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Specific Features of Solvation and Chromophore Properties of Some *meso*-Substituted Porphyrins

D. B. Berezin

Ivanovo State University of Chemical Engineering, Ivanovo, Russia
Institute of Chemistry of Solutions, Russian Academy of Sciences, Ivanovo, Russia

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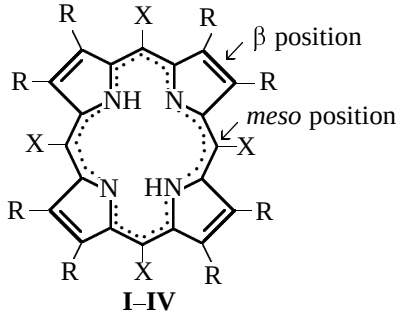
Abstract — The thermochemistry of solution and solvation of *meso*-substituted porphyrin ligands in three solvents differing in the donor–acceptor properties (benzene, chloroform, dimethylformamide) was studied. The results are correlated with the steric structure of the macrorings. Regular trends in variation of the electronic absorption spectra of the free porphyrins (H_2P) and their dications (H_4P^{2+}) upon *meso* substitution were revealed.

As compared to aromatic porphyrins H_2P containing substituents at β-positions (compound **I**), *meso*-substituted porphyrins **II**–**V** differ more significantly in the steric structure and properties from the simplest representative of the series, unsubstituted porphine (R = X = H). However, by now the most studied *meso*-substituted porphyrins are still tetraphenylporphine **II** and its symmetrical *o*-, *m*-, and *p*-substituted derivatives. Recent studies [1] showed that introduction into the H_2P molecule of bulky *meso*-alkyl or *meso*-aryl substituents often affects its properties more significantly than does, e.g., introduction of donor or acceptor substituents into the phenyl rings of **II**.

In this study we examined the thermochemistry of solution and solvation of *meso*-tetraphenylporphine **II**, *meso*-tetraisopropylporphine **III**, and *meso*-tetra(α-naphthyl)porphine **IV** in inert (benzene), proton-donor (chloroform), and proton-acceptor (dimethylformamide) solvents (Table 1). We also estimated the solvatochromic effect of porphyrins **I**–**V** and their double-protonated species H_4P^{2+} in these solvents (Table 2).



I–**IV**

R = C_2H_5, X = H (**I**); R = H, X = C_6H_5 (**II**), *iso*-C_3H_7 (**III**), α-$C_{10}H_7$ (**IV**), *cyclo*-C_6H_{11} (**V**).

An advantage of alkyl and aryl substituents is that they exert characteristic electronic and steric effects and, at the same time, do not alter the character of the specific solvation at the macroring periphery, because they contain no polar groups or bonds capable of specific interactions. Thus, the contribution of the specific solvation to the total solvation of such H_2P molecules can be provided by only the –N= and –NH centers. This contribution can be affected only by the above-mentioned electronic and steric effects of the substituents.

The calorimetric data (Table 1) show that the enthalpies of solution ΔH_s^0 of β-octaethylporphine **I**, *meso*-tetraphenylporphine **II**, and *meso*-tetraisopropylporphine **III** in benzene, especially those of the alkyl derivatives (**I**, **III**), are large and positive. The universal solvation of the porphyrin macroring with benzene involves the π–π* electronic interaction of the aromatic systems of H_2P and the solvent [2]. We believe that introduction of conformationally labile alkyl substitu-

Table 1. Enthalpies of solution (ΔH_s^0) and relative solvation (ΔH_{tr}^0) of β- and *meso*-substituted porphyrins **I**–**IV**, kJ mol^{-1}

Comp. no.	Benzene, ΔH_s^0	Chloroform		DMF	
		ΔH_s^0	$-\Delta H_{tr}^0$	ΔH_s^0	$-\Delta H_{tr}^0$
I	39.8 ± 3.1	17.1 ± 3.0	22.7	25.7 ± 0.9	14.1
II	20.7 ± 0.2	9.9 ± 0.2	10.8	10.9 ± 0.2	9.8
III	34.4 ± 3.3	24.5 ± 0.4	9.9	8.3 ± 0.4[a]	26.1
IV	–10.8 ± 0.6	–21.2 ± 0.5	10.4	–25.2 ± 0.2	14.4

[a] Estimated.

