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Synthesis and Coordination Properties of the Zinc Complex of Dimeric Porphyrin in Reactions with Imidazole, 2-Methylimidazole, and the Pyridine in Benzene

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Abstract—Dimeric porphyrin(2,6-bis[15'-(3",5"-di-*tert*-butylphenol)-3',7',13',17'-tetramethyl-2',8',12',18-tetraethylporphin-5'-yl]-4-*tert*-buthylphenol) and its binuclear zinc complex were obtained from 4,4'-dimethyl-3,3'-diethyldipyrrolylmethane, 2,6-diformyl-4-*tert*-butylphenol and 3,5-di-*tert*-buthylbenzaldehyde. Coordina-tion properties of dimeric zincporphyrin in the intermolecular reaction with nitrogen-containing bases (imidazole, 2-methylimidazole, and pyridine) in benzene were studied. Geometry and electronic structure of the zincporphyrin and its molecular complexes were calculated by a quantum-chemical method. Energy characteristics of the intermolecular reaction of the dimeric zincporphyrin with bases were determined. The calculated energies of the central metal atom interaction with the nitrogen atom of an extra-ligand agree well with the stability of the Zn-porphyrin molecular complexes. The influence of the deformation distortions of the porphyrin ligand on the strength of the metal–extra-ligand σ-bond was established.

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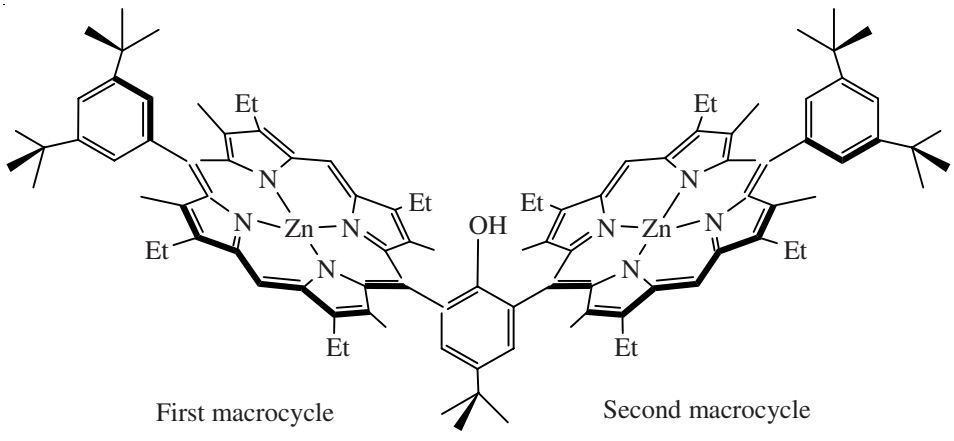
Properties of metalporphyrins are governed by their structural diversity, conformation transformations of macrocycles and the ability of a central metal atom to interact with various donor ligands [1–4]. In the present work we continue the study of the steric macrocycle stress influence on coordination properties of metalporphyrins. We describe here the synthesis of the dimeric zincporphyrin (ZnP), 2,6-bis[zinc 15'-(3'',5''-di-*tert*-butyl-phenyl)-3',7',13',17'-tetramethyl-2',8',12',18'-tetraethylporphin-5'-yl]-4-*tert*-buthyl-phenol with a slightly strained macrocycle and the regularities of its intermolecular interaction with nitrogen bases–extra-ligand [(L = imidazole (Im), 2-methylimidazole, and pyridine (Py)].



The reaction ZnP + L_n = Zn(L)$_n$P was carried out in benzene at 295 K, which was used owing to its inertness. This solvent does not solvate the metal atom and does not render essential influence on the ability of the metalporphyrin to coordinate an additional molecular ligand.

Coordination properties of dimeric ZnP were studied using spectrophotometric titration [5, 7–10] and computer simulation [11–14]. The spectrophotometric method allows evaluation of con-centrations of absorbing species, metalporphyrins and their extra-complexes, as their dilute solutions obey Bouguer–Beer law (1).

$$A = \varepsilon cl. \quad (1)$$

Here A is optical density of a solution; ε is molar absorption coefficient; c is concentration of absorbing material, M; l is width of a solution layer.

The constant of extra-complex stability was calculated by equation (2) for three-component equilibrium systems.

$$K_{st} = \frac{(A_{eq} - A_0)/(A_\infty - A_0)}{1 - (A_{eq} - A_0)/(A_\infty - A_0)} \times \frac{1}{(c_L - c^0_{MP})[(A_{eq} - A_0)/(A_\infty - A_0)]}. \quad (2)$$

Here c^0_{MP} is the initial concentration of a metalporphyrin in a solution; A_{eq} is optical density of an equilibrium solution; A_0 is optical density of a free metalporphyrin solution; A_0 is optical density of an equilibrium solution with the maximal extra-ligand concentration.

