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Effect of Linear Benzannelation on the Spectral Appearance of Octaaza Substitution in Phthalocyanine and Its Metal Complexes

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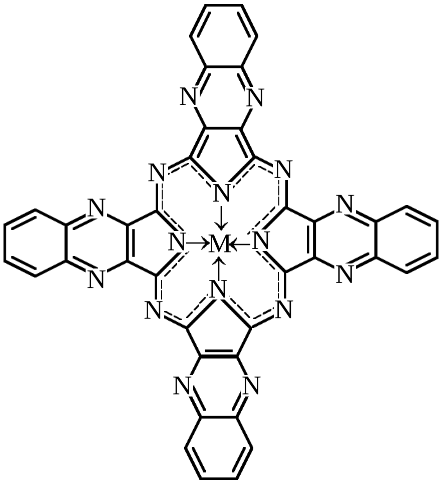
Abstract—The effect of linear benzannelation on the spectral appearance of peripheral octaaza substitution in phthalocyanine molecules in going from tetrapyrazinoporphyrazines to tetra-2,3-quinoxalinoporphyrazines in protic and aprotic solvents, such as H_2SO_4, high-percentage oleum, DMSO, and DMF) is intricate and does not allow the contribution of such ligand modification to be assigned exclusively to decreased electron-acceptor power of its periphery.

The electronic absorption spectra of phthalocyanines and their structural analogs have been well docimented. In particular, spectral characteristics of a series of metal complexes of 2,3- naphthalocyanine (2,3-NcM) [1], tetra-2,3-pyridinoporphyrazine (2,3-PycM) [2], tetrapyrazinoporphyrazine (PZCM) [3], tetra-2,3-quinolinoporphyrazine (2,3-QycM) [4, 5], and tetra-2,3-quinoxalinoporphyrazine (I) (2,3-QxcM) [6, 7] in organic solvents (DMSO, quinoline, dimethyl sulfate) have been reported.

It is noted that whereas introduction of nitrogen into phthalocyanine benzene ring produces a strong hypsochromic shift of the long-wave absorption maximum, increasing from tetra- to octaaza derivatives [2, 3], linear benzannelation of phthalocyanine and its aza analogs results in a strong bathochromic shift of this band, which compensates the effect of aza substitution. Thus, isometallic complexes of tetra(areno)- and tetra(azaareno)porphyrazines can be arranged in the following order: 2,3-NcM > 2,3-QycM > 2,3-QxcM > PcM > 2,3-PycM > PzcM, in terms of the position of the principal absorption maximum.

To assess the effect of linear benzannelation of the spectral properties of tetrapyrazinoporphyrazines, in the present work we obtained and analyzed the electronic absorption spectra of tetra-2,3-quinoxalinoporphyrazine (**Ia**) and its metal complexes **Ib**–**Ih** in protic and aprotic solvents (H_2SO_4, high-percentage oleum, DMSO, and DMF).

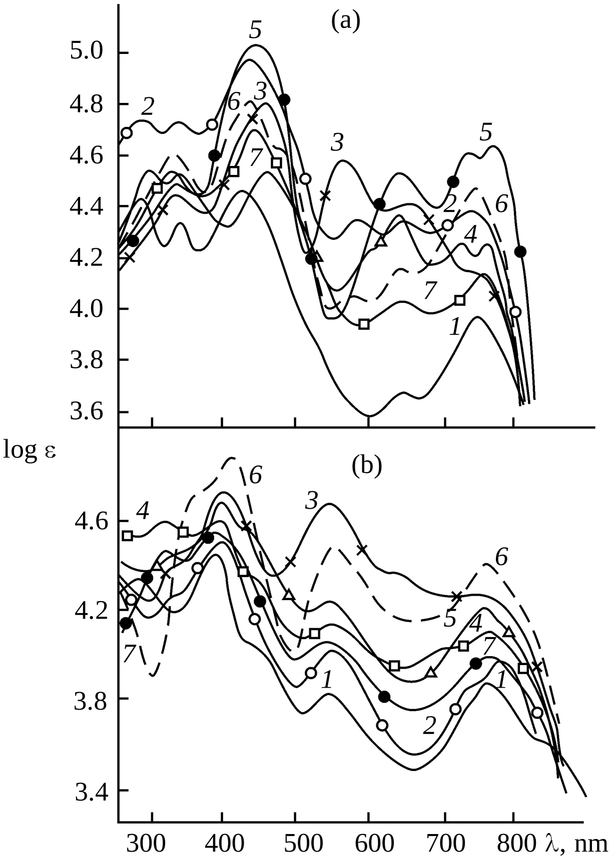


Ia–**Ih**

M = H_2 (**a**), M = Cu(II) (**b**), M = Co(II) (**c**), M = Ni(II) (**d**), M = Fe(II) (**e**), M = Fe(III) (**f**), M = Zn (**g**), M = Mg (**h**).

In aprotic solvents, the visible absorption spectra of tetrapyrazinoporphyrazines and tetra-2,3-quinoxalinoporphyrazines are similar to each other and have, except for iron(II), cobalt(II), and metal-free compounds, a normal “phthalocyanine” pattern.

Linear benzannelation of tetrapyrazinoporphyrazine does not affect the anomalous spectral pattern of the latter, i.e. the *Q* band is still nonspilt, unlike what is observed with phthalocyanine. Moreover, additional absorption bands appear at 470 nm [OxcFe(II) and OxcCo(II)] and, with OxcFe(III), one more band at 565 nm. At the same time, the first absorption band of PzcH2 and its metal complexes suffers a strong bathochromic shift: by 79–111 nm in DMSO and by



Electronic absorption spectra of (a) 2,3-QxcM in 17.8 M H_2SO_4 and (b) high-percentage oleum. (*1*) 2,3-$QxcH_2$, (*2*) 2,3-QxcCu, (*3*) 2,3-QxcCo, (*4*) 2,3-QxcNi, (*5*) 2,3-QxcFe, (*6*) 2,3-QxcZn, and (*7*) 2,3-QxcMg.

66–83 nm in DMF. Therewith, the intensity of the visible absorption gets much weaker.

Linear benzannelation in Oxc derivatives results in that the optical properties in their solutions get much solvent-dependent, unlike what is observed with PzcM. The solvatochromism of 2,3-QxcM reveals itself even in going from DMSO to DMF. If in the former solvent the Q band shifts from that in 2,3-$QxcH_2$ (700 nm) by –17 [2,3-QxcCo(II)] to +58 nm [2,3-QxcNi(II)], in the latter neither complex formation in itself nor the nature of the metal have almost no effect on the position of the *Q* band (707 ± 3 nm).

With phthalocyanine, complex formation always makes the first absorption band to shift hypsochromically, whereas in going from octaaza-substituted phthalocyanine to its metal complexes the spectra in DMSO reveal an anomalous bathochromic shift by 2 nm with PzcZn and by 26 nm with PzcNi(II). Linear benzannelation not only enhances this spectral anomaly in 2,3-QxcZn and 2,3-QxcNi(II) (3 and 58 nm, respectively), but even is responsible for it in 2,3-QxcFe(II) (8 nm). Probably, benzannelation of octaazaphthalocyanine complexes of these metals results in flattening of the π-electron framework of the ligand molecule and its denser population.

The spectra of tetra-2,3-quinoxalinoporphyrazines in conc. H_2SO_4 and high-percentage oleum (see figure) showed that in protic media linear benzannelation still stronger affects the spectral pattern typical of PzcM.

In solutions of 2,3-$QxcH_2$, $PzcH_2$, and their metal complexes in conc. H_2SO_4, the first absorption band is generally shifted bathochromically (compared with its position in organic solvents), which is normal and corresponds to the present notion of the protonation-induced polarization of the principal chromophore as a reason for the spectral changes observed in going from solutions of phthalocyanines in aprotic solvents to those in protic solvents. Therewith, in the case of 2,3-QxcM, the shift is much larger than in the case of isometallic complexes of tetrapyrazinoporphyrazine, which results from the enlargement of the π-electron system of the ligand and enhancement of its polarizability, produced by linear benzannelation.

At the same time, octaaza substituion in PzcNi(II) and PzcFe(II) shifts their first absorption band hyprochromically, which is probably associated with a strong protonation-induced disturbance of the planarity of the ligand. Note that linear benzannelation in nickel(II) complexes renders this anomaly still more pronounced, that is the hypsochromic shift gets larger. Linear benzannelation in PzcFe(II) not only increases the spectral shift in absolute value, but also changes its sign.

Like with solutions of 2,3-QxcM in DMSO, the position of the first absorption band in the spectra of H_2SO_4 solutions is metal-dependent. Coordination of 2,3-$QxcH_2$ with most of the metals studied (except for Ni and Zn) most commonly shifts the first band hyprochromically, and many authors considered this phenomenon as a spectral criterion of the strength of macrocyclic complexes.

Linear benzannelation enhances the bathochromic shift in the case of the zinc complex (the only of PzcM whose *Q* band is shifted bathochromically on coordination in H_2SO_4 solutions) and gives rise to a bathochromic shift in the case of the nickel complex. However, in going from DMSO to H_2SO_4, these complexes change places in terms of the value of the bathochromic shift.

Thus, by the value of the shift of the *Q* band (nm) in the spectra of H_2SO_4 solutions in going from 2,3-

$QxcH_2$ to 2,3-QxcM, the metals can be arranged in the following order: Zn (+23), Ni(II) (+13), Fe(II) (–3), Mg (–5), Co(II) (?8), Cu(II) (–18), and Fe (III) (–35).

In general, linear benzannelation renders the spectra of tetrapyrazinoporphyrazines much more intricate (except for 2,3-$QxcH_2$ and 2,3-QxcMg).

The spectra of tetra-2,3-quinoxalinoporphyrazines in conc. H_2SO_4 clearly tend to lose their "phthalocyanine" character and change from two-band (strong *Q* and Soret bands) to four-band: ~750 (*Q* band), ~610, ~550, and ~400 nm (Soret band). Thus, in the spectra of 2,3-$QxcH_2$ and its Zn, Mg, and Fe(II) complexes, one additional band appears at ~610 nm, with Fe(III) complex, at ~550 nm, and with complexes Co(II), Ni(II), and Cu(II), both additional bands take place, therewith, in the latter complex the band at ~610 nm is shifted bathochromically by ~80 nm. In certain cases, these two bands compare in intensity (2,3-QxcCu) with or are even stronger [2,3-QxcCo(II), 2,3-QxcFe(III), and 2,3-QxcNi(II)] than the *Q* band which, in its turn, exhibit tendency for strong broadening and, with 2,3-QxcZn and 2,3-QxcNi(II), for broadening and splitting.

Contrary to expectations, in going from conc. H_2SO_4 to high-percentage oleum, the linear benzannelation–induced bathochromic shift of the *Q* band: In both ligand series, it varies within 15 nm, except for 2,3-QxcCu(II) (50 nm).

Nevertheless, in the spectra in high-percentage oleum, too, linear benzannelation in tetrapyrazinoporphyrazines appears rather unusually. Whereas the spectra of the latter [except for PzcCo(II)] in high-percentage oleum are almost identical to those in H_2SO_4, linear benzannelation makes the visible part of the spectrum three-band, including the Soret band. The spectra of 2,3-$QxcH_2$ and its metal complexes are no longer "phthalocyanine," since they contain bands near 550 nm, that compare in intensity with the *Q* band, and have the Soret band bathochromically shifted and three visible bands strongly broadened. Such pattern is quite untypical of the other members of the tetrapyrazinoporphyrazine series.

The interpretation of bands in this region [weak in the spectra of PzcCo(II) and PzcFe(II) in conc. H_2SO_4 and oleum] as an intramolecular metal-to-ligand charge-transfer band, proposed by Berezin *et al.* [3], seems unlikely in view of the appearance of a band at 541 nm in the spectrum of 2,3-$QxcH_2$.

The intricate effect linear benzannelation exerts on the spectral properties of tetrapyrazinoporphyrazines shows that such modification of the heterocyclic ligand should not be only considered as a kind of "electronic damping" that compensates for the effect of octaaza substitution in the immediate ("primary") environment of the porphyrazine, i.e. reducing the electron-acceptor ability of the periphery. It is more reasonable to consider the additional aromatic rings ("secondary" environment) as an "electronic reservoir," whose response to changes in the coordination center of the molecule or to solvent and the sensitivity to these factors, i.e. the degree of involvement of the "secondary" environment into the electronic structure of the principal chromophore depends on the properties of its "primary" environmrnt.

EXPERIMENTAL

The electronic absorption spectra were taken on a Perkin–Elmer Lambda-20 spectrophotometer in quartz rectangular cells 10 mm thick, for ~10^{-5} M solutions.

The valence state of Co and Fe in compounds **Ic**–**If** was established by ESR spectroscopy.

Tetra-2,3-quinoxalinoporphyrazines were prepared as described in [7, 8]. Compounds **Ie** and **If** were synthesized from Fe(II) oxalate and sulfate, respectively.

Compounds **Ia**–**Ih** were purified by extraction of admixtures with hot water and acetone in a Soxhlet apparatus, followed by triple reprecipitation form conc. H_2SO_4 (except for 2,3-QxcMg), washing with water to neutral and sulfate-free washings, and drying to constant weight at 323 K.

2,3-$QxcH_2$ and metal complexes were obtained as hydrates, and, therefore, they was subjected to thermal vacuum treatment at 423–523 K and 10^{-4} MPa. Completeness of dehydration was controlled by thermal analysis.

Tetraquinoxalinoporphyrazines are black fine crystals with metallic shine. They do not melt up to 400°C.

Tetraquinoxalinoporphyrazine (**Ia**). Yield 68%. Found, %: C 66.90; H 2.50; N 31.02. $C_{40}H_{18}N_{16}$. Calculated, %: C 66.89; H 2.49; N 31.03. Copper(II) tetraquinoxalinoporphyrazine (**Ib**). Yield 61%. Found, %: C 60.70; H 1.93; Cu 8.10; N 28.01. $C_{40}H_{16}CuN_{16}$. Calculated, %: C 61.26; H 2.04; Cu 8.11; N 28.59. Cobalt(II) tetraquinoxalinoporphyrazine (**Ic**). Yield 78%. Found, %: C 62.20; H 2.01; Co 6.99; N 28.34. $C_{40}H_{16}CoN_{16}$. Calculated, %: C 61.62; H 2.05; Co 7.57; N 28.76. Nickel(II) tetraquinoxalinoporphyrazine (**Id**). Yield 81%. Found, %: C 61.00; H 2.02; N 28.76; Ni 8.10. $C_{40}H_{16}N_{16}Ni$. Calculated, %: C 61.64; H 2.05; N 28.77; Ni 7.54. Iron(II) tetraquinoxalinoporphyrazine (**Ie**). Yield 72%. Found, %: C 61.50; H

2.01; Fe 7.50; N 28.78. $C_{40}H_{16}FeN_{16}$. Calculated, %: C 61.86; H 2.06; Fe 7.22; N 28.86. Iron(III) tetraquinoxalinoporphyrazine hydrosulfate (**If**). Yield 70%. Found, %: C 55.43; H 2.07; Fe 6.10; N 26.14. $C_{40}H_{17}FeN_{16}O_4S$. Calculated, %: C 54.98; H 1.95; Fe 6.41; N 25.66. Zinc tetraquinoxalinoporphyrazine (**Ig**). Yield 65%. Found, %: C 61.40; H 2.13; N 28.01; Zn 8.40. $C_{40}H_{16}N_{16}Zn$. Calculated, %: C 61.11; H 2.04; N 28.52; Zn 8.33. Magnesium tetraquinoxalinoporphyrazine (**Ih**). Yield 48%. Found, %: C 64.99; H 2.50; Mg 3.22; N 29.80. $C_{40}H_{16}MgN_{16}$. Calculated, %: C 64.52; H 2.15; Mg 3.23; N 30.11.

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REFERENCES

1. Mikhailenko, S.A. and Luk’yanets, E.A., *Zh. Obshch. Khim.*, 1969, vol. 39, no. 11, p. 2554.
2. Bykova, V.V., *Cand. Sci. (Chem.) Dissertation*, Ivanovo, 1981.
3. Berezin, B.D., Klyuev, V.N., and Korzhenevskii, A.B., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1977, vol. 20, no. 3, p. 357.
4. Korzhenevskii, A.B., Markova, L.V., and Koifman, O.I., *Khim. Geterotsikl. Soedin.*, 1992, no. 8, p. 1068.
5. Markova, L.V., Korzhenevskii, A.B., Koifman, O.I., and Gal’pern, M.G., *Zh. Khim. Nevodn. Rastvorov*, 1992, vol. 1. no. 2, p. 207.
6. Markova, L.V., Korzhenevskii, A.B., Koifman, O.I., and Panova, M.V., Avstracts of Perers, *XVII Vsesoyuznogo chugaevskogo soveschaniya po khimii kompleksnykh soedinenii* (XVII Russian Chugaev Meeting on Chemistry of Complex Compounds), Minsk, 1990, part 2, p. 382.
7. Gal’pern, M.G. and Luk’yanets, E.A., *Zh. Obshch. Khim.*, 1969, vol. 39, no. 11, p. 2536.
8. Markova, L.V., *Cand. Sci. (Chem.) Dissertation*, Ivanovo, 1991.