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The Effect of Functional Substitution on Thermal Stability of Pyridinylporphyrins under Argon Atmosphere

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Abstract—The data on thermal stability under argon atmosphere of a series of porphyrin ligands containing meso- and β-positioned electron-donor (Me, Et, or Ph) groups as well as electron-acceptor pyridinyl substituents differing in the heteroatom location are presented. Thermogravimetric analysis and electron absorption spectroscopy studies have shown that pyridinylporphyrins are thermally stable at heating to 360–500°C depending on the functional substitution in the molecule.

Keywords: pyridinylporphyrin, degradation, thermal stability, argon, thermogravimetric analysis, electron absorption spectroscopy

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Porphyrins and their structural analogs have been applied as catalysts of various chemical, electrochemical, and photochemical processes [1–3], as therapeutic and diagnostic compounds [4–7], brilliance-forming additives [7], dyes [8, 9], optical materials [10], chemical sensors [10–12], etc.

Pyridinyl-substituted porphyrins and their complexes with *d*-metals are especially attractive, owing to the capacity of the pyridine nitrogen atom bearing a lone-electron pair to form bonds with electron-acceptor molecules, cations, etc.

The estimation of the pyridinylporphyrins potential for practical applications requires the information on their stability under diverse conditions; the relevant data have been almost absent in the literature so far [13, 14]. For instance, the technology of production of oxygen cathodes of fuel cells includes the stage of thermal treatment of the catalyst, and the information of thermal stability of potential catalysts is of topical importance.

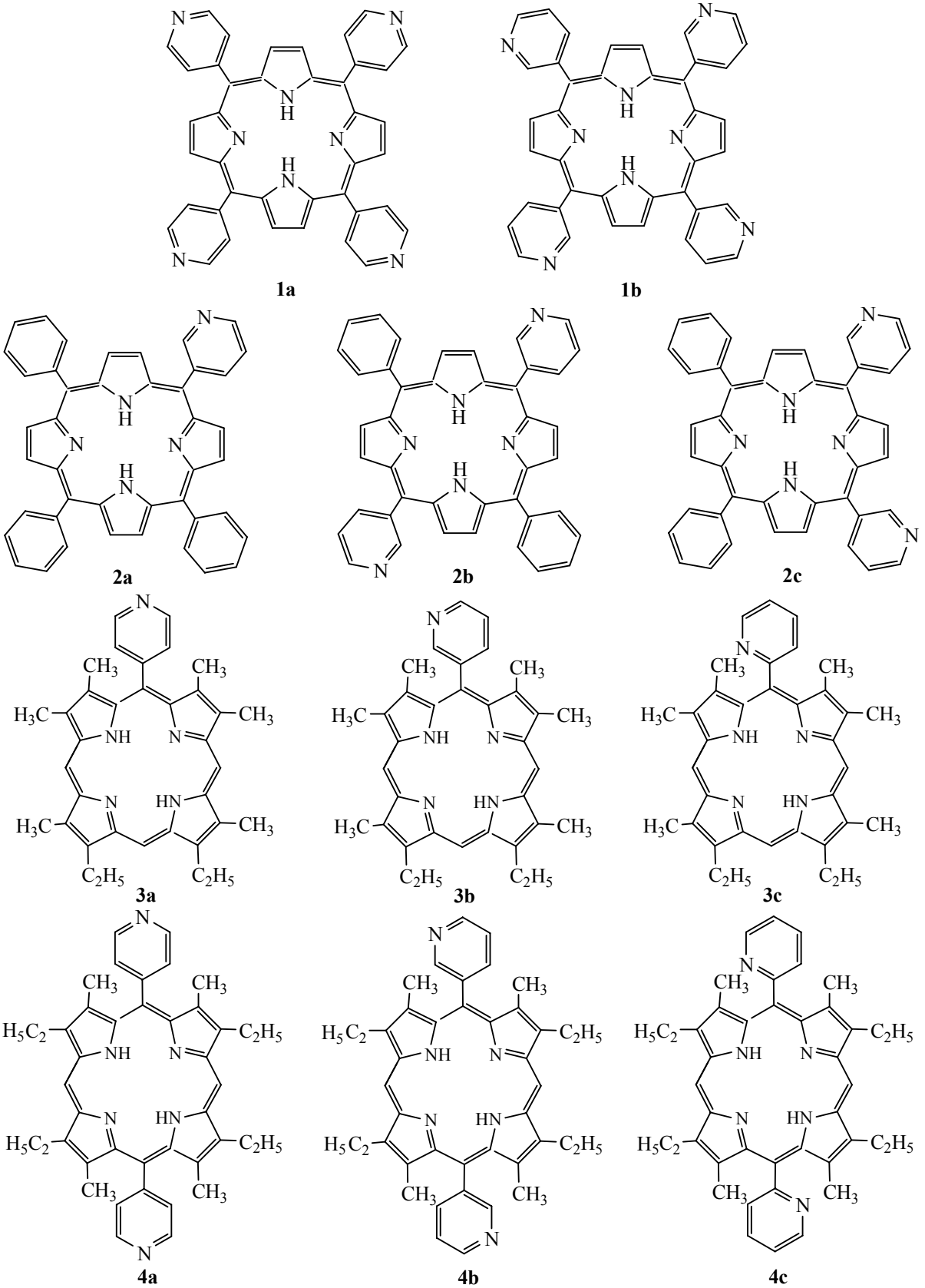
In order to analyze the effects of the nature and the number of functional substituents in porphyrin molecules, we performed thermogravimetric analysis of solid porphyrins **1–4** under conditions of thermal decomposition at linear heating in an inert atmosphere (Scheme 1).

Introduction of additional electron-acceptor substituents to the molecule of porphyrin generally reduces the thermal stability of the macrocycle due to the decrease in the electron density. This observation was confirmed in this study (see the table). For example, mono-, di-, and tetrasubstituted pyridinylporphyrins (except for compound **1a**) exhibited the lower onset of thermal decomposition (t_{start}) as compared to the unsubstituted analog.

In the case of the *meso*-substituted porphyrins even the substitution of one of the phenyl groups with the π-acceptor pyridinyl group (compound **2a**) resulted in the t_{start} decrease by 15°C by comparison with the parent compound H_2TPhP. Further increase in the number of the electron-acceptor groups (compounds **2b**, **2c**, **1b**) led to the decrease in t_{start} by 12–22°C.

The data on the thermal stability of the porphyrins differing in the spatial arrangement of the pyridinyl substituents with respect to the porphine macrocycle demonstrated that the t_{start} value for the 5,10-isomer (**2c**) was slightly higher than in the case of the isomer with the substituents in positions 5 and 15 (**2b**).

Scheme 1.



Thermogravimetric analysis data on decomposition of pyridinylporphyrins **1–4** and tetraphenylporphyrin (H_2TPhP) under argon atmosphere[a]

Compound	m_o, mg	t_{start}, °C	t_{max}, °C	t_{end}, °C	m_{a1}^{exp}, %	t_{start}, °C	t_{max}, °C	t_{end}, °C	m_{a2}^{exp}, %
H_2TPhP [16]	5.631	–	–	–	–	470.2	486.1	498.5	51.54
1a	3.883	304.15	328.96	345.64	3.43	501.0	501.31 525.25	531.2	49.62
1b	2.187	–	–	–	1.39	458.5	467.3	472.5	41.51
2a	3.140	–	–	–	–	455.0	467.7	478.1	44.95
2b	1.920	–	–	–	–	448.2	456.7	465.5	40.04
2c	4.458	–	–	–	–	452.5	460.4	468.2	40.46
3a	1.465	–	–	–	–	416.7	411.1 437.1	445	67.45
3b	3.135	183.6	249.7	276	6.07	400.8	412.8	421.2	59.03
3c	2.730	236.8	287.2	297.8	5.91	387.5	402.1	411.0	55.40
4a	2.416	–	–	–	–	365.1	375.9	395.6	55.24
4b	2.492	210.7	259.3	267.6	2.07	363.6	373.5	388.5	51.46
4c	2.256	232.2	257.6	275.8	2.13	360.9	369.5	389.1	52.56

[a] $t_{start,}$ temperature of the onset of the process; t_{max}, temperature of the maximum endoeffect; t_{end}, temperature of the end of the process; m_{a1}^{exp} and m_{a2}^{ex}, experimental value of weight loss.

It was found that thermal stability of the studied compounds decreased with the nitrogen atom of the pyridinyl fragment located closer to the macrocycle (within each of the compounds groups **3a–3c** and **4a–4c**, see the table). For example, the onset of the thermal decomposition of the 3N-isomer of the monopyridinylporphyrin **3b** was almost by 17°C lower than that of the 4N-isomer **3a**, and that of the 2N-isomer **3c** was by further 13°C lower than in the case of the 3N-isomer **3b**. That was evidently due to the redistribution of the electron density over the macrocycle. The same trend was observed for compounds **4a–4c**.

