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Synthesis and Spectral Parameters of Tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazine and Its Metal Complexes

S. V. Efimova[a], **A. B. Korzhenevskii**[b], **and O. I. Koifman**[b]

[a] *Ivanovo State University of Chemical Technology, pr. F. Engel'sa 7, Ivanovo, 153000 Russia*
e-mail: sef@isuct.ru

[b] *Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia*

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Abstract—Tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazine and its complexes with bivalent metals were synthesized for the first time by template tetramerization of 6-*tert*-butylquinoxaline-2,3-dicarbonitrile. The obtained macrocyclic compounds are soluble in hydrophobic solvents. Their electronic absorption spectra in organic solvents and the spectra of the corresponding protonated forms in sulfuric acid were studied.

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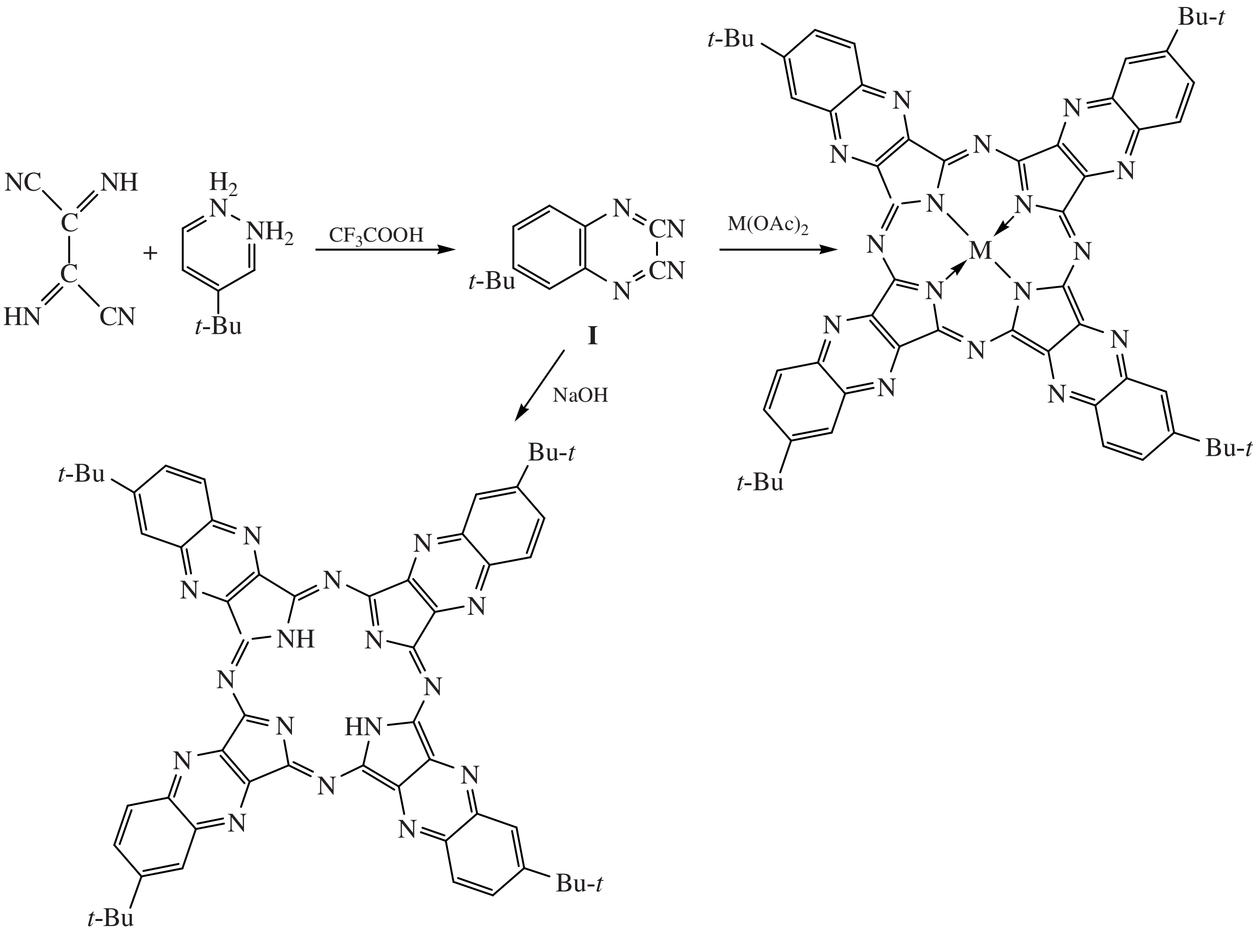
Potential structural diversity of tetraarenoporphyrazines, as well as diversity of practically useful properties of already prepared compounds of this series, determines the necessity of further synthesis of new derivatives and studies on their properties with a view to develop materials of new generation for various fields of practical application. Undoubtedly, aza analogs of naphthalocyanine attract strong interest from the viewpoints of both fundamental science and possible practical use. However, studies and application of known octaaza-2,3-naphthalocyanines, i.e., tetra-2,3-quinoxalinoporphyrazines are considerably limited, or (in some cases) they become impossible because of very poor solubility of these compounds in organic solvents [1].

