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Regioselective Nitration of 5–Phenyl–2,3,7,8,12,18–hexamethyl–13,17–diethylporphine

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Dedicated to Professor Michael Hanack on the occasion of his 80th Anniversary

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*Nitration system NaNO$_2$-TFA for regioselective nitration of the meso-positions of 5-phenyl-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**1**) was examined. The degree of nitration is easily controlled by the amount of NaNO$_2$ used and by the reaction time. All compounds are characterized by MS, UV-Vis-, and ^{1}H NMR-spectroscopy as well as mass-spectrometry. Protonation of transannular protons of some synthesized porphyrins is discussed.*

Keywords: Porphyrin, nitration, *meso*-nitroporphyrins, trifluoroacetic acid, sodium nitrite.

Introduction

Porphyrins (Ps), due to their peculