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Complex Formation and Spectral Properties of *meso*-Phenyltetrabenzoporphyrins in Pyridine and *N,N*-Dimethylformamide

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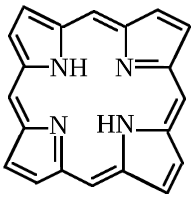
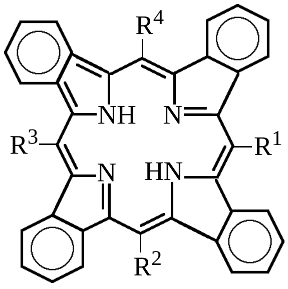
Abstract—Contributions of structural (macroring distortion) and polarization (in asymmetrically substituted derivatives) effects into the reactivity and chromophoric properties of substituted porphyrins were revealed on the basis of the kinetics of complex formation of nona-, deca-, undeca-, and dodecasubstituted porphyrins (*meso*-phenyltetrabenzoporphyrins) with $Zn(OAc)_2$ in pyridine and the electronic absorption spectra of the ligands and their complexes with Zn(II) and Cu(II) in pyridine and *N,N*-dimethylformamide (DMF). Dodecaphenyl substitution produces a weaker ring distortion in the more aromatic tetrabenzoporphyrin compared with porphyrins themselves. Irrespective of the degree of macroring nonplanarity, the Zn (II) and Cu complexes of tetrabenzoporphyrins with increasing degree of *meso*-phenyl substitution meet a spectral stability criterion.

Over the last two decades benzoporphyrins have attracted interest due to the recognized propects for their practical application [1], in particular, as materials with nonlinear optical properties, semiconductors, photogenerators of singlet oxygen in photodynamic therapy and engineering, as well as models in studies on photosynthetic processes. Nevertheless, until the present time benzoporphyrins seem to be the least explored group of compounds of the entire class of porphyrin (**I**) derivatives. This is caused by the complexity of their synthesis and purification.

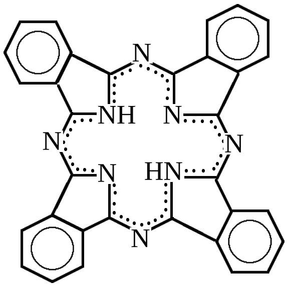
Tetrabenzoporphyrin (**II**) and its analogs **III**–**VI** present interest, since they occupy an intermediate place between porphyrin (**I**) and phthalocyanine (**VII**) in terms of structure and properties [3]. This is proved by quantum-chemical calculations [4], calculations of bond π-electron charges in molecule **II** [3], photoelectron spectral data on the ionization potentials of nitrogen atoms in the molecules [5], and also data on their coordination properties [6]. According to [4, 6], there is a weak π-electron interaction between the macrocyclic and fused benzene chromophores in molecule **II** (the order of the C^{α}–C^{β} π bond is as low as 0.386 [3, 4]). Therewith, the multicontour conjugated system characteristic of porphyrins themselves [7, 8] is disturbed. Thus, compound **II** and its derivatives are rigid aromatic macrorings combining in their strucure stable benzene and macrocyclic conjugated π sysems, which are almost independent of each other.



I



II–**VI**



VII

$R^1 = R^2 = R^3 = R^4 = H$ (**II**), $R^1 = R^2 = R^3 = H$, $R^4 = Ph$ (**III**), $R^1 = R^3 = H$, $R^2 = R^4 = Ph$ (**IV**), $R^1 = H$, $R^2 = R^3 = R^4 = Ph$ (**V**), $R^1 = R^2 = R^3 = R^4 = Ph$ (**VI**).

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Table 1. Characteristics of the electronic absorption spectra of tetrabenzoporphyrins **II**–**VI** in pyridine and DMF [λ_{max}, nm (log ε)].