The molecule symmetry strongly affected the onset of the thermal decomposition as well. In particular, in the cases of symmetrical porphyrins **1a** and **4a** the decomposition started at higher temperature as compared to the unsymmetrical analogs **1b**, **4c**, or **3a–3c**.

Thermal decomposition of the ligands studied in this work occurred in a single stage and was accompanied by complete decomposition of the molecule (Fig. 1). Several of the studied compounds exhibited slight mass loss at relatively low temperature. This process was not connected with the substance decomposition, as confirmed by the unchanged electron absorption spectra of the specimen after heating (Fig. 2).

In summary, the obtained data on the thermal stability of the pyridinyl-substituted porphyrins in the solid state under argon atmosphere revealed the correlation between the molecular structure of the compound and its thermochemical properties within the isomers group, but not for the whole set of the

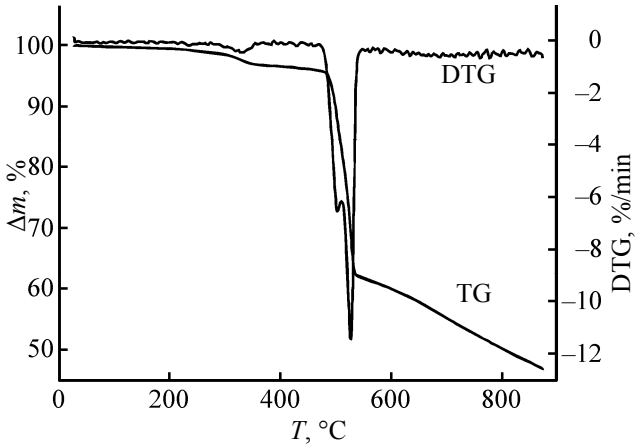


Fig. 1. Thermogram of porphyrin **1a** under argon atmosphere.

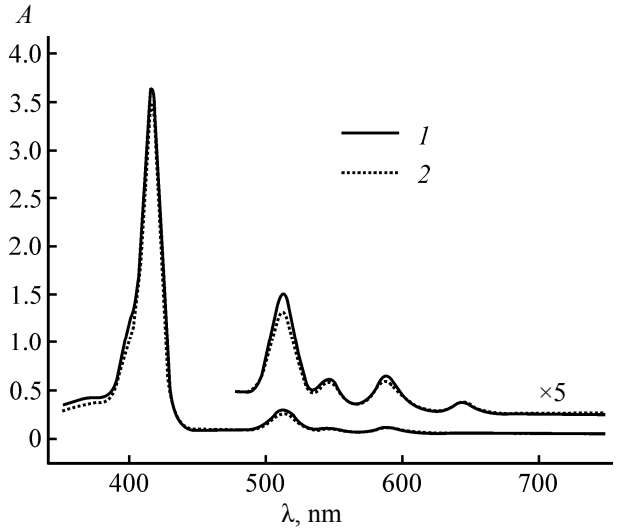


Fig. 2. Electron absorption spectrum (chloroform) of porphyrin **2a** (*1*) before and (*2*) after heating to 365°C.

studied ligands. Thermal stability of the studied porphyrins under inert atmosphere was higher than at their heating in air [15].

EXPERIMENTAL

Thermogravimetric analysis experiments were performed at the Upper-Volga Regional Center for Physicochemical Studies using a DSC 204 F1 differential scanning calorimeter equipped with a TG 209 F1 Iris thermobalance (NETZSCH, Germany). A weighed specimen (2–5 mg) was placed in a platinum crucible and heated under static argon atmosphere at a heating rate of 10 K/min over the 298–1223 K range. Prior to the experiment, the specimens were dried in a vacuum (<1 mmHg) during 1 day at room temperature. Electron absorption spectra were recorded using an SF-56 spectrophotometer. ^{1}H NMR spectra were recorded using a Bruker-500 instrument.

Compounds **1**, **3**, and **4** were synthesized as described elsewhere [17–20].