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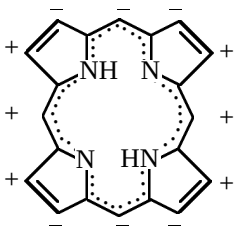
Table 2. Parameters [λ, nm (log ε)] of the electronic absorption spectra of *meso*-substituted porphyrins **I**–**V** and their dications **Ia**–**Va**

Comp. no.	Soret band (*B*)	Band I (*Q*)	$\Delta\lambda_I$, nm[a]	Solvent
I	395 (5.30)	621 (3.81)	–	C_6H_6
Ia	395 (5.41)	590 (3.90)	–31	C_6H_6
I	393 (5.27)	619 (3.74)	–2	$CHCl_3$
Ia	392 (5.43)	591 (3.96)	–29	$CHCl_3$
I	387 (5.31)	619 (3.74)	–2	DMF
Ia	392 (5.41)	589 (3.77)	–30	DMF
II	418 (5.58)	647 (3.68)	–	C_6H_6
IIa	438 (5.62)	654 (4.72)	7	C_6H_6
II	418 (5.67)	646 (3.55)	–1	$CHCl_3$
IIa	436 (5.69)	652 (4.73)	6	$CHCl_3$
II	416 (5.62)	646 (3.68)	0	DMF
IIa	438 (6.12)	656 (5.21)	11	DMF
III	417 (5.18)	661 (3.51)	–	C_6H_6
IIIa	424 (5.27)	639 (4.36)	–22	C_6H_6
III	419 (5.18)	657 (3.60)	–4	$CHCl_3$
IIIa	427 (5.20)	640 (4.30)	–17	$CHCl_3$
III	415 (5.19)	657 (3.54)	–4	DMF
IIIa	419 (5.11)	638 (4.18)	–19	DMF
IV	420 (5.22)	655 (3.76)	–	C_6H_6
IVa	447 (5.00)	645 (4.42)	–10	C_6H_6
IV	423 (5.15)	654 (3.69)	–1	$CHCl_3$
IVa	453 (5.02)	646 (4.36)	–8	$CHCl_3$
IV	421 (5.21)	653 (3.49)	–2	DMF
IVa	450 (4.91)	644 (4.13)	–9	DMF
V	420 (5.05)	663 (3.31)	–	C_6H_6
Va	429 (5.21)	649 (4.37)	–14	C_6H_6
V	424 (5.12)	660 (3.61)	–3	$CHCl_3$
Va	430 (5.15)	648 (4.25)	–12	$CHCl_3$
V	420 (5.03)	659 (3.17)	–4	DMF
Va	429 (5.01)	646 (3.89)	–13	DMF

[a] For solutions of dications **Ia**–**Va**, the shift of band I in going from the ligand H_2P to its dication H_4P^{2+} ($\Delta\lambda_I^{H+}$); for solutions of **I**–**V**, the shift of band I of the ligand in the given solvent ($\Delta\lambda_I$) relative to C_6H_6.

ents into the β- or *meso*-positions of the macroring prevents such solvation. Furthermore, these alkyl substituents, apparently, increase the energy consumption for formation of a cavity in the structure of the solvent (benzene) to accommodate the solute molecule [3]; this factor also makes a positive contribution to ΔH_s^0. In the case of *meso*-tetraphenylporphine **II**, the possible additional π–π* solvation of the phenyl fragments with benzene somewhat decreases ΔH_s^0.