Porphyrin	Solvent	λ_{Soret}	λ_3	λ_2'''	λ_2''	λ_2'	λ_1
II	DMF	413 (4.70), 428 (4.75)	569 (3.84)	598.5 sh (4.13)	605.5 (4.19)	613.5 sh (4.18)	661.5 (4.06)
	Pyridine	416 (4.46), 431 (4.51)	570 (3.59)	600 sh (3.86)	608.5 (3.95)	615.5 (3.96)	664 (3.82)
III	DMF	417 (4.11), 432 (4.21)	529.5 (2.47), 569 (2.97)	601.5 sh (3.49)	608.5 (3.57)	614 sh (3.54)	664.5 (3.33)
	Pyridine	421 (4.79), 434.5 (4.89)	530 (3.30), 571.5 (3.73)	602.5 sh (4.17)	611 (4.29)	616.5 (4.28)	666 (4.07)
IV	DMF	422 (4.77), 432 (4.93)	524 (3.41), 570.5 (5.24)	602 sh (4.16)	609 (4.23)	616 sh (4.22)	665 (4.02)
	Pyridine	422 (4.56), 434 (4.71)	573 (3.55)	604 sh (3.94)	611.5 (4.04)	618.5 (4.06)	666.5 (3.84)
V	DMF	423 (5.12), 436.5 (5.26)	530 (3.64), 572 (5.10)	604 sh (4.48)	612 (4.59)	616 sh (4.58)	667 (4.24)
	Pyridine	426 (4.94), 440 (5.13)	531 (3.53)	605 sh (4.31)	613 (4.39)	618.5 sh (4.38)	666.5 (4.16)
VI	DMF	462.5 (4.68)	584 (3.70)	622 sh (3.89)	631 (3.91)	649.5 sh (3.87)	695 (3.47)
	Pyridine	465.5 (4.57)	543 (3.22), 590.5 (3.38)	627 sh (3.73)	637 (3.75)	651 sh (3.71)	697 (3.13)

Dodeca substitution in molecule **I**, i.e. substitution of all the twelve its peripheral hydrogen atoms, is one of the most effective ways of distorting the planar structure of the aromatic molecule [9]. Consecutive *meso*-phenyl substitution in molecule **II**, leading, in the limit, to dodeca-substituted tetraphenylbenzoporphyrin **VI**, too, disturbs the planar structure of the parent molecule. This effect is opposite to benzo substitution. The nonplanar structure of the Zn(II) complex of compound **VI** follows from the X-ray diffraction data [10]. By dynamic ^{1}H NMR spectroscopy [11] it was shown that the distorted structure of compound **VI**, its Zn complex, and "acid" dication is preserved in solution.

The aim of the present work was to reveal specific features of distortion of molecules more aromatic than porphyrins themselves and also to estimate the electronic and structural contributions of substituents to variation in the spectral and complex-forming properties of compound **II** upon its consecutive *meso*-phenyl substitution.

When benzene rings are introduced into the porphyrin macroring, a tetraisoindole macroring **II** arises instead of a tetrapyrrole macroring **I**. The macrocyclic chromophore in **II** experiences a weak electron-acceptor effect of fused benzene rings. It is supposed that, despite the fact that the electronic absorption spectrum of compound **II** differs considerably from those of porphyrins themselves in band structure, they are close to each other in the nature of electronic transitions [7]. This can be considered as evidence for the similarity of the chromophoric systems of compounds **I** and **II**. Thus, bands 1 and 2" (Table 1, Fig. 1) are formed by two π–π^* ($A_{1g} \longrightarrow B_{3u}$ and $A_{1g} \longrightarrow B_{2u}$) transitions, polarized at a right angle to each other in the molecular plane, whereas bands 2' and 2" are assigned as their vibrational satellites ($A_{1g} \longrightarrow \overline{B}_{2u}$ and $A_{1g} \longrightarrow \overline{B}''_{3u}$). As found by polarization measurements, both components of the Soret band of **II** relate to two different electronic transitions ($A_{1g} \longrightarrow B'_{2u}$ and $A_{1g} \longrightarrow B'_{3u}$ [12]), the long-wave component being polarized similarly to band 1, and the short-wave, similarly to the $A_{1g} \longrightarrow B_{2u}$ transition (band 2") [7].

The π–π bands of **II** are much stronger than the respective bands of porphyrins themselves, and the quasiforbidenness of the $A_{1g} \longrightarrow B_{3u}$ and $A_{1g} \longrightarrow B_{2u}$ transitions is already lifted as the first fused benzene fragment appears (monobenzoporphyrin) [13, 14]. Therewith, splitting of the Soret band into components is a characteristic of tetrabenzoporphyrins only and does not take place in the case of monobenzoporphyrin [13], *cis*- and *trans*-dibenzoporphyrins [14, 15], as well as their naphthyl analogs

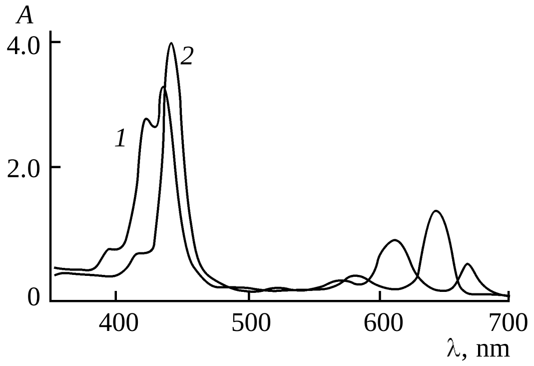

Fig. 1. Electronic absorption spectra of (*1*) *meso*-phenyltetrabenzoporphyrin (**III**) and (*2*) its zinc complex in pyridine.

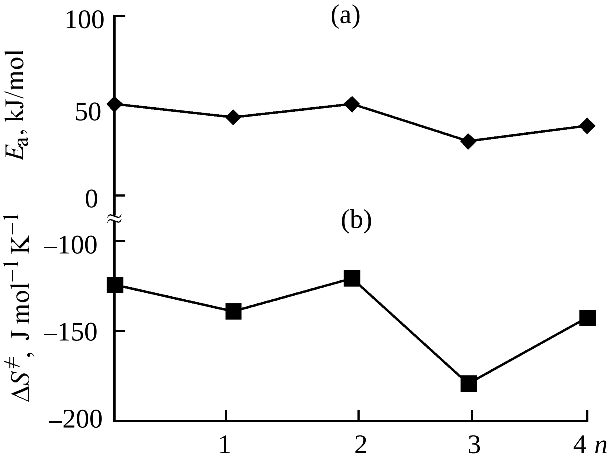

Fig. 2. Changes in (a) E_a and (b) $\Delta S^{\neq}$ upon complex formation along the series of *meso*-phenytetrabenzoporphyrins **II**–**VI**. *n* is the number of *meso*-phenyl groups in tetrabenzoporphyrin.

[16]. In spite of the obvious symmetry of molecule **II**, apparently, there is some nonequivalence of isoindole (N–H bonds) and isoindolenine (–N= atoms) fragments, which reveals itself in anomaly in certain photophysical properties of the molecule [7].

We established for the first time that consecutive *meso*-phenyl substituion in compound **II** makes the components of the Soret band closer together until they coalesce in the spectrum of compound **VI**. Apparently, the Soret band in the latter spectrum is also split, but this splitting is not evident because of the higher conformational flexibility of the molecule (the bands are more diffuse). All bands in the visible region of the electronic absorption spectrum of compound **II** shift bathochromically with *meso*-phenyl substitution (the Soret band and band 1 by 36 and 34 nm, respectively, for compound **VI** compared to compound **II**), the strongest changes produced by introduction of the fourth phenyl group [transition **V** $\longrightarrow$ **VI** (26 and 28 nm, respectively)].

Complex formation of tetrabenzoporphyrins **II**–**VI** with 3*d*-metal salts is accompanied by a cardinal change in their electronic absorption spectra: The spectra of the complexes contain no other bands than the Soret band and two visible bands (Fig. 1) belonging, supposedly, to purely electronic transitions [7]. The simplification of the electronic spectrum is associated with increase in the molecular symmetry and also, probably, with suppression of vibrational states on complex formation. The positions of bands in the electronic absorption spectra of metal complexes is determined by the type and strength of M–N chemical bonds.

Karavaeva *et al.* [17] established that the spectral stability criterion whose physical sence has been described in the monograph [3] applies to metal complexes of **II**. According to this criterion, the thermodynamic stability of metal complexes in a series of similar compounds is the higher, the larger is the hypsochromic shift of band 1 of metal porphyrin (MP) in comparison to band 1 of the porphyrin ligand (H_2P) ($\Delta\lambda_1^{MP} = \lambda_1^{MP} - \lambda_1^{H_2P}$). Based on the basis of the electronic absorption spectra and kinetic data, we can contend that the spectral stability criterion applies to all the tetrabenzoporphyrin complexes studied in the present work, irrespective of the distortion degree. Thus, band 1 of the more covalent Cu(II) complexes [3] exhibits a larger hyprochromic shift compared to the respective band for the less stable Zn(II) complex whose M–N bonds are more ionic (Table 2).

The electronic absorption spectra of tetrabenzoporphyrins **II**–**VI** in pyridine and DMF (Table 1) revealed a very weak solvatochromic effect in these solvents for the whole series of compounds. Analysis of the log ε values for benzoporphyrin ligands **II**–**VI** (Table 1) shows that band 1 in the spectra of asymmetrically substituted ligands **III**, **V** is always stronger than in the spectra of symmetrical ligands **II**, **IV**, and **VI**, which points [3] to polarization effects in **III** and **V**.

We have studied the kinetics of complex formation of phenylbenzoporphyrins **II**–**VI** with $Zn(OAc)_2$ in pyridine (Py). The salt was taken in a 100-fold molar excess compared to porphyrin (H_2P), which allowed us to describe the reaction by a pseudo-first-order equation. The linear character of the dependences $\log(c^0_{H_2P}/c_{H_2P}) = f(\tau)$ (Fig. 2) points to a first reaction order in porphyrin. The true rate constant (k_v,

Table 2. Electronic absorption spectra of tetrabenzoporphyrins **II**–**VI** and their complexes with Cu(II) and Zn(II) in pyridine (λ_{max}, nm)

Porphyrin (metal porphyrin)	λ_{Soret}	λ_3	λ_2'''	λ_2''	λ_2'	λ_1	$\Delta\lambda_1$[a]
II	415.0, 430.0	570.0	600.0 sh	605.5 sh	615.5	663.0	
II(Cu)	428.0					625.0	–38.0
II(Zn)	433.0				584.0	631.5	–31.5
III	422.0, 434.0	529.0	605.0 sh	611.0	617.0 sh	668.0	
III(Cu)	433.5					628.0	–40.0
III(Zn)	438.0				586.0	633.5	–34.5
IV	423.0, 434.0	573.0	605.0 sh	612.0	617.5	667.5	
IV(Cu)	435.0				583.5	629.0	–38.0
IV(Zn)	436.0				592.0	633.5	–34.0
V	428.0, 440.0	534.5	605.0 sh	613.0	617.5 sh	669.0	
V(Cu)	438.5					632.5	–36.5
V(Zn)	444.5				593.0	637.0	–32.0
VI	466.0	542.0, 589.0	627.0 sh	636.0	652.0	697.0	
VI(Cu)	448.0				sh	652.0	–45.0
VI(Zn)	445.0				612.0	656.0	–41.0

[a] $\Delta\lambda_1$ is the bathochromic shift of band 1 in the electronic spectrum of tetrabenzoporphyrins upon complex formation ($\Delta\lambda_1^{MP} = \lambda_1^{MP} - \lambda_1^{H_2P}$).

