down relatively to the average plane of the molecule (Fig. 6). The N_4 plane has a rhombic shape that is consistent with the data of X-ray structural analysis [11]. Its perimeter equals to 11.6536 Å. Average deviation of the macrocyle skeleton atoms from its average plane along *Z* axis ($|\Delta Z_{av}|$) equals to 0.0934 Å. For ZnP(II) and ZnP(III) the values of $|\Delta Z_{av}|$ are 0.1585 Å and 0.2837 Å respectively. The deformation screwing grows in the series: ZnP(I) < ZnP (II) < ZnP(III). By the comparison of stability of these zinc-porphyrin molecular complexes the following sequence is obtained: ZnP(III)< ZnP(II) < ZnP(I) [8–10] (Tables 1 and 2). The absence of ZnP(IV) in these series is due to the electronic activity of OCH_3 groups and to the steric factor originating from the inclination of these groups toward N_4 plane narrowing the cavity of coor-dination interaction.

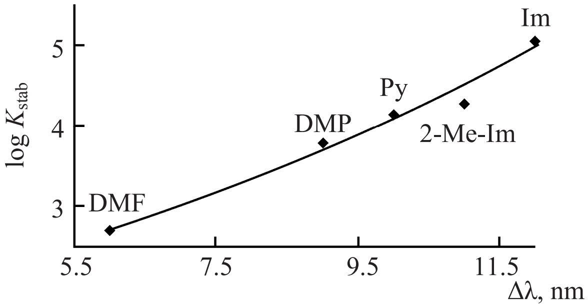


Fig. 5. Plot of log K_{stab} of complex (L)ZnP(I) vs. the values of shift of basic absorption band in electronic spectra.

Table 2. Selected geometric characteristics of ZnP(I) and its molecular complexes

Complex	Bond length, Å							
	Zn–N_1 Zn–N_3	Zn–N_2 Zn–N_4	N_1–N_3 N_2–N_4	C_{m1}–C_{m3} C_{m2}–C_{m4}	Zn–N_L	Zn–Ct	P^a	$l_{N-N}{}^b$
ZnP(I)	2.0346	2.0630	4.0679	7.1245		0.0355	11.6536	10.2797
	2.0340	2.0868	4.1714	6.8150				
(Im)ZnP	2.1203	2.1013	4.1362	7.1199	2.0829	0.3982	11.7043	10.2847
	2.0913	2.1335	4.1443	6.7831				
(2-MeBzIm)ZnP	2.1266	2.1050	4.1387	7.1214	2.1516	0.4480	11.6394	10.7581
	2.1080	2.1302	4.1142	6.7368				
(MeIm)ZnP	2.0910	2.1271	4.1252	7.1225	2.1071	0.4121	11.7012	10.1917
	2.1157	2.1109	4.1539	6.7798				
(Py)ZnP	2.1168	2.1082	4.1347	7.1208	2.1075	0.3972	11.7048	10.5115
	2.0935	2.1316	4.1557	6.7991				
(Hi)ZnP	2.0979	2.1386	4.1051	7.1557	2.1471	0.4573	11.7169	10.3859
	2.1079	2.1533	4.1851	6.7771				
(DMP)ZnP	2.1038	2.1124	4.1254	7.1119	2.1203	0.4011	11.6993	10.9310
	2.0989	2.1234	4.1519	6.7965				
(DMF)ZnP	2.1327	2.0990	4.1389	7.1213	2.2179	0.4795	11.6872	10.7277
	2.1059	2.1409	4.1300	6.7902				
(Prd)ZnP	2.1089	2.0865	4.1399	7.1190	2.1590	0.3903	11.6956	10.2102
	2.0913	2.1172	4.1348	6.7874				
(Prm)ZnP	2.1162	2.1020	4.1337	7.1224	2.1290	0.3817	11.7021	10.5648
	2.0874	2.1320	4.1446	6.7919				
$(Prz)_3(ZnP)_2$	2.0917	2.0794	4.1992	7.1267	2.2246	0.1774	11.8226	10.3691
1 macrocycle	2.1161	2.1001	4.1645	6.7988	2.5093			
	2.0945	2.0984	4.2000	7.1392	2.5024	0.1721	11.8199	10.3003
2 macrocycle	2.1127	2.0782	4.1624	6.7799	2.2300			

[a] Perimeter of N_4 coordination plane; [b] distance between nitrogen atoms of NO_2 groups.