The formation of a binuclear complex (L)$_n$ZnP results in a red shift of the basic absorption bands of the chromophore in the electronic spectrum and in the variation of their intensity (Fig. 1), that allows us to use the spectral method in studying coordination properties of the dimeric zincporphyrins. Equilibrium in the metalporphyrin–base system is reached practically instantaneously. The coordination process, as well as any other reversible reaction, obeys the mass action law and is ruled by stability constant (3).

$$K_{st} = [(L)_nMP]/[MP][L]^n. \quad (3)$$

In spite of the fact that the retention of isobestic points in electronic spectra of complexes with extra-ligands proves the presence of two colored compounds in a solution under study, absorption spectra of metalporphyrins with one and two extra-ligands are very close to each other, and the displacement of the isobestic point is comparable with the experimental error. Therefore we used the Bent-French method [5] to determine a number of attached ligands. In all cases (coordination of Im, 2-MeIm, and Py) the dependences of log $[(A_{eq} - A_0)/(A_\infty - A_{eq}]$ on log c_L are linear. The slope of these straight lines is 1.052, 1.139, and 0.998, respectively, that corresponds to unity within the limits of experimental error (Fig. 2). Thus, a complex (L)ZnP is formed in the course of the inter-molecular interaction. The attachment of one base molecule, despite of the presence of two complex-forming centers, seems to be connected with certain hindrances caused by mutual screening of reaction centers by macrocycles arranged under an angle to each other. Possible orientation of a nitrogen base in (L)ZnP complexes will be considered below.

The resulting stability constants (K_{st}) and calculated structure and energy parameters of the zinc complexes are given in Tables 1 and 2. The analysis of these data allows us to estimate the strength of binding nitrogen bases with the dimeric Zn-porphyrin and to obtain the stability series: (Im)ZnP > (Py)ZnP > (2-MeIm)ZnP. This trend is caused by weakening basic properties of extra-ligands on passing from imidazole to pyridine and by steric hindrances (in the case of 2-MeIm the

Table 1. Stability constants of extra-complexes of dimeric zincporphyrin, shift of their characteristic absorption bands in benzene, and calculated energy of the zinc atom bond with the nitrogen atom of the base

Complex	K^{295}_{st}, M	pK_{ex}+[a]	Δλ, nm	E_b (Zn–N_L), kcal mol^{-1}
(Im)ZnP	52200±4780	6.65	11.0	–18.23[b], –18.11[c]
(Py)ZnP	5860±427	5.29	10.0	–14.94[b], –14.63[c]
(2-MeIm) ZnP	1950±179	5.89	7.9	–13.53[b], –13.49[c]

[a] The value found by the potentiometric method in water at 298 K [18]. [b] Isomer **A**. [c] Isomer **B**.

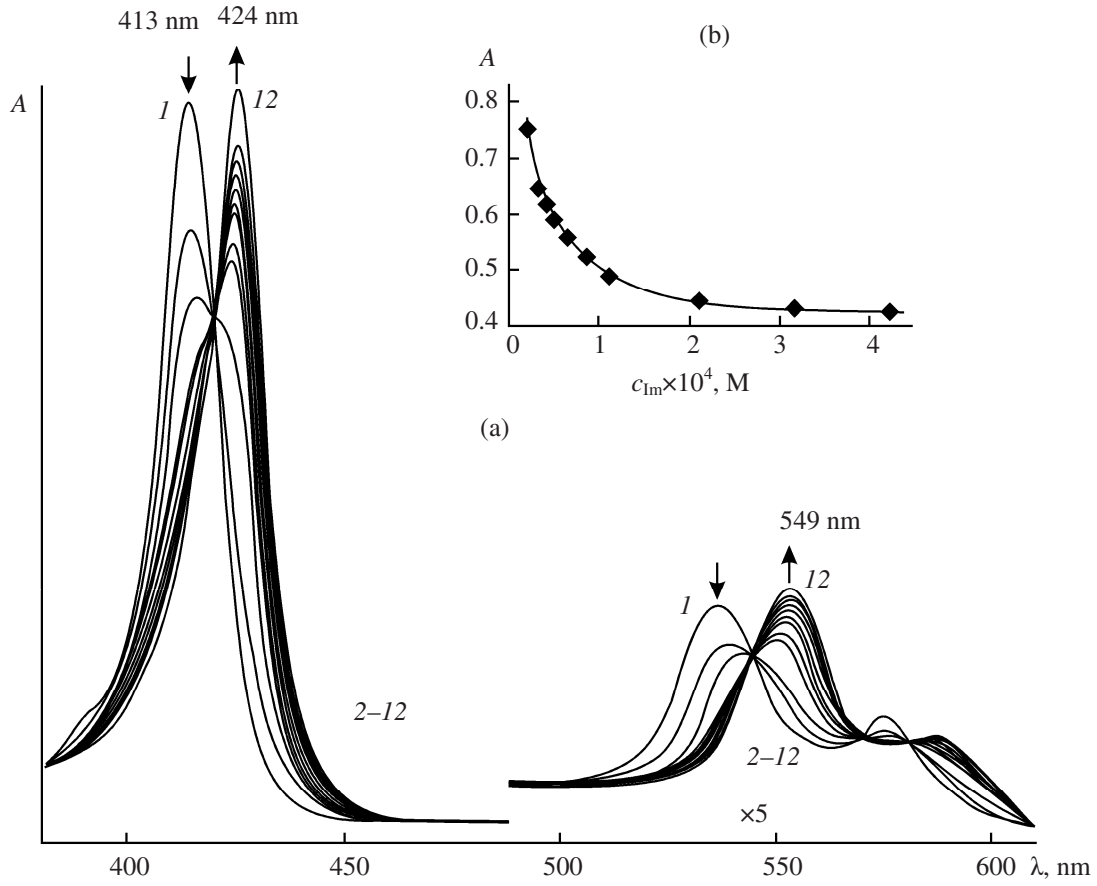


Fig. 1. (a) Electron absorption spectrum (EAS) of dimeric zincporphyrin (ZnP) with imidazole in benzene: (*1*) ZnP without adding imidazole (c_{ZnP} 5.52 × 10^{-6} M); (*2–11*) ZnP with intermediate imidazole concentrations (c_{ZnP} 5.52 × 10^{-6} M; c_{Im} 2.11 × 10^{-5}–4.21 × 10^{-4} M); (*12*) ZnP with imidazole excess (c_{Im} 2.42 × 10^{-3} M). (b) Corresponding titration curve; λ 413 nm.

methyl group is in the *ortho*-position of the base) affecting the coordination. The comparison of K_{st} values for dimeric and monomeric zinc complexes shows that the stability of those latter is much lower [6]. It results both from the electron effects of substituents and macrocycles (in the case of a dimer) and from the deformation strain of a macrocyclic ligand.

It was found that the stability constant depends on the basicity of an additional molecular ligand described by the value of pK_{ex+}.

The comparison of K_{st} for zinc extra-complexes with the variation of absorption bands positions in the electronic spectra of metalporphyrins ($\Delta\lambda_{max}$) shows that these values correlate with each other (Fig. 3). The undirectional dependence described by the equation:

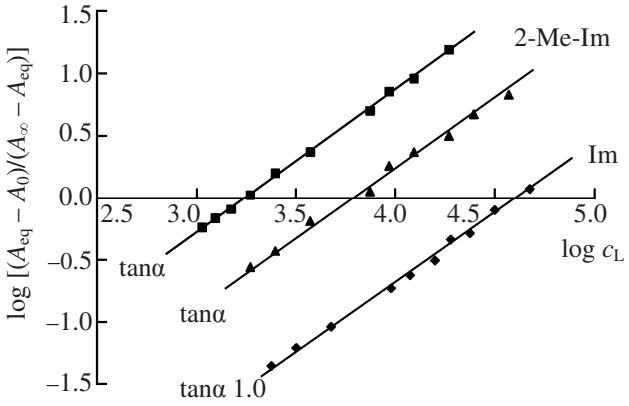


Fig. 2. Dependences of log $[(A_{eq} - A_0)/(A_\infty - A_{eq}]$ on log c_L for the intermolecular reaction of dimeric ZnP with a nitrogen base; A_∞, A_{eq}, and A_∞ are optical densities of solutions on a working wavelength for metalporphyrin and for equilibrium mixtures at certain concentrations of the base and the complex.

Table 2. Certain calculated characteristics of optimized molecules of dimeric ZnP extra-complexes

Complex	q_{Oph},[a] units	O_{ph}–Zn_1[b] Oph–Zn_2[b] Å	P_1[c] P_2[c] Å	Macrocycle 1					Macrocycle 2				
				N_1–N_3 N_2–N_4 Å	Zn–N_1 Zn–N_3 Å	Zn–N_2 Zn–N_4 Å	Zn–N_L, Å	Zn–Ct[d], Å	N_1–N_3 N_2–N_4 Å	Zn–N_1 Zn–N_3 Å	Zn–N_2 Zn–N_4 Å	Zn–N_L, Å	Zn–Ct, Å
ZnP	–0.214	5.6248	11.6131	4.1014	2.0684	2.0458		0.0128	4.0816	2.0674	2.0602		0.0704
		5.1906	11.5836	4.1139	2.0331	2.0682			4.1100	2.0166	2.0493		
(Im)ZnP	–0.237	5.5430	11.6081	4.0970	2.0672	2.0501		0.0128	4.1352	2.1200	2.1093	2.0859	0.4288
(isomer **A**)		5.1088	11.6775	4.1147	2.0298	2.0647			4.1258	2.1032	2.0897		
(isomer **B**)	–0.227	5.3162	11.7086	4.1429	2.1168	2.1006	2.0917	0.3976	4.0783	2.0666	2.0553		0.0818
		5.2636	11.5763	4.1411	2.1017	2.1137			4.1023	2.0151	2.0482		
(Py)ZnP	–0.231	5.5575	11.6105	4.0969	2.0672	2.0497		0.0119	4.1336	2.1185	2.1115	2.1116	0.4273
(isomer **A**)		5.0660	11.6717	4.1149	2.0298	2.0653			4.1224	2.1025	2.0848		
(isomer **B**)	–0.215	5.3862	11.7311	4.1431	2.1154	2.0961	2.1146	0.3941	4.0798	2.0667	2.0567		0.0738
		5.2134	11.6196	4.1403	2.1020	2.1145			4.1044	2.0155	2.0485		
(2-MeIm)	–0.218	5.5803	11.6104	4.0972	2.0675	2.0496		0.0128	4.1328	2.1247	2.1155	2.1145	0.4326
ZnP		5.0165	11.6738	4.1151	2.0298	2.0655			4.1276	2.0977	2.0916		
(isomer **A**)	–0.226	5.3159	11.7057	4.1407	2.1162	2.0999	2.1197	0.4096	4.0789	2.0668	2.0558		0.0798
(isomer **B**)		5.2538	11.5770	4.14	2.1048	2.1188			4.1033	2.0153	2.0485		

[a] Charge on O_{ph} atom of bridging phenol. [b] Zn_1 and Zn_2 are central atoms of the first and the second macrocycles, respectively. [c] Perimeter of coordination plane N_4 of the first and the second macrocycle, respectively. [d] Ct – centre of a macrocycle coordination cavity.

log K_{st} = 0.1538 $(\Delta\lambda_{max})^2$ – 2.477$\Delta\lambda_{max}$ + 13.299 (r 0.96), differs in character from the linear dependence for the case of ZnTPP [7]. The deviation from linearity, as in the above-described case, is caused by an increase in steric strain in dinuclear ZnP on the coordination of an external ligand. The non-planarity of the ZnP structure and the change in the extent of the macrocycle deformation on the coordination with an extra-ligand were also confirmed by the quantum-chemical calculations.

Quantum-chemical calculations allow prediction of the course of the intermolecular interaction of the

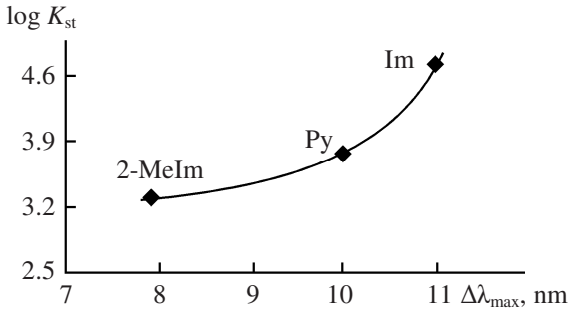


Fig. 3. Dependence of log K_{st} of dimeric ZnP molecular complexes on the shift of basic absorption bands in EAS.

compound under study with a base, to understand the reasons of variations in stability of formed complexes of binuclear zincporphyrin from the position of structural and energy characteristics of the metalporphyrin and the extra-ligand (Table 2). We have found on the basis of the calculated data that the dimeric zincporphyrin is nonplanar and strained (Fig. 4). The angle between macrocycles in the complex under study is 112°. The phenyl groups are oriented to the plane of tetrapyrrole fragments under an angle of 84°–86°. Alkyl substituents pairwise protrude into a solvent on the both sides of the macrocycle under an angle of 60°–62°. It is necessary to note that deformation strains of macrocycles are ambiguous. One fragment has a rather planar structure of a coordination center with a small deviation of the metal atom from the plane. The structure of the second macrocycle is nonplanar with dominating saddle-like deformation (Fig. 4). The perimeter of its coordination plane N_4 is less by 0.295 Å than that of the first macrocycle.

We believe that the difference in the extent of deformation of two macrocycles is connected both with their mutual influence and the orientation of the OH group of bridging phenol (Fig. 4). The proximity of oxygen to the N_4 plane of the second tetrapyrrole

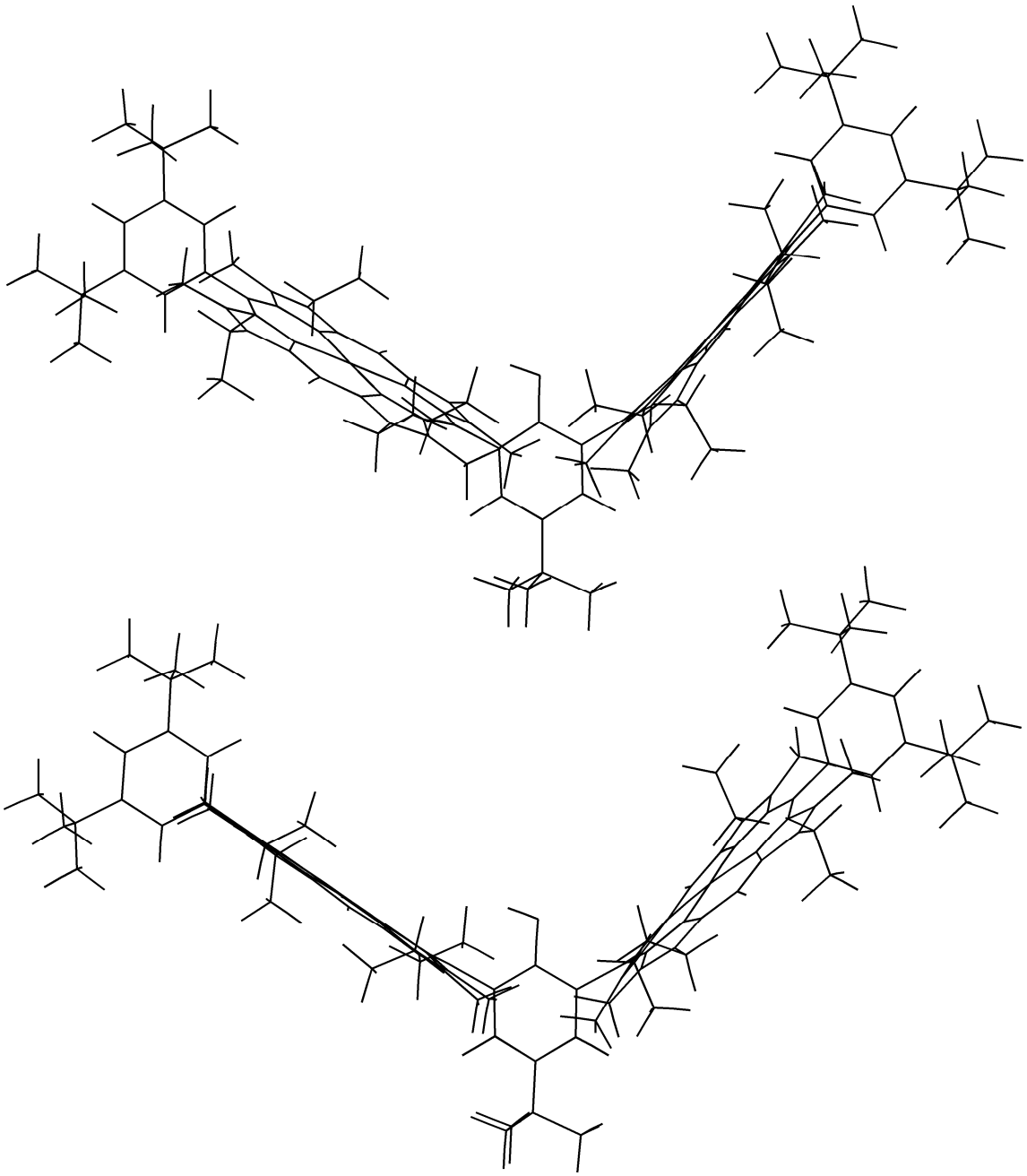


Fig. 4. Structure of a dimeric ZnP molecule calculated by the PM3 quantum-chemical method in various projections.

fragment (closer by 0.4336 Å than to the first fragment) affects the structure of the coordination cavity and causes a redistribution of electron density on neighboring atoms. The charge on the zinc atom in this case is less by 0.01 units than the charge of the central metal atom of the first macrocycle.

The formation of the molecular complex is accompanied by a change in the extent of dimeric porphyrin deformation, axial and torsional strains of macrocycles increasing (Table 2, Fig. 5).

On the basis of the quantum-chemical calculations we have found that isomers of the molecular complexes are formed in the reaction course. The existence of structures A and B (Fig. 6) is most energy favorable. The conformation conversion of these forms for (Im)ZnP, (Py)ZnP, and (2-MeIm)ZnP corresponds

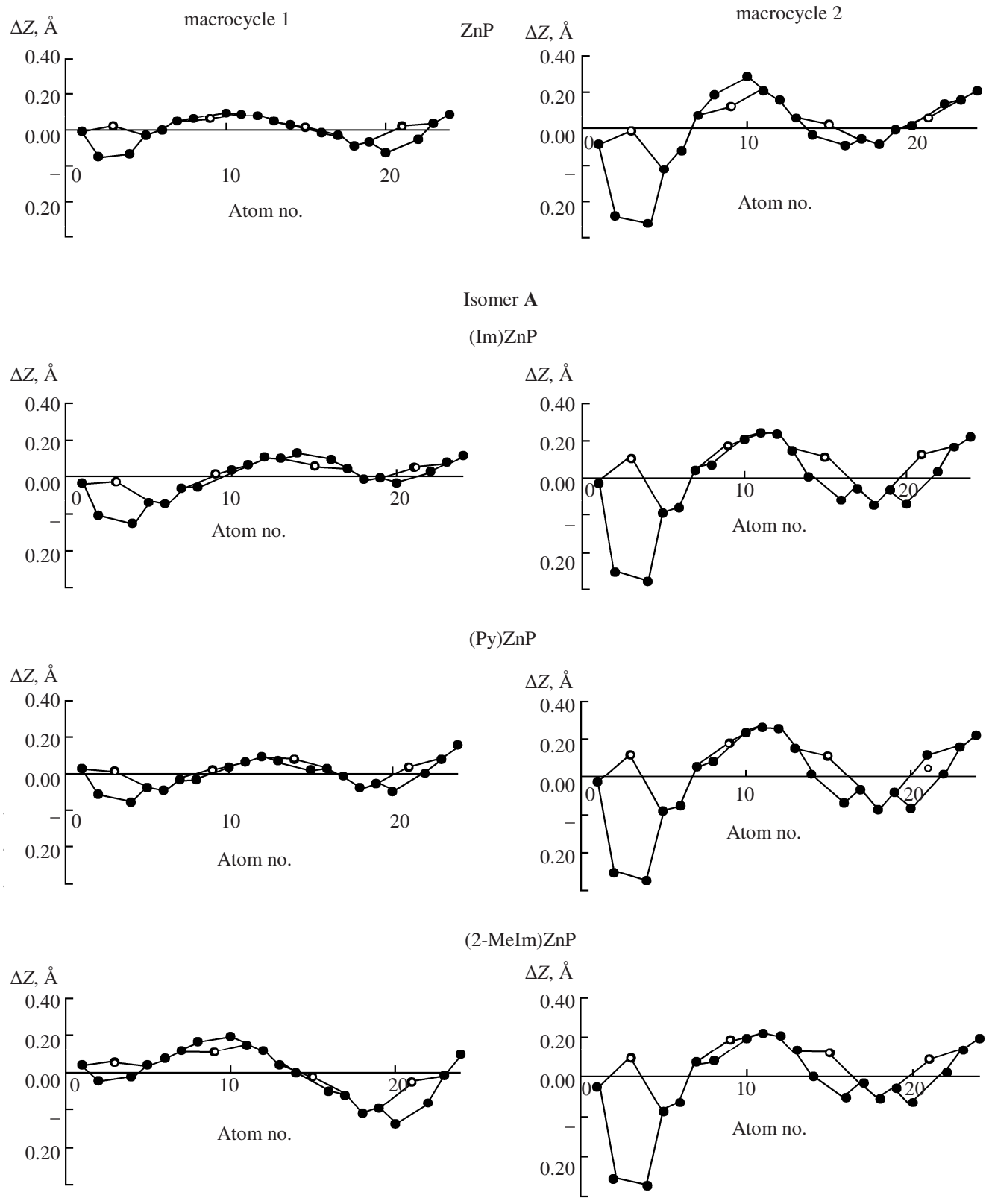


Fig. 5. Deviations of porphyrin macrocycle skeletal atoms in dimeric ZnP and in its molecular complexes with nitrogen-containing bases from the molecule medial plane (ΔZ) as calculated by the PM3 quantum-chemical method.

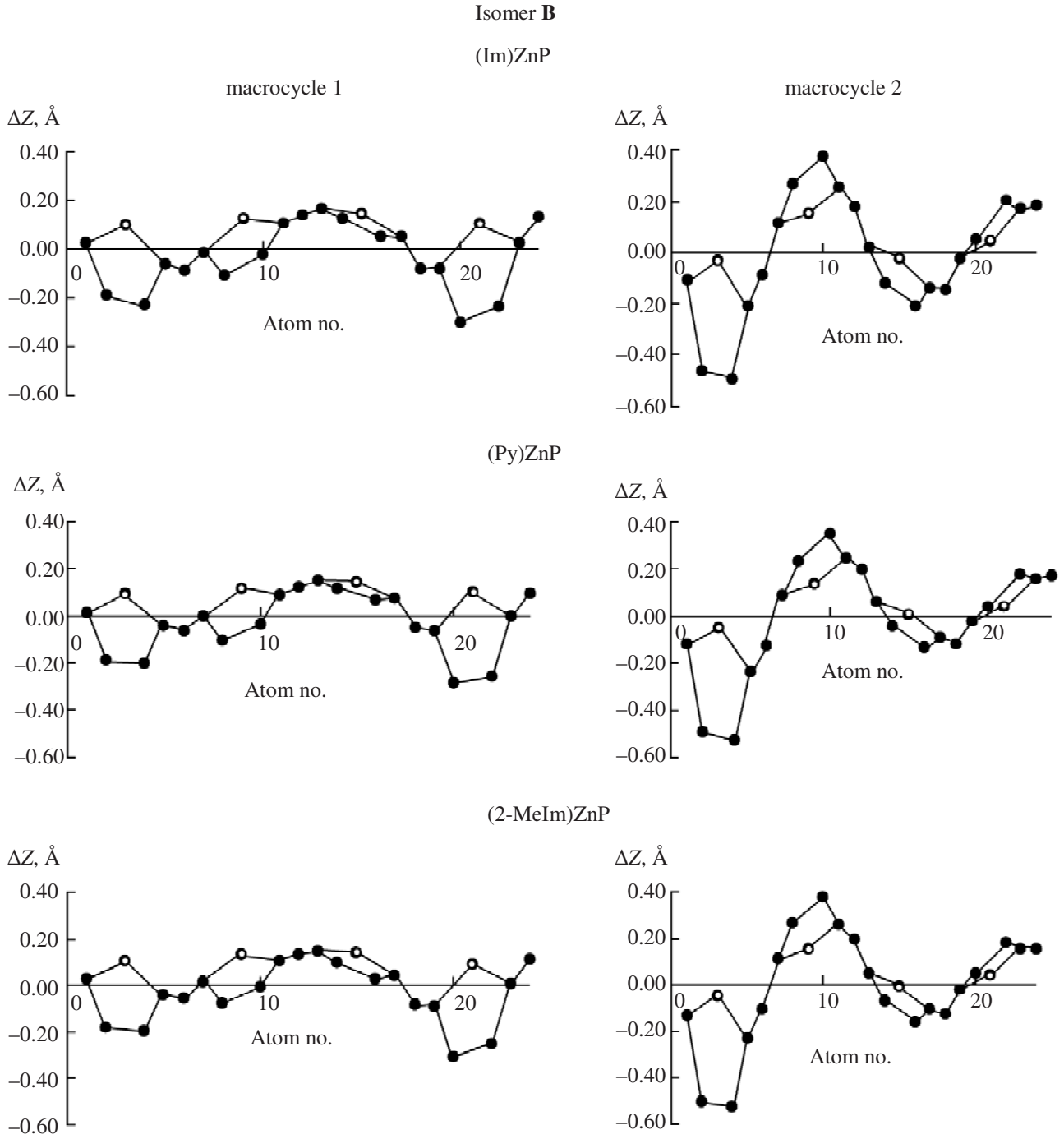

Isomer **B**
(Im)ZnP
macrocycle 1
macrocycle 2
ΔZ, Å
0.40
0.20
0.00
–0.20
–0.40
–0.60
0
10
20
Atom no.
(Py)ZnP
(2-MeIm)ZnP

Fig. 5. (Contd.)

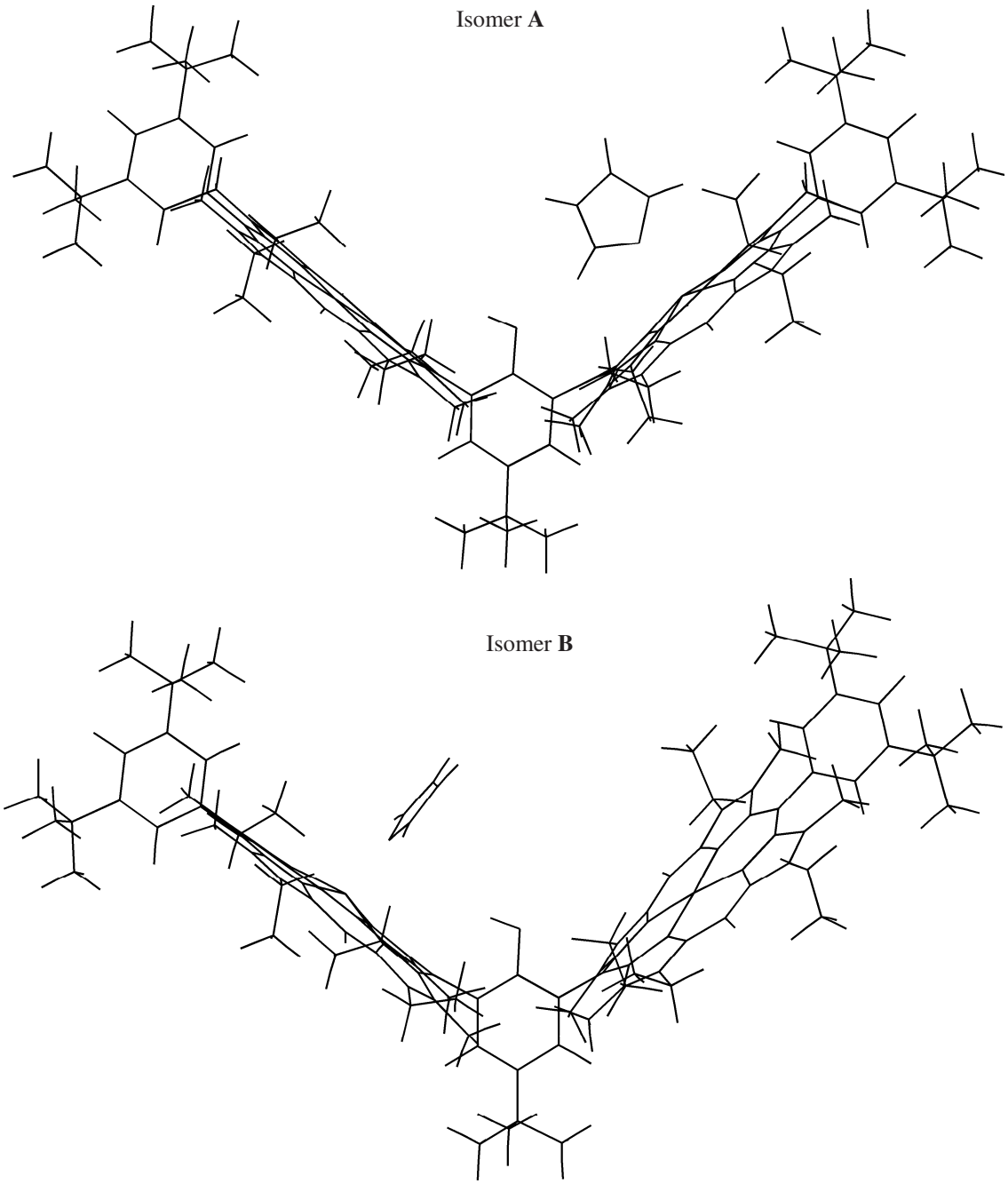


Fig. 6. Structure of isomers of (Im)ZnP complex calculated by the PM3 quantum-chemical method.

to 0.12, 0.31, and 0.4 kcal mol^{-1}, respectively (Table 2). The molecule of a base interacts with a zinc atom, being in a cavity between macrocycles. Such orientation is caused by the metal atom (Zn–Ct) protruding into the same cavity. In dimeric ZnP the coordination in the position of the second macrocycle proceeds easier, as the Zn–Ct distance in it is longer by 0.068 Å than in the first macrocycle. In the course of the intermolecular interaction the angle between macrocycles decreases: for (Im)ZnP, (2-MeIm)ZnP, and (Py)ZnP by 9°–10°, 4°–5°, and 6°–7°, respectively. In the case of B isomers the slope of phenyl fragments to the N_4 plane changes. In the first macrocycle this value is 89°–90° and in the second 80°–82°. The attachment of a base results in an increase in the coordination plane area of the macrocycle involved in the coordination and in a decrease in the area of the N_4 plane of the neighboring

macrocycle, except for (Py)ZnP B isomer (Table 2). The effective charge on the reactive center of the neighboring macrocycle also decreases: for (Im)ZnP, (2-MeIm)ZnP, and (Py)ZnP by 0.005–0.01, 0.006–0.009, and 0.005–0.007 units, respectively. An increase in the Zn–Ct distance is characteristic for the molecular complexes: for **B** isomers in the both macrocycles and for **A** isomers in the macrocycle involved in the base bonding (Table 2).

The extent of the molecular complex strain depends both on the nature of the base and on its orientation (Table 2 and Fig. 5). The formation of the $Zn–N_L$ bond leads to a change in the type of the macrocycle deformation. A mixed deformation type, dome- and saddle-shaped, with slight waviness is characteristic of the second macrocycle in the case of isomer **A**. For isomer **B** the dominanting dome-shaped deformation increases in the first macrocycle (Figs. 5 and 6).

The analysis of the experimental and calculated data has shown that the energy of the $Zn–N_L$ bond formation (E_b) in the molecular complex varies in direct proportion to its stability. The resulting dependences are described by equations (4) and (5) for isomers **A** and **B**, respectively (Tables 1 and 2, Fig. 7).

The increase in E_b in the series of complexes (2-MeIm)ZnP > (Py)ZnP > (Im)ZnP corresponds to the increase of compounds stability on passing from 2-methylimidazole to imidazole. A similar trend is also characteristic for the $Zn–N_L$ bond energy. In the series of the nitrogen-containing bases 2-MeIm > Py > Im the stability of the complexes increases as the strength of the $Zn–N_L$ σ-bond increases. However, in this series there is no correlation between the metal deviation from the N_4(Zn–Ct) plane and the $Zn–N_L$ bond strength (Table 2). The mutual influence of ligands

$$\log K_{st} = -0.2998E_b - 0.7362, \quad (4)$$

$$\log K_{st} = -0.3029E_b - 0.7457. \quad (5)$$

fairly strongly manifests itself in molecular complexes. The appearance of a $Zn–N_L$ bond with one macrocycle results in essential weakening of the $Zn–N_p$ bond in it and to its strengthening in the other macrocycle (Table 2).

The aforesaid suggests that deformation strains of tetrapyrrole fragments, alongside with the nature of bases and the electron effects of substituents and

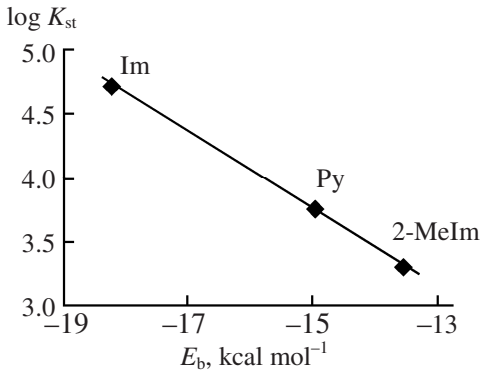


Fig. 7. Correlation between E_b and the molecular complex stability (for isomer **A**).

macrocycles, essentially affect coordination properties of dimeric zincporphyrins.

EXPERIMENTAL

Optical density for a series of solutions with a constant metalporphyrin concentration and various extra-ligand concentrations was measured at 413 and 425 nm for (2-MeIm)ZnP and (Im)ZnP and at 413 and 424 nm for (Py)ZnP at 259 K in cells of 1 cm in thickness. The inaccuracy of thermostating was no more than 1 K. The electron absorption spectra were taken on a Cary-100 spectrophotometer within the range from 400 up to 650 nm and recorded as graphs and tables for the subsequent mathematical treatment.

The optimization of K_{st} values and the determination of root-mean-square deviations were carried out using the least squares method. The relative error in the determination of K_{st} did not exceed 8–10%.

Quantum-chemical calculations were fulfilled by the PM3 semiempirical method, using a combination of the conjugate gradient Fletcher-Reeves and Polak–Ribiere methods [14.] The calculation was terminated on reaching a gradient of 0.01 kcal mol^{-1} Å.

(2,6-Bis[15'-(3'',5''-di-*tert*-butylphenol)-3',7',13',17'-tetramethyl-2',8',12',18'-tetraethylporphin-5'-yl]-4-*tert*-buthylphenol) (I) was synthesized using the procedure [15–17]. At room temperature a solution of 0.2 g of trichloroacetic acid in 10 ml of acetonitrile was added with stirring in an argon atmosphere to a solution of 0.5 g of 4,4'-dimethyl-3,3'-diethyldipyrrolylmethane, 0.05 g of 2,6-diformyl-4-*tert*-butylphenol, and 0.42 g of 3,5-di-*tert*-

butyl-benzaldehyde in 30 ml of acetonitrile. The mixture was stirred for one day under these conditions; a solution of *p*-chloranil in 30 ml of THF was added and stirred for 4 h. The solvents were distilled off in vacuum of a water-jet pump; a residue was washed out with water and dried in air at 70°C. The residue was dissolved in chloroform and chromatographed on aluminum oxide (grade II) with chloroform as an eluent. The second band of the dimeric porphyrin was gathered. The solutions were evaporated up to a minimal volume and chromatographed repeatedly on silica gel. After evaporation to a minimal volume the porphyrins were precipitated by methanol, filtered off, and dried. Dimeric porphyrin yield 12.8 mg (1.6%). EAS, λ_{max}, nm (log ε): 626 (3.52); 574 (4.08); 542 (3.97); 509 (4.45); 412 (5.56) (chloroform). Molecular weight 1480.185.

2,6-Bis[zinc-15'-(3'',5''-di-*tert*-butylphenol)-3',7',13',17'-tetramethyl-2',8',12',18'-tetraethylporphin-5'-yl]-4-*tert*-buthylphenol (II). Porphin (10 mg) was dissolved in 50 ml of benzene, then a tenfold excess of zinc acetate was added to the porphyrin solution. The reaction mixture was heated and boiled for 40-50 min. The reaction course was monitored by the variation of the electron absorption spectrum of the mixture. The disappearance of porphyrin absorption bands and the appearance of absorption bands of its metal complex allowed to judge the completion of the reaction. After the reaction termination the resulting mixture was cooled, and excess salt was extracted by water. The benzene solution of a zinc complex was evaporated and chromatographed on silica gel (eluent–chloroform). The crystalline complex was isolated by precipitation from chloroform. Yield 91%. EAS (benzene), λ_{max}, nm (log ε): 573.0 (4.14), 538.0 (4.47), 413.0 (5.28). ^{1}H NMR spectrum, ($CDCl_3$, internal standard TMS, δ, ppm: 11.45 s (1H, OH–Ph); 10.25 with (4H, *meso*-H), 8.40 d (4H, H^o); 8.28 t (4H, H^n); 4.33 q (16H, CH_2CH_3), 2.43 s (24H, CH_3), 1.50 s (36H, *t*-Bu); 1.75 t (24H, CH_2CH_3), 1.45 s (9H, *t*-BuPh). Found, %: C 76.2, H 7.39, N 7.20. $C_{98}H_{114}Zn_2N_8O$. Calculated, %: C 75.97, H 7.36, N 7.23.

ACKNOWLEDGMENTS

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