It is known that introduction of various peripheral substituents into tetraarenoporphyrazine molecules makes them better or lesser soluble in different solvents, depending on the substituent nature and their number. Introduction of *tert*-butyl groups into the phthalocyanine molecule is known to considerably improve the solubility in organic solvents, whereas the electronic and geometric structure remains almost unchanged, as follows from almost complete identity of the electronic absorption spectra of the substituted and parent compounds in both DMF and H_2SO_4 [2]. Such liophilization could extend not only the set of methods applicable for studying physicochemical properties of these compounds but also the scope of their application in various fields, from chemistry and medicine to optoelectronics. Although some *tert*-butyl-substituted tetra(azaareno)porphyrazines, namely tetra(6-*tert*-butyl-3,4-pyridino)porphyrazine [3] and tetra(5-*tert*-butyl-2,3-pyrazino)porphyrazine [4] and their metal complexes have been synthesized and characterized by spectral methods, syntheses of copper and vanadyl complexes of tetra(*tert*-butylquinoxalino)porphyrazine have been reported only in [5, 6].

The goal of the present study was to synthesize tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazine (**II**) and its complexes **III**–**V** with bivalent metals and examine their spectral parameters. Compounds **II**–**V** were prepared as shown in Scheme 1.

Compounds **II**–**V** were not reported previously; they were isolated as dark green powders which did not melt up to 350°C. Compounds **II**–**V** are much better soluble in DMF and DMSO as compared to unsubstituted analogs and, unlike the latter, are soluble in chloroform, benzene, and alcohol. Therefore, it was possible to purify them by column chromatography on silica gel. Tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazine (**II**) and its metal complexes **III**–**V** were isolated as crystal hydrates. Before studying their spectral properties, they were subjected to thermal treatment at 423–523 K under a residual pressure of 10^{-4} MPa. The

Scheme 1.



II, M = H_2; **III**, M = Cu; **IV**, M = Co; **V**, M = Zn.

completeness of dehydration was checked by thermogravimetric analysis.

It was interesting to examine the effects of the central metal ion and solvent nature on the spectral parameters of compounds **II**–**V** in solution. The electronic absorption spectra of tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazine (**II**) and its metal complexes **III**–**V** in aprotic solvents (benzene, chloroform; Fig. 1) contained strong bands in the yellow–red and UV regions, which is typical of phthalocyanines. Unfortunately, among common aprotic solvents, only DMF and DMSO can be used for studying the spectra of tetra(2,3-quinoxalino)porphyrazines and their tetra-*tert*-butyl-substituted analogs. Therefore, we were able to estimate the effect of peripheral alkyl groups on the electronic absorption spectra only in DMF. In the spectrum of **II**, as well of its unsubstituted analog, the first *Q*-band is not split. The same is characteristic of phthalocyanine. Unlike the spectra of unsubstituted metal complexes, which lack Soret band, complexes **III**–**V** displayed a strong absorption band at λ ~350 nm.