Compounds 2a–2c. A mixture of 6.9 mL (0.072 mol) of 3-pyridinylcarbaldehyde, 7.6 mL (0.072 mol) of benzaldehyde, and 10 mL (0.144 mol) of pyrrole was gradually added to a mixture of 350 mL of acetic acid, 150 mL of nitrobenzene, and 10.5 mL (0.111 mol) of acetic anhydride. The reaction mixture was refluxed during 1.5 h, and nitrobenzene was removed via steam distillation. The precipitate was filtered off, washed with water, and dried in air at 70°C. The obtained porphyrins mixture was extracted with chloroform using a Soxhlet apparatus and purified by chromatography on alumina (Brockman type II) collecting the first fraction of 5,10,15,20-tetraphenylporphyrin (yield 1.72 g, 7.7%) and the second fraction of the pyridinylporphyrins. The product was then additionally purified by chromatography on silica gel 60 (0.063–0.2 mm, 70–230 mesh, ASTM) eluting with chloroform.

5-(Pyridin-3-yl)-10,15,20-triphenylporphyrin (2a). Yield 1.95 g (8.74%). Electron absorption spectrum (chloroform), λ_{max}, nm (log ε): 646 (3.56), 590 (3.78), 550 (3.87). 515 (4.31), 415 (5.66). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.53 d (1H, 2'-H_{Py}, *J* = 1.8), 9. 08 d.d (1H, 6'-H_{Py}, *J* = 5.0, 1.8), 8. 95 d (2H, 3,7-H, *J* = 4.5), 8.92 s (4H, 12,13,17,18-H), 8.85 d (2H, 2,8-H, *J* = 4.5), 8.57 d. t (1H, 4'-H_{Py}, *J* = 5.0, 1.8), 8.28 d (6H, 2",6"-H_{Ph}, *J* = 6.4), 7.85–7.77 m (10H, 5'-H_{Py}, 3",4",5"-H_{Ph}), –2.73 s (2H, NH).

5,15-Bis(pyridin-3-yl)-10,20-diphenylporphyrin (2b). Yield 0.37 g (1.65%). Electron absorption spectrum (chloroform), λ_{max}, nm (log ε): 647 (3.60), 590 (3.72), 550 (3.83), 515 (4.19), 417 (5.43). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.55 s (2H, 2'-H_{Py}), 9.11 d (2H, 6'-H_{Py}, *J* = 4.8), 8.99 d (4H, 3,7,13,17-H, *J* = 3.1), 8.89 d (4H, 2,8,12,18-H, *J* = 3.1), 8.59 d (2H, 4'-H_{Py}, *J* = 4.8), 8.29 d (4H, 2",6"-H_{Ph}, *J* = 7.3), 7.86–7.77 m (8H, 5'-H_{Py}, 3",4",5"-H_{Ph}), –2.71 s (2H, NH).

5,10-Bis(pyridin-3-yl)-15,20-diphenylporphyrin (2c). Yield 0.98 g (4.4%). Electron absorption spectrum (chloroform), λ_{max}, nm (log ε): 646 (3.71), 589 (3.86), 550 (3.98), 514 (4.34), 417 (5.51). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.54 s (2H, 2'-H_{Py}), 9.10 d (2H, 6'-H_{Py}, *J* = 5.5), 8.98 d (2H, 3,12-H, *J* = 4.4), 8.94 s (2H, 7,8-H), 8.91 s (2H, 17,18-H), 8.87 d (2H, 2,13-H, *J* = 4.4), 8.57 d (2H, 4'-H_{Py}, *J* = 5.5), 8.29 d (4H, 2",6"-H_{Ph}, *J* = 6.0), 7.86–7.78 m (8H, 5'-H_{Py}, 3",4',5'-H_{Ph}), –2.72 s (2H, NH).

5,10,15-Tris(pyridin-3-yl)-20-triphenylporphyrin. Yield 0.56 g (2.5%) ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.50 s (3H, 2'-H_{Py}), 9.10 d.d (3H, 6'-H_{Py}, *J* = 5.5, 1.4), 8.95 d (2H, 8,12-H, *J* = 4.5), 8.89 s (4H, 3,7,13,17-H), 8.85 d (2H, 2,18-H, *J* = 4.5), 8.57 d (3H, 4'-H_{Py}, *J* = 5.5), 8.26 d (2H, 2",6"-H_{Ph}, *J* = 6.0), 7.86–7.79 m (6H, 5'-H_{Py}, 3",4",5"-H_{Ph}), –2.79 s (2H, NH).

5,10,15,20-Tetrakis(pyridin-3-yl)porphyrin. Yield 0.21 g (0.95%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.50 s (4H, 2'-H), 9.10 d.d (4H, 6'-H, *J* = 5.6,

1.4), 8.56 d (4H, 4'-H, J = 5.6), 7.81 t (4H, 5'-H, J = 5.6), –2.80 s (2H, NH).

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