Proceeding from the calculated characteristics we conclude that the type of the molecular complex formed at the axial binding of metalloporphyrin and organic base is respectively (L)ZnP(I) and $(Prz)_3$·$[ZnP(I)]_2$, in good agreement with the experimental data.

Appearance of Zn–N_L bond leads to a change in the structural mode of the coordination node from planar to tetragonal bipyramid with rhombic N_4 base. Notable steric screwing of the zinc-porphyrin macrocycle (Figs. 6 and 7, Table 2) is observed. The deformation mode is changed from saddle to a mixed: dome (dominates) with a small fractions of saddle and riffle (Fig. 7). It should be noted that while deformations of different (L)ZnP(I) complexes are of the same type the bond angles in their methylene bridges and angles of inclination of pyrrole fragments toward average macrocycle plane are different (Fig. 7). Axial binding of base with the metalloporphyrin leads also to extension of coordination plane N_4 by weakening of the bond between zinc atom and intracyclic nitrogen atoms of the macrocycle. Also a change occurs in the distance between nitrogen atoms of NO_2 groups (Table 2) and in the values of the angle of inclination of phenyl fragments to *XY* plane by 2°–20°.

For the complex $(Prz)_3[ZnP(I)]_2$ a presence is characteristic of two nonplanar macrocycles with dominating dome type deformation (Figs. 6 and 7). The angle of inclination of phenyl fragments to *XY* plane is 84°–85° in both the zinc-porphyrin molecules.

Analysis of the experimental and calculated data allows to note that the value of K_{stab} correlates with the Zn–N_L bond length. Increase in the strength of Zn–N_L σ-bond in the coordination center favors increase in the stability of the molecular complexes (Tables 1 and 2).

However, there is no dependence between deviation of zinc atom from N_4 plane (Ct–Zn) and Zn–N_L bond length (Table 2). In the molecular complex a *cis* effect is noted. The increase in the Zn–N_L bond strength leads to the weakening of the bond between the zinc and porphyrin nitrogen atom (Zn–N_p) (Table 2).

The energies of formation of Zn–N_L bond (E_{bond}) in the composition of the molecular complex calculated by quantum-chemical method vary in parallel with its stability (Table 1). In the series of the complexes: (DMF)ZnP(I) < (Prd)ZnP(I) < (Prm)ZnP(I) < (DMP) ZnP(I) < (Py)ZnP(I) < (2-MeIm)ZnP(I) < (Im)ZnP(I) the E_{bond} grows. This points to the increase in the stability of compounds in going from dimethylformamide to imidazole.

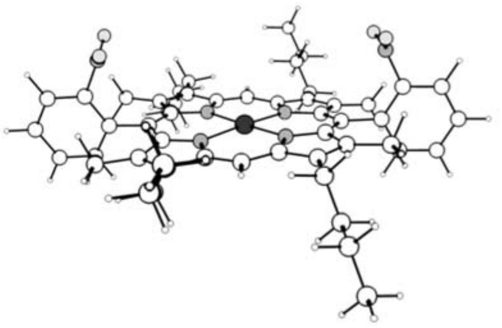
On the basis of the above said it can be concluded that both electronic and deformational factors contribute considerably to the coordination properties of the studied zinc-porphyrins in their reactions with organic bases.