Introduction of *tert*-butyl groups almost does not change the position of the first absorption band in the spectra of metal-free compound **II** and its copper and zinc complexes **III** and **V**, while cobalt complex **IV** is characterized by blue shift of that absorption maximum ($\Delta\lambda_{max}$ = 11 nm). On the other hand, its vibrational satellite in the spectra of copper and zinc complexes **III** and **V** is resolved better, the shift of the absorption maximum being minimal ($\Delta\lambda_{max}$ = 3 and –7 nm, respectively), but it disappears from the spectra of ligand **II** and cobalt complex (**IV**) (the corresponding unsubstituted analogs show an inflection point).

Interestingly, the spectra of modified tetra-2,3-quinoxalinoporphyrazines (except for zinc complex **V**) contain fairly intense absorption bands in the region λ

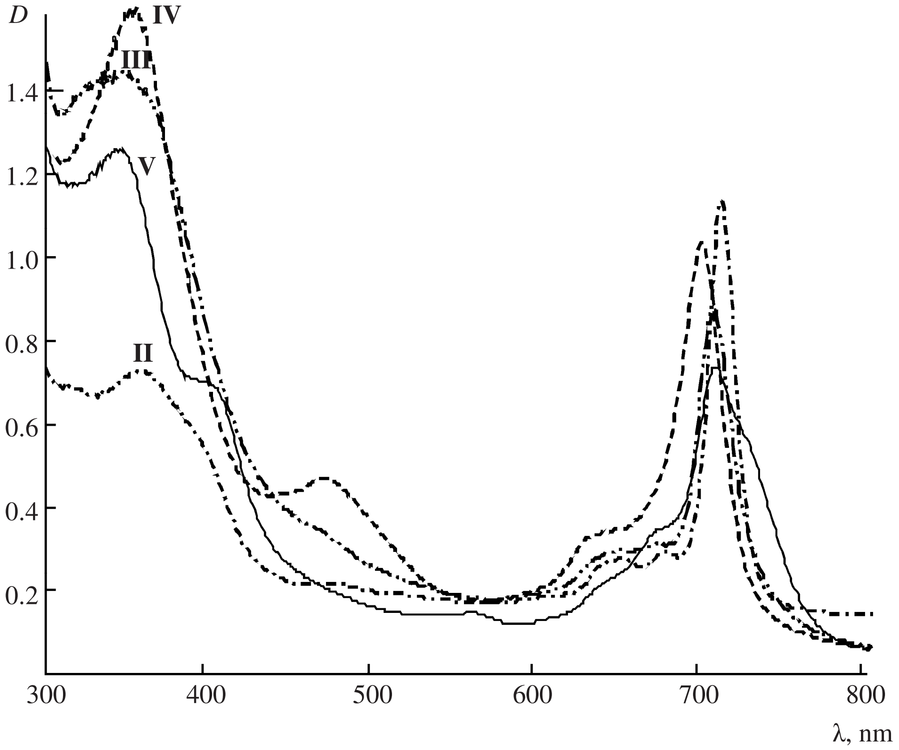


Fig. 1. Electronic absorption spectra of tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazines **II**–**V** in DMF.

640–650 nm, whose origin was not identified. Analogous bands were also observed in chloroform (**II**, **V**) and benzene (**III**–**V**). Complexation of porphyrazine **II**, as well as of its unsubstituted analog, with copper and zinc is not accompanied by shift of the *Q*-band, while the *Q*-band in the spectrum of cobalt complex **IV** is displaced by 11 nm toward shorter wavelengths.

Solvatochromic effect (see table; Figs. 1, 2) for the alkyl-substituted macrorings is reflected in the appearance of absorption bands at λ 640–650 nm and vibrational satellite of the *Q*-band, position of the Soret band (the strongest effect is observed for complex **III**: $\Delta\lambda_{max} = -22$ nm in going from DMF to benzene), and absorption intensities. The position of the *Q*-band in the spectra of solutions of the ligand and metal complexes almost does not change: the maximal Δλ value (+10 nm) was found for complex **V** in going from chloroform to benzene.