Table 3. Kinetic parameters of complex formation of tetrabenzoporphyrins **II**–**VI** with $Zn(OAc)_2$ in pyridine (298 K, $c_{\mathbf{II-VI}}$ 2.6×10^{-5}, $c_{Zn(OAc)_2}$ 2.6×10^{-3} M)

Porphyrin	λ_{exp}, nm	$k_v\times10^2$, $l\,mol^{-1}\,s^{-1}$ [a]	E_a, kJ/mol	$\Delta S^{\neq}$, $J\,mol^{-1}\,K^{-1}$
II	631.5	0.69	50.8 ± 0.1	-124 ± 6.0
III	633.5	2.56	43.2 ± 2.6	-139 ± 2.0
IV	633.5	1.38	50.5 ± 1.7	-120 ± 6.0
V	637.0	4.71	29.6 ± 1.1	-179 ± 9.0
VI	656.0	10.03	38.5 ± 0.7	-143 ± 2.5

[a] Obtained by extrapolation.

$l\,mol^{-1}\,s^{-1}$) was calculated as $k_v = k_{app}/c_s$ (k_{app} is the apparent rate constant, s^{-1}, and c_s is the molar concentration of salt, M). Consecutive *meso*-phenyl substitution inceases the rate and decreases the activation energy (E_a) and $\Delta S^{\neq}$ (enhanced solvation of the transition state) of reaction (1) (Table 3). However, as seen from Table 3, there is no regular trend in the complex-forming ability of compounds **II**–**VI**.

$$H_2P + M(OAc)_2(Py)_{n-2} \longrightarrow [H_2P\cdots Zn(OAc)_2(Py)_{n-2}]^{\neq} \longrightarrow ZnP + 2HOAc + (n-2)Py.$$

Even though the rate of reaction (1) changes rather steadily (Fig. 2), the activation parameters show that asymmetrical *meso* substitution favors the process. Thus, E_a decreases by 7 kJ/mol and $\Delta S^{\neq}$ decreases by 15 $J\,mol^{-1}\,K^{-1}$ in passing from **II** to **III**. When the second phenyl group is introduced in **III** *trans* to the first phenyl group, E_a and $\Delta S^{\neq}$ return to values characteristic of **II**. Presumably, the symmetrical *trans*-diphenyl substitution in **IV** results in symmetrization of the coordination cavity [18], and, consequently, of the electron density in the macroring. In passing from **IV** to **V**, E_a and $\Delta S^{\neq}$ decrease again and grow again in passing to **VI**. These changes may be associated with polarization of the macroring in **II** by asymmetrical *meso*-phenyl substitution. Similar effects has been observed with *meso*- phenyloctaethylporphyrins on their complex formation in DMF and Py [18] and also with *meso*-alkyloctaethylporphirins in acetonitrile [19].

Decrease in E_a of reaction (1) always entails decrease in $\Delta S^{\neq}$ (Fig. 2). However, in force of structural distinctions between compounds **II**–**VI**, we failed to reveal a compensation kinetic effect [3] in the complex formation. Conventionally speaking, **II**, **IV**, **VI**, on the one hand, and **II**, **III**, **V** on the other, form two groups of molecules differing by the character of electron density distribution and macroring distortion. It should be noted that no correlation was found between changes in reaction rate and band shifts in the electronic absorption spectrum on consecutive *meso*-

phenyl substitution in **II**. This result suggests that chromophoric and coordination properties are differently affected by structural and electronic factors.

In the case of asymmetrical substitution, as, for example, in **V**, the polarization factor shows up in the coordination properties of phenylbenzoporphyrins. Thus, the energy of the process is most strongly affected by the asymmetrical triphenyl substitution in compound **V** for which the activation energy of reaction (1) is the lowest (Table 3, Fig. 2), rather than the dodecaphenyl substitution in compound **VI** whose macroring is distorted to the greatest extent [10, 11]. Apparently, such an asymmetrical substitution results in that the molecule can adopt one of the most reactive asymmetrically distorted conformations with a higher degree of of N–H bond polarization. Evidence for the low symmetry of the conformation of compound **V** comes from the observation in the ^{1}H NMR spectrum of nonequivalence of endocyclic NH protons already at 298 K [20]. The substitution by phenyl groups of three *meso*-hydrogen atoms in molecule **II** accelerates reaction (1) almost 7 times and decreases its E_a by more than 20 kJ/mol and $\Delta S^{\neq}$ by 55 J mol^{-1} K^{-1}. The symmetric tetraphenyl substitution in compound **VI** appears to be less effective in this regard. Though the reaction rate increases compared to unsubstituted tetrabenzoporphyrin **II** by a factor of ~15, the E_a and $\Delta S^{\neq}$ values decrease by as little as 13 kJ/mol and 19 J mol^{-1} K^{-1}, respectively.