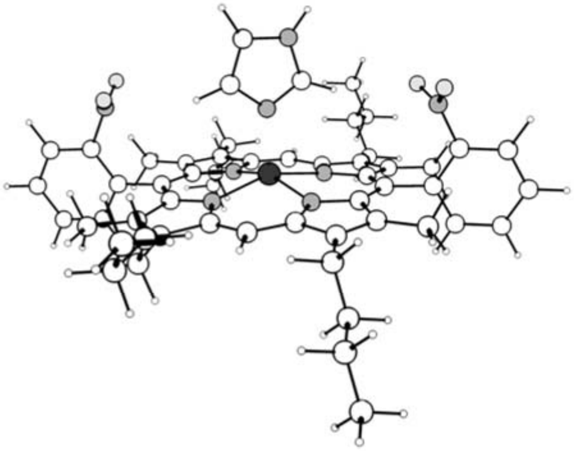
EXPERIMENTAL

Reaction ZnP + L_n = $Zn(L)_nP$ was carried out at 298 K using benzene as an inert solvent. The experimental and calculation procedures are described in detail in [1, 12–14]. Optical density of series of solutions with constant concentration of metalloporphyrin and varied concentration of extra ligand was measured at the operating wavelengths 413–417 and 421–426 nm. The measurements were carried out at 298K using cells of 1 cm thickness. Errors in the temperature control are 1 K or less. Electronic absorption spectra were registered on a Cary-50 spectrophotometer in the range 380 to 700 nm. The spectra were registered as diagrams and tables for further mathematic treatment.

The treatment of dependences was carried out by the least square method. Relative error in determination of $K_{stab.}$ value is not higher than 8–10%.

The quantum-chemical calculations were carried out by PM3 method [2–4, 7] with PC version [15] of Gamess program package [16]. The condition of cancellation of the calculation was the value of gradient 0.002 kJ mol^{-1} $Å^{-1}$. Initial data were prepared and results of calculation were treated using ChemCraft version 1.3 program (author G.A. Zhurko). As initial approximation, the bond and angles of porphyrin macrocycle were taken those of an average metalloporphyrin structure [11], those of phenyl rings and alkyl substituents at porphyrin and nitrogen bases were taken from [17]. The butyl substituents were designated in the initial approximation in the form of


ZnP(I)


(Im)ZnP(I)

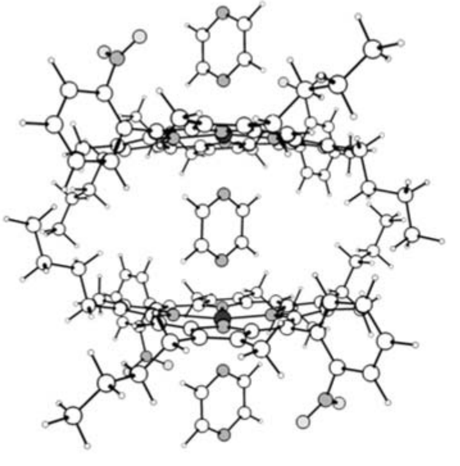

$(Prz)_3ZnP(I)_2$

Fig. 6. Structures of ZnP(I) and of its molecular complexes with imidazole and pyrazine (quantum-chemical PM3 calculation).