Depending on the substitution of the H_2P molecule (at β- or *meso*-positions, or at the intracyclic NH positions), it can either remain planar or take one of the characteristic nonplanar conformations. The most frequent types of of distortion of the planar chromophore are corrugation and saddle-, dome-, and wave-shaped distortions, as well as their combinations [1]. In particular, whereas octa-β-substituted porphyrins are essentially planar [4], *meso*-substituted porphyrin ligands and their Zn(II) and Ni(II) complexes occur in the crystal in the corrugated conformation which, according to resonance Raman [1] and ^{1}H NMR [5] spectroscopy, is preserved in solution. The corrugated conformation is characterized by alternating upward (+) and downward (–) displacements of the *meso*-positions of H_2P relative to the initial planar molecule (structure **VI**). The mean shift ΔC_{meso} of the *meso*-C atoms from the initial macroring plane can serve as a quantitative measure of corrugation. According to the X-ray structural and spectroscopic data, macrocycles **I**–**V** can be ranked in the following order with respect to the extent of their nonplanarity: **I** < **II** ≈ **IV** < **III** < **V**. Whereas octaethylporphine **I** and tetraphenylporphine **II**, as well as their Ni(II) complexes, are essentially planar and their distortion is due to the crystal packing effects (ΔC_{meso} 0.04 and 0.38 Å, respectively[1]) [4], *meso*-tetraisopropylporphine **III** and *meso*-tetracyclohexylporphine **V** (ΔC_{meso} 0.74 and 0.77 Å, respectively) exist in the crystal in the nonplanar corrugated conformation [1, 6]. However, despite the corrugated structure of the macroring, ΔH_s^0 of **III** in benzene remains large and positive (Table 1). Apparently, large negative values of ΔH_s^0 are characteristic of distorted porphyrins only, e.g., for dodeca-substituted porphyrins having a saddle-shaped structure [1]. For **IV**, ΔH_s^0 (in particular, in benzene) unexpectedly was large and negative. The X-ray structural data for this macrocycle are lacking; however, there are no grounds to assume that this compound is less planar than **II**. Apparently, the most probable structure of **IV** is that with the relatively planar core and almost perpendicular arrangement of the *meso*-α-naphthyl substituents relative to the macroring plane [7].



VI

Another criterion of the increasing nonplanarity (decreasing aromaticity) of macrorings **I**–**V** is a down-

[1] Here and hereinafter, data for the Ni(II) complexes.

field shift of the ^{1}H NMR signals (δ_{NH}, ppm) of the intracyclic NH protons, indicative of the decreased ring current (π-electronic shielding) in the series of related compounds: **I** (–3.74) > **II** (–2.76) ≈ **IV** (–2.53) > **III** –1.80 > **V** (–1.60) [7–9] (solvent $CDCl_3$).

The following factors may be responsible for the fact that the dissolution of **IV** in benzene is more exothermic than that of **II** (Table 1): additional π–π* solvation of the bulkier *meso* substituent; smaller energy required for breaking the solvent structure, because of no rotation of the *meso* fragments around the C_{meso}–C_{naphth} bond; less strong crystal lattice of **IV** becuase of the bulkier *meso* substituent.

The latter factor is, apparently, the most significant, because compound **IV** dissolves with the heat release not only in the inert, universally solvating benzene, but also in the proton-donor chloroform and electron-donor dimethylformamide. The enthalpies of transfer (ΔH^0_{tr}) of porphyrin **IV** from the standard solvent (benzene) into DMF and $CHCl_3$, or the relative enthalpies of solvation of **IV** with these solvents, are close to those of **II**, which is consistent with the classical concept of specific solvation of the =N– and –NH centers of H_2P witgh electron-donor and electron-acceptor solvents [2]. Previous studies of the thermochemistry of solution of natural and synthetic (mainly planar) porphyrins showed that the solvation of the =N– and –NH centers in these molecules is weak because of their shielding with the π-electron system of the planar aromatic macroring, i.e., because of the macrocyclic solvation effect [2]. The enthalpies of transfer (ΔH^0_{tr}) of **I** and **II** into proton-donor chloroform, characterizing the enthalpy of solvation of **I** and **II** with this solvent relative to the standard solvent, are consistent with the basicity of these porphyrins. Owing to the transfer of the σ-electron density to the macroring from the eight electron-donor groups at the β-positions, the tertiary nitrogen atoms in **I** are more basic than those in **II** [1]. Despite the expected increase in the basicity of nonplanar porphyrin **III** due to its decreased aromaticity, the distortion of the planar structure of the chromophore core in **III** is not manifested in the enthalpies of its solution and transfer (Table 1).