Study on the electronic absorption spectra of tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazines **II**–**V** in concentrated sulfuric acid (Fig. 3) showed that peripheral alkylation almost does not affect the mode of protonation. Like unsubstituted tetraquinoxalinoporphyrazine and its metal complexes, the first band in

Electronic absorption spectra of tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazines **II**–**V**

Solvent	λ_{max}, nm (log ε)			
	II	**III**	**IV**	**V**
DMF	707 (4.61)	704 (4.52)	695 (4.78)	707 (4.32)
	–	670 (4.02)	–	669 (4.11)
	640 (4.32)	647 (4.12)	648 (4.34)	–
	350 (4.78)	352 (4.65)	348 (4.79)	347 (4.41)
$CHCl_3$	712 (4.78)	707 (4.65)	704 (4.62)	704 (4.58)
	679 (4.41)	664 (4.19)	660 (4.38)	671 (4.25)
	644 (4.32)	–	–	645 (4.15)
	347 (4.72)	344 (4.68)	342 (4.75)	357 (4.78)
Benzene	710 (4.25)	708 (4.12)	698 (4.08)	714 (4.18)
	665 (3.78)	–	–	667 (3.68)
	–	648 (3.63)	647 (3.54)	650 (3.52)
	347 (4.45)	329 (4.38)	350 (4.28)	348 (4.34)
H_2SO_4	750 (4.21)	745 (4.48)	746 (4.25)	768 (4.72)
	612 (4.08)	–	603 (4.58)	605 (4.63)
	–	544 (4.51)	535 (4.62)	560 (4.52)
	378 (4.86)	395 (4.88)	402 (4.89)	390 (5.12)
	264 (4.78)	251 (4.91)	268 (4.85)	256 (4.93)
	205 (4.93)	207 (4.89)	–	–