We are the first to study the complex-forming properties of *meso*-phenyltetrabenzoporohyrins, and, in particular, compound **VI**. As follows from published data [21], compound **VI** synthesized by the procedure in [22] and studied in a number of works, for example, [23], was a mixture of *meso*-substituted tetrabenzoporphyrins, mainly **IV** and **V** [21]. Compound **VI** as a single product can be obtained by the procedure in [24]. We found that, under comparable conditions, individual porphyrin **VI** reacts with Zn(OAc)$_2$ in pyridine almost 2.5 times faster compared with the mixture in [23], with lower E_a (by 10 kJ/mol) and $\Delta S^{\neq}$ (by 25 J mol^{-1} K^{-1}), i.e. with a stronger solvation of the transition state.

We can contend that two main factors, electronic and steric, are responsible for the enhanced complex-forming ability of *meso*-substituted benzoporphyrins. *meso*-Phenyl substituents, as established in studies on their acid–base and coordination properties [3, 25], act as electron acceptors in relation to the porphyrin macroring. In the case of benzoporphyrin **II** derivatives, *meso*-phenyl groups, too, actively participate in electron density distribution. Thus, the spin electron density in the π-radical cation of the zinc complex of **VI** is substantially redistributed into *meso*-phenyl rings, whereas in the similar species involving compound **II** it is basically localized in the $C_{12}N_4$ macroring [26]. Apparently, in view of the decreased electron density in the macroring in tetrabenzoporphyrin **II** compared with porphyrin **I**, the meso-phenyl substituent exerts a very weak electron-donor effect in the former. Therefore, in the case of symmetrical tetra-*meso*-phenyl substitution, the polarization factor is insignificant and the increased complex-forming ability of compound **II** is defined by the distorting effect of phenyl groups on the aromatic macroring. The ^{1}H NMR spectral data point to a strong deshielding of NH protons in **VI** (δ 1.2 ppm) [21] compared to **I** (δ –3.76 ppm) [27]. Nevertheless, the reaction rate with Zn(OAc)$_2$ in pyridine increases in passing from **II** to **VI** by a factor of 15 only, which may result from a weak macroring distortion compared to dodecasubstituted porphyrins themselves, where k_v increased several orders of magnitude [18]. In fact, according to X-ray diffraction data, the macroring in the Zn complex of octaethyltetraphenylporphyrin is distorted stronger than in metal-free compound **VI**. The deviation of C^{β} atoms from the macroring mean plane is more than 1 Å in the former [28] and is only 0.765 Å in the latter [10]. Therewith, both the macrorings have a saddle-type of distortion. The moderate macroring distortion in the Zn(II) complex of compound **VI** is attributable to the aromaticity, i.e. resistance to deformations, of the parent macroring **II**.

EXPERIMENTAL

Spectral and kinetic measurements were carried out on Specord M-40 and Hitachi U-2000 spectrophotometers. The technique of kinetic measurements has been described in [23].

Phenylbenzoporphyrins **III**–**VI** were obtained by the procedures in [20, 24, 29, 30]. Purity control was performed by ^{1}H NMR and electronic spectroscopy, as well as by TLC on Silica F-60, eluent $CHCl_3$–Me_2CO.

Tetrabenzoporphyrin **II** was synthesized as described in [31]. *N*,*N*-Dimethylformamide and pyridine (chemical grade) were dehydrated before use by refluxing over $MgSO_4$ and KOH, respectively, followed by distillation. Zinc and copper acetates (analytical grade) were recrystallized from glacial AcOH and handled in a desiccator over concentrated H_2SO_4.

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