The enthalpies of transfer (ΔH^0_{tr}) of **I**, **II**, and **IV** into dimethylformamide are similar and low. Compound **III** is poorly soluble in DMF, and ΔH^0_s of **III** in DMF is an estimated quantity; therefore, ΔH^0_{tr} of **III** into DMF may be somewhat overestimated.

β- and *meso*-Alkyl-substituted porphyrin ligands **I** and **III**–**V** exhibit a classical electronic absorption spectrum (four bands in the visible range and the Soret band, Table 2); the assignments were made in [10, 11]. In going from free porphyrins to their double-protonated species [$H_2P_{(solv)} + 2H^+_{(solv)} \rightleftarrows H_4P^{2+}_{(solv)}$] existing in an organic solvent in the presence of strong acids, the absorption spectrum in the visible range becomes two-band owing to the degeneration of the electronic levels with an increase in the molecular symmetry from D_{2h} to D_{4h}. Band I (*Q* band) is shifted hypsochromically relative to the neutral ligand (Fig. 1). The extent of the hypsochromic shift is usually correlated with the stability of the H_4P^{2+} dication and is considered as a measure of the molecular nonplanarity [12]. However, *meso*-tetraphenylporphine **II**, in contrast to *meso*-alkyl porphine derivatives, e.g., the tetracyclohexyl analog **V**, shows a bathochromic shift of band I ($\Delta\lambda_I^{H+}$) upon protonation (Table 2). This is apparently due to the capability of the *meso*-phenyl substituent to act as a π-electron buffer: its partial conjugation with the π system of the protonated macroring delocalizes the excess positive charge [12]. As a result of extension of the chromophore system of **II**, band I is shifted bathochromically. In the case of *meso*-tetra(α-naphthyl)porphine **IV**, such a π conjugation is impossible for steric reasons; therefore, band I in the protonated species of **IV** is also shifted hypsochromically, and the intensity of the electron transfer in the Soret band decreases (Table 2).

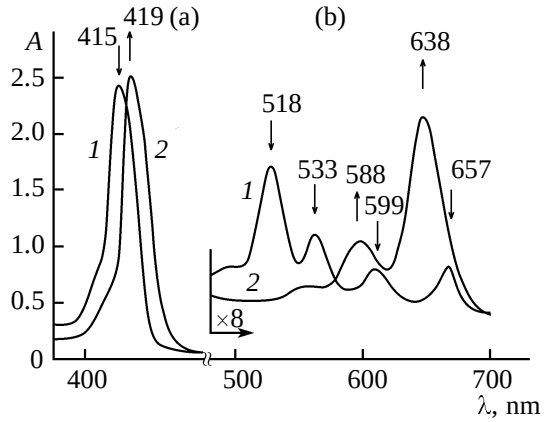


Fig. 1. Electronic absorption spectra of (*1*) **III** and (*2*) its dication **IIIa** in DMF (acidifying agent 3.6 M CF_3COOH): (a) Soret band (*B*) and (b) band I (*Q*).

Aryl- (**II**, **IV**) and alkyl-substituted (**I, III, V**) porphyrins can be readily distinguished by the bathochromic shift of the Soret band upon protonation: ~20–30 and less than 10 nm, respectively.

Porphyrins **I**–**V** show a weak solvatochromic effect upon solvent replacement [the shift of band I of the electronic absorption spectrum ($\Delta\lambda_I$) is within 4 nm], characteristic of the majority of classical porphyrins (Table 2). This fact shows that the first excited (S_1^*)

states of **I**–**V** differ insignificantly from the ground (S_0) state in the solvation with nonpolar with nonpolar (benzene, chloroform) and polar (DMF) solvents. The solvatochromic effect of H_4P^{2+} dications **Ia**–**Va** is virtually as weak as that of the neutral H_2P species (Table 2). Furthermore, we have not observed any correlation of $\Delta\lambda_I^{H+}$ with the solvent polarity, reported previously [12] for dications of porphyrins of other structural groups. The lack of such a correlation may be due to efficient delocalization of the positive charges of protons over the π system of the dication in the case of *meso*- substituted porphyrins with alkyl or aryl substituents.

EXPERIMENTAL

Porphyrins **I**–**V** were prepared, purified, and identified as described in [6, 7, 9–11]. Solvents were dehydrated and purified by standard procedures [13]. The calorimetric experiment was performed with a precision ampule calorimeter with an isothermal jacket, following the procedure described in [14]. The electronic absorption spectra of porphyrins **I**–**V** and their dications were recorded on a Hitachi U-2000 spectrophotometer.

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REFERENCES

1. Senge, M.O., *The Porphyrin Handbook*, Smith, K.M., Kadish, K.M., and Guilard, R., Eds., San Diego: Academic, 2000, vol. 1, p. 239.
2. V'yugin, A.I. and Krestov, G.A., in *Rastvory neelektrolitov v zhidkostyakh* (Solutions of Nonelectrolytes in Liquids), Moscow: Nauka, 1989, p. 137.
3. Hildebrand, G.H. and Scott, R.L., *The Solubility of Non-Electrolytes, New* York: Dover, 1964.
4. Scheidt, W.R., *The Porphyrin Handbook*, Smith, K.M., Kadish, K.M., and Guilard, R., Eds., San Diego: Academic, 2000, vol. 3, p. 49.
5. Medforth, C.J., Muzzi, C.M., Shea, K.M., Smith, K.M., Abraham, R.J, Jia, S., and Shelnutt, J.A., *J. Chem. Soc., Perkin Trans. 2*, 1997, no. 4, p. 839.
6. Senge, M.O., Bischoff, I., Nelson, N.Y., and Smith, K.M., *J. Porphyrins Phthalocyanines*, 1999, vol. 3, no. 2, p. 99.
7. Vodzinskii, S.V., *Cand. Sci. (Chem.) Dissertation*, Odessa, 1990.
8. Medforth, C.J., *The Porphyrin Handbook*, Smith, K.M., Kadish, K.M., and Guilard, R., Eds., San Diego: Academic, 2000, vol. 5, p. 1.
9. Veyrat, M., Ramasseul, R., Turowska-Tyrk, I., Scheidt, W.R., Autret, M., Kadish, K.M., and Marchon, J.-C., *Inorg. Chem.*, 1999, vol. 38, no. 8, p. 1772.
10. Gurinovich, G.P., Sevchenko, A.N., and Solov'ev, K.N., *Spektroskopiya khlorofilla i rodstvennykh soedinenii* (Spectroscopy of Chlorophyll and Related Compounds), Minsk: Nauka i Tekhnika, 1968.
11. Berezin, D.B., Andrianov, V.G., and Semeikin, A.S., *Opt. Spektrosk.*, 1996, vol. 80, no. 4, p. 618.
12. Andrianov, V.G, Malkova, O.V., and Berezin, D.B., *Uspekhi khimii porfirinov*, Golubchikov, O.A., Ed., St. Petersburg: Nauchno-Issled. Inst. Khimii Sankt-Peterb. Gos. Univ., 2001, vol. 3, p. 107.
13. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
14. Berezin, M.B., *Doctoral (Chem.) Dissertation*, Ivanovo, 1993.