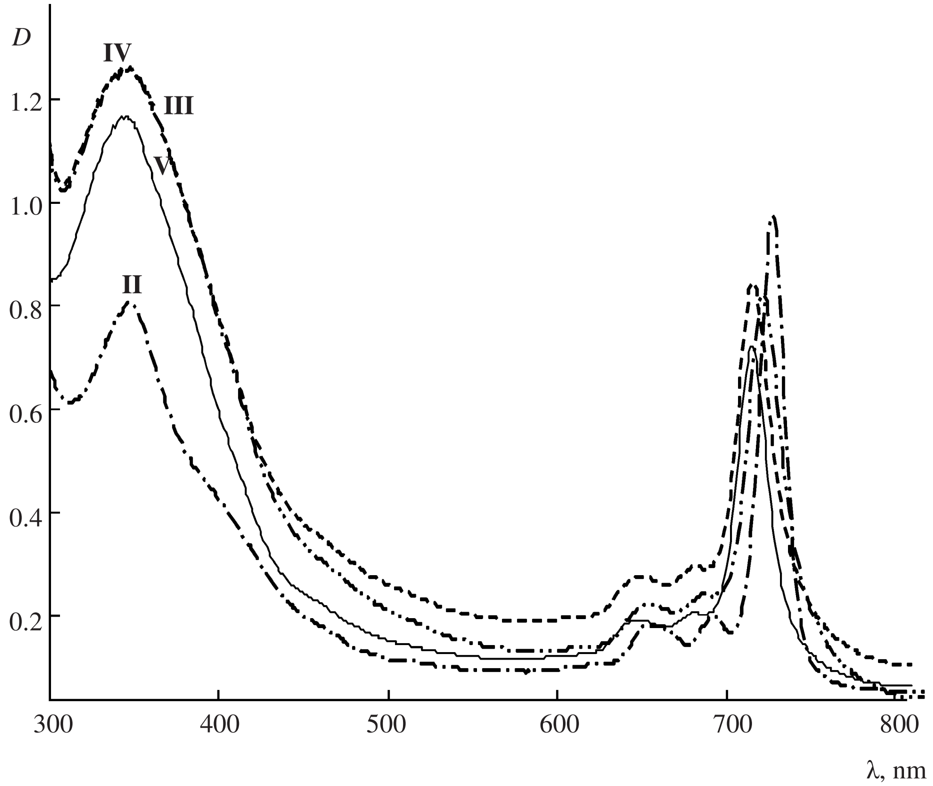


Fig. 2. Electronic absorption spectra of tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazines **II**–**V** in chloroform.

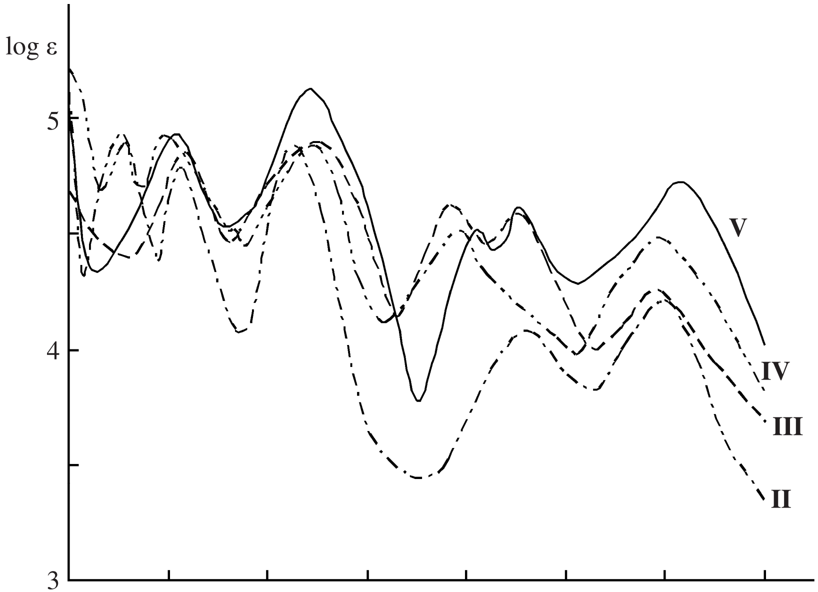


Fig. 3. Electronic absorption spectra of tetra(6-*tert*-butyl-2,3-quinoxalino)porphyrazines **II**–**V** in 17.5 M H_2SO_4.

the electronic absorption spectra of **II**–**V** in sulfuric acid shifts red relative to its position in the spectra recorded from organic solutions, which is quite consistent with the up-to-date concepts on polarization of the main chromophore upon protonation. The magnitude of the red shift is almost the same for the substituted and unsubstituted compounds. As in the spectra in DMF, coordination of ligand **II** to the examined metals in sulfuric acid solution leads to a blue shift of the first absorption band whose position is weakly related to the metal nature.

EXPERIMENTAL

The electronic absorption spectra were measured on a Perkin–Elmer Lambda 20 spectrophotometer using rectangular cells with a cell path length of 0.1 to 1 cm; concentration 10^{-4}–10^{-6} M. The IR spectra were obtained from samples pelleted with KBr on an Avatar 360 FT-IR ESP spectrometer with Fourier transform. The elemental compositions were determined on a FlashEATM 1112 analyzer.

2,3-Diiminosuccinonitrile was synthesized by oxidation of 2,3-diaminomaleonitrile with dichlorodicyanobenzoquinone [7]. Yield 92%, mp 165–166°C. Found, %: C 45.55, 45.69; H 1.90, 1.88; N 52.55, 52.43. $C_4H_2N_4$. Calculated, %: C 45.28; H 1.88; N 52.83.