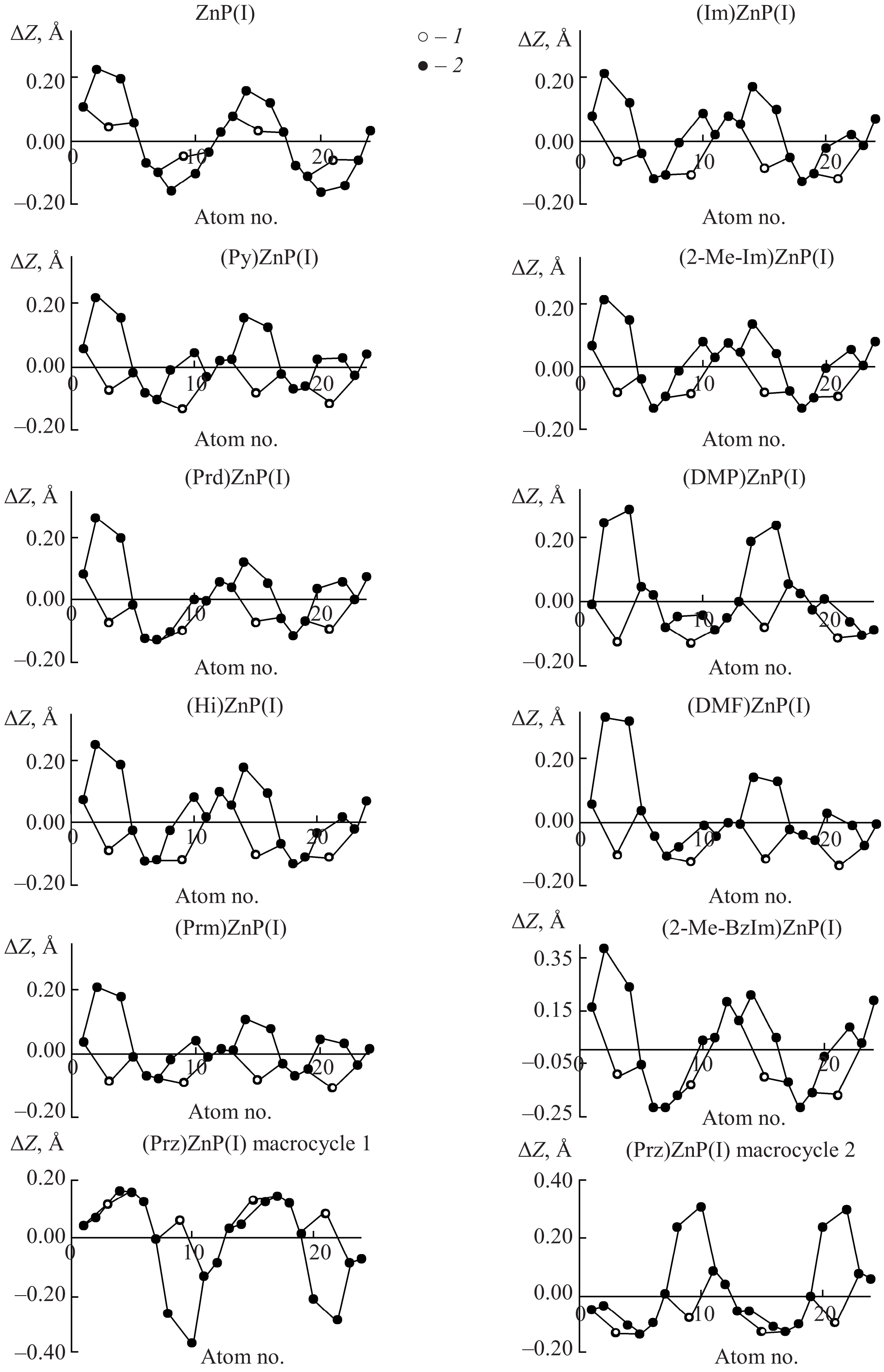


Fig. 7. Deviation of the skeleton atoms from the average plane of porphyrin macrocycle (ΔZ) for the complexes ZnP(I) and $(L)_n$ZnP(I) (quantum-chemical PM3 calculation): (*1*) nitrogen atoms and (*2*) carbon atoms.

frozen *trans* isomers. The average plane of phenyl rings was oriented at the right angle to the average macrocycle plane. Orientation of the nitrogen bases was assigned to provide orthogonal orientation of the average plane of axial ligand and average plane of the porphyrin macrocycle (for dimethylformamide parallel orientation) and the orientation of nitrogen atom with its lone electron pair toward central metal atom.

5,15-Di(*o*-nitrophenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin was synthesized [18] and provided by Professor Semeikin (Ivanovo Chemical Technological University).

Zinc complex of 5,15-di(*o*-nitrophenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin [ZnP(I)] was synthesized by th reaction of porphyrin with 10-fold excess of zinc acetate in benzene at 40–50 min of reflux. The reaction was monitored by registration of electron absorption spectra of the reaction mixture. Disappearance of porphyrin absorption bands and appearance of those of its zinc complex allowed monitoring of the reaction progress. After the reaction completion the reaction mixture was cooled and excess of salts was removed by extraction with water. The obtained solution of zinc complex in benzene was evaporated. The zinc complex was purified by chromatography on silica gel (eluent benzene) followed by recrystallization from chloroform. Electronic absorption spectrum, λ_{max}, nm (log ε): 580.0 (4.16), 545.0 (4.24) 416.0 (5.28) (benzene). R_f (Silufol): 0.85 (benzene). ^{1}H NMR spectrum ($CDCl_3$, internal HMDS), δ, ppm: 10.16 s (*meso*-H), 8.41 m, 8.16 m, 7.99 m (PhH), 3.99 t, 2.11 m, 1.65 m, 1.14 m (C_4H_9) 2.43 s (CH_3).

ACKNOWLEDGMENTS

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