

Axial Coordination of Imidazoles by *meso*-Nitro Substituted Zn-Octaethylporphyrins

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Dedicated to Academician A. I. Konovalov on the occasion of his 80th birthday

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The study of complex formation between mono-, di-, tri- and tetranitro meso-substituted Zn-octaethylporphyrins with imidazole and 1-methylimidazole by UV-Vis titration method showed that binding ability of the Zn-porphyrins towards investigated N-containing small organic molecules depends on the number of electron-withdrawing nitro-groups in the macrocycle. Taking into account the fact that binding is accompanied by a clear and easily identifiable response in the UV-Vis spectra of the reaction mixture, tri- and tetranitro substituted Zn-porphyrins could be considered as molecular optical sensing devices for small heterocyclic substrates.

Keywords: Zn-octaethylporphyrin, *meso*-nitro substituted porphyrins, electron withdrawing groups, axial coordination, binding ability, stability constant.

Аксиальная координация имидазолов мезо-нитрозамещёнными Zn-октаэтилпорфиринами

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Исследованием комплексообразования моно-, ди-, три- и тетра мезо-замещённых Zn-октаэтилпорфиринов с имидазолом и 1-метилимидазолом методом спектрофотометрического титрования показано, что комплексообразующая способность перечисленных Zn-порфиринов по отношению к исследованным N-содержащим малым органическим молекулам определяется числом электроноакцепторных нитро-групп в макроцикле. Принимая во внимание то обстоятельство, что комплексообразование сопровождается четким и легко идентифицируемым откликом в спектрах поглощения реакционной системы, три- и тетра-нитро замещённые Zn-октаэтилпорфирины могут рассматриваться в качестве молекулярных оптических устройств для распознавания малых гетероциклических субстратов.

Ключевые слова: Zn-октаэтилпорфирин, мезо-нитрозамещённые порфирины, электроноакцепторные группы, аксиальная координация, связывающая способность, константа устойчивости.

Introduction

Axial coordination in metalloporphyrins is a main driving force of processes of molecular recognition and self-organization of tetrapyrrolic macrocycles into supramolecular ensembles. According with the literature^[1-4] and our own experimental data^[5-11] it is mainly determined by a structure of porphyrin macrocycle, basicity of an extra-ligand and nature of a solvent. Among the listed factors a structure of tetrapyrrole macrocycles renders the highest influence on the metalloporphyrin's ability to additional coordination of a ligand, first of all, due to an electronic influence of the substituents. Besides, a chemical modification porphyrin structure can create steric hindrances for ligands axial coordination, or, on the contrary, form intramolecular cavities favorable for additional ligands binding.^[11-15] Stability constants of complexes between the correspondingly modified porphyrins and organic ligands of different nature, in comparison with porphyrins of relatively simple structures, can differ by several orders.

This work is devoted to UV-Vis studying of the influence of step-by-step *meso*-nitro substitution in Zn-octaethylporphyrin on its binding ability towards imidazole (**L1**) and 1-methylimidazole (**L2**) in toluene.

Experimental

Zn-5-nitro-2,3,7,8,12,13,17,18-octaethylporphyrin (**2**), Zn-5,15-dinitro-2,3,7,8,12,13,17,18-octaethylporphyrin (**3**), Zn-5,10,15-trinitro-2,3,7,8,12,13,17,18-octaethylporphyrin (**4**) and Zn-5,10,15,20-tetranitro-2,3,7,8,12,13,17,18-octaethylporphyrin (**5**) were obtained according to the known procedures.^[16,17] 2,8,12,18-Tetrabutyl-3,7,13,17-tetramethylporphyrin (**6**), 5,15-diphenyl-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (**7**) and 5,10,15,20-tetraphenyl-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (**8**) were obtained according to^[18]. Zn-2,3,7,8,12,13,17,18-octaethylporphyrin (**1**) was obtained by complexation of the corresponding porphyrin ligand (2,3,7,8,12,13,17,18-octaethylporphyrin) with zinc acetate in boiling dimethylformamide and showed the best correlation with the spectral data presented for this compound according to^[19]. 2,3,7,8,12,13,17,18-Octaethylporphyrin, imidazole, 1-methylimidazole and toluene from Sigma-Aldrich were used without purification. UV-Vis spectra of the porphyrinates and their evolution upon addition of the ligands were measured on a Carry 100 spectrophotometer.

The UV-visible absorption spectral studies reveal red shifted Soret and visible bands upon addition of the ligands to a solution of the investigated porphyrins confirming that the *N*-containing entity of the ligands binds to the Zn-cation of the coordination centre of the tetrapyrrolic macrocycle.

The stability constant of the metalloporphyrin complexes with the ligands in ratio of 1:1 (K_{assoc}) according to the literature^[7,8] were calculated based on spectrophotometric data at

two wavelengths (decreasing and increasing) using the following relationship:

$$K_{assoc} = \frac{[A-B]}{[A] \cdot [B]} = \frac{1}{[B]} \left(\frac{\Delta A_{i,\lambda_1}}{\Delta A_{o,\lambda_1}} \cdot \frac{\Delta A_{o,\lambda_2}}{\Delta A_{i,\lambda_2}} \right) \cdot M^{-1},$$

where, λ_1 is the decreasing wavelength, λ_2 is the increasing wavelength, $[A]$ is the Zn-porphyrin concentration, $[B]$ is the ligand concentration, ΔA_0 is the maximal change of the optical density at the given wavelength, ΔA_i is the change of the optical density of the solution at a given wavelength at a given concentration.

Results and Discussion

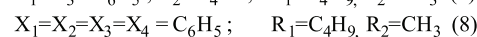
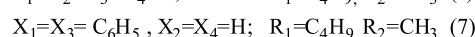
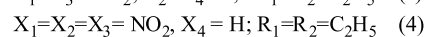
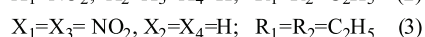
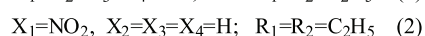
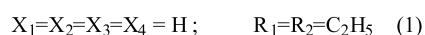
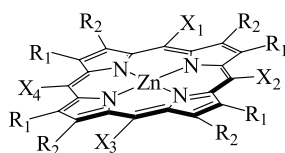
Axial coordination of **L1** and **L2** on Zn-porphyrins (**1-5**) is accompanied by characteristic red shift of absorption bands in the UV-Vis spectra of the system porphyrinate-ligand. It should be noted that upon complexation of the porphyrinates with the monodentate ligands, over a wide concentration range of the ligands ($C_L = 0 \div 3 \cdot 10^{-4}$ M), changes in the UV-Vis spectra of the reaction mixture occur with the formation of one family of spectral curves with one set of isosbestic points. The details of spectrophotometric titration upon investigation of the *host-guest* interactions are described in our previous works.^[7-10] The titration curve has one step, which indicates the formation of a single type of complexes in a ratio of 1:1. The changes in the UV-Vis spectra of the system **1-L1** and corresponding binding isotherms are depicted in Figures 1, 2 as an example.

It was found out that step-by-step *meso*-substitution of the tetrapyrrolic core by one (**2**), two (**3**), three (**4**) and four (**5**) nitro groups leads to the essential increasing of the stability constants of 1:1 complexes between the porphyrinates **2-5** and monodentate ligands **L1** and **L2** as compared with the similar complexes of porphyrinate **1** (Table 1, Figure 3).

Table 1. Stability constants of 1:1 complexes (K_{assoc} , M^{-1}) between porphyrinates **1-5** and monodentate ligands **L1**, **L2** in toluene, $C_{ZnP} = 1.1 \cdot 10^{-5}$ M.

No	L1	L2
1	25100	32800
2	41900	67200
3	88700	127000
4	188000	196700
5	294000	329000
6	25700	–
7	26200	–
8	26540	–

The error in determining of the stability constants was 5-7 %.^[18]



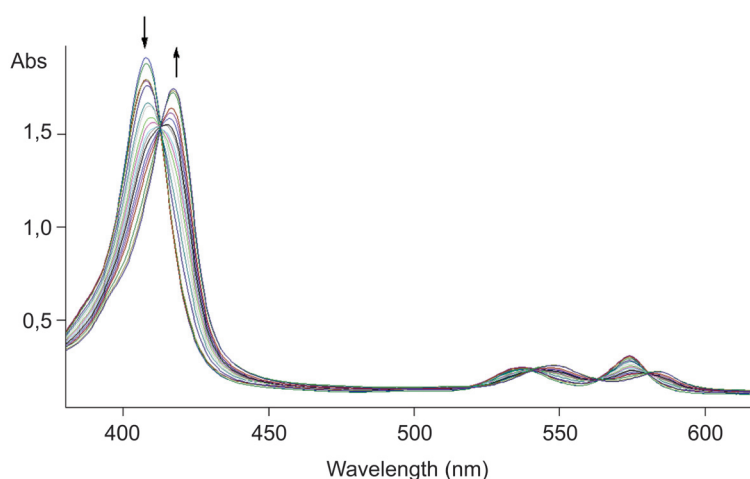


Figure 1. Changes in the UV-Vis spectra of the system **1-L1** in toluene at 20 °C, $C_1 = 1.0 \cdot 10^{-5}$ M.

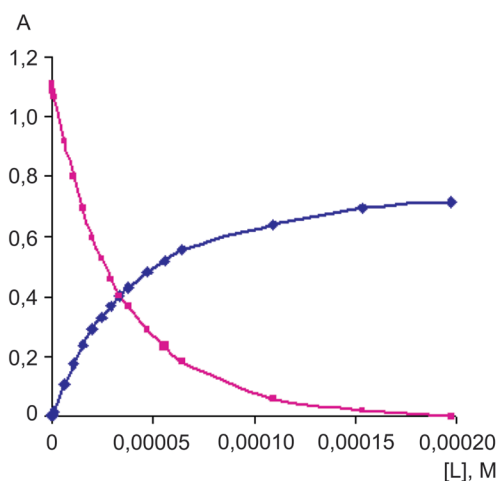


Figure 2. Binding isotherms of the system **1-L1** on the decreasing (400 nm) and the increasing (426 nm) waves lengths in toluene at 20 °C, $C_1 = 1.0 \cdot 10^{-5}$ M.

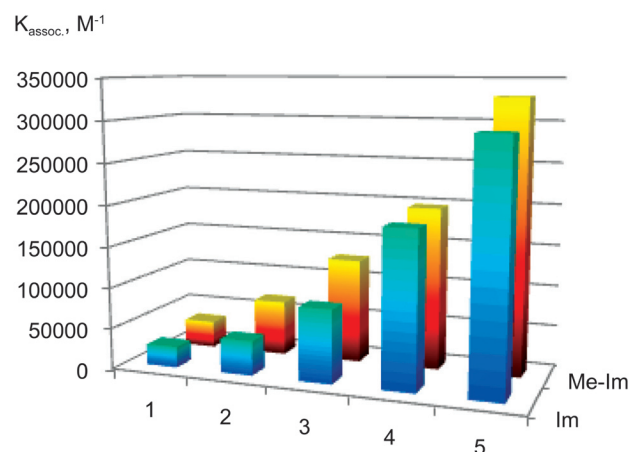


Figure 3. Dependence of the stability constants of porphyrinates **1-5** with the ligands **L1** and **L2** on the nature of small *N*-containing organic molecules in toluene, 25 °C.

It should be noted that *meso*-nitro substitution could have strong influence on a porphyrin π -electronic system both due to an electronic effect of the substituents, and deformation of the tetrapyrrolic macrocycle. Step-by-step introduction into the Zn-octaethylporphyrin of one, two, three and four nitro-groups has accompanied by essential distortion of the porphyrinate molecule. Red shift of absorption bands in UV-Vis spectra in going from **1** to **2-5** testifies in favor of this assumption (Table 2).

Similar dependence is known in the case of step-by-step *meso*-phenyl substitution in a porphyrin macrocycle.^[5] However, unlike *meso*-phenyl substitution of Zn-octaalkylporphyrins [in going from 2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (**6**) to 5,15-diphenyl-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (**7**) and 5,10,15,20-tetraphenyl-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin (**8**)] in the case of *meso*-nitro substituted Zn-porphyrinates **2-5** the chemical modification is accompanied

by essential increasing in binding ability of the porphyrinates towards the ligands **L1** and **L2** (Table 1).

Table 2. Position of the bands in UV-Vis spectra of Zn-porphyrins **1-5** in dichloromethane.^[16,17]

№	λ , nm				
1	331	402	490	532	569
2	350	401	497	534	573
3	352	404	503	539	576
4	264	360	413	510	571
5	260	370	426	520	580

Probably, the nitro-groups, except macrocycle deformation, have strong electronic influence on π -electronic system of tetrapyrrolic macrocycle. It is known that the higher is an electronic density of delocalized π -electronic

system of porphyrin macrocycle, the stronger are the N-Zn bonds of porphyrinate coordination center, and, as a result, donor-acceptor interactions between porphyrinate zinc cation and nitrogen atom of a ligand (Zn-L) is weaker.^[1] The acceptor nitro-groups, decreasing an electronic density of the π -electronic system, simultaneously increase a partial positive charge on the porphyrinate zinc cation and facilitate Zn-L interactions. The more nitro-groups are in a macrocycle, the higher is a corresponding binding constant (Table 1).

Conclusions

Thus, the influence of step-by-step *meso*-nitro substitution in Zn-octaethylporphyrin on its binding ability towards imidazole and 1-methylimidazole was investigated by the method of UV-Vis titration in toluene. The stability constants of the resulting complexes and concentration intervals of their existence were determined. Taking into account the fact that binding is accompanied by a clear and easily identifiable response in the UV-Vis spectra of the reaction mixture, tri- and tetranitro substituted Zn-porphyrins could be considered as molecular optical sensing devices for small heterocyclic substrates.

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