4-*tert*-Butylbenzene-1,2-diamine was synthesized by successive nitration and reduction of 4-*tert*-butylaniline [8]. Yield 67%, mp 96–97°C. Found, %: C 71.37, 71.40; H 9.62, 9.61; N 19.01, 18.99. $C_{10}H_{16}N_2$. Calculated, %: C 71.42; H 1.53; N 19.05.

6-*tert*-Butylquinoxaline-2,3-dicarbonitrile (I). A mixture of 0.5 g of 2,3-diiminosuccinonitrile and 0.5 g of *tert*-butylbenzene-1,2-diamine was added over a period of 30 min to 10 ml of trifluoroacetic acid, maintaining the temperature not exceeding 20°C. The resulting suspension was left to stand at room temperature, Trifluoroacetic acid was removed under reduced pressure, and the residue was washed with water, dried, and recrystallized from benzene. Yield 0.73 g (52%), mp 110–112°C. IR spectrum (KBr), ν, cm^{-1}: 3242 (C=N), 2978–2875 (C–H), 2252 (C≡N). Found, %: C 68.45, 68.58; H 5.02, 5.01; N 26.53, 26.41. $C_{14}H_{12}N_4$. Calculated, %: C 68.85; H 4.91; N 26.22.

($2^{4(5)}$,$7^{4(5)}$,$12^{4(5)}$,$17^{4(5)}$-Tetra-*tert*-butyl-5,10,15,20-tetraazatetraquinoxalino[2,3-*b* : 2′,3′-*g* : 2″,3″-*l* : 2‴, 3‴-*q*]porphyrin) (II). A mixture of 1 g of 6-*tert*-butylquinoxaline-2,3-dicarbonitrile (**I**) and 1 g of anhydrous sodium hydroxide was heated to 200–220° C, and the melt was kept for 10–15 min at that temperature. The mixture was cooled and ground with distilled water, and the precipitate was filtered off. The product was washed on a filter in succession with distilled water (until neutral washings), 50 ml of hydrochloric acid (slowly), and water again and subjected to chromatography on silica gel using chloroform was eluent, and the eluate was evaporated to dryness. Yield 75%. Found, %: C 70.95, 71.00; H 5.26, 5.29; N 23.77, 26.71. $C_{56}H_{50}N_{16}$. Calculated, %: C 71.04; H 5.28; N 23.67.

($2^{4(5)}$,$7^{4(5)}$,$12^{4(5)}$,$17^{4(5)}$-Tetra-*tert*-butyl-5,10,15,20-tetraazatetraquinoxalino[2,3-*b* : 2′,3′-*g* : 2″,3″-*l* : 2‴, 3‴-*q*]porphyrin) metal complexes III–V *(general procedure)*. A mixture of 0.23 g of 6-*tert*-butylquinoxaline-2,3-dicarbonitrile (**I**), 0.25 mmol of copper(II), cobalt(II), or zinc(II) acetate, and a catalytic amount of ammonium molybdate was heated to 200–220°C, and the melt thus formed was kept for 30 min at that temperature. The mixture was cooled and treated in succession with boiling 5% hydrochloric acid and boiling 5% aqueous ammonia, and the precipitate was filtered off and subjected to chromatography on silica gel using chloroform as eluent. Complexes **III**–**V** were isolated as dark green finely crystalline substances with metal luster, which did not melt up to 400°C; compounds **III**–**V** are readily soluble in organic solvents.

Complex **III**. Yield 68%. Found, %: C 66.67, 66.62; H 4.75, 4.79; N 22.25, 22.28. $C_{56}H_{48}N_{16}Cu$. Calculated, %: C 66.70; H 4.76; N 22.23.

Complex **IV**. Yield 57%. Found, %: C 66.97, 66.99; H 4.75, 4.79; N 22.34, 22.32. $C_{56}H_{48}N_{16}Co$. Calculated, %: C 67.00; H 4.78; N 22.33.

Complex **V**. Yield 74%. Found, %: C 66.62, 66.61; H 4.73, 4.74; N 22.22, 22.23. $C_{56}H_{48}N_{16}Zn$. Calculated, %: C 66.60; H 4.75; N 22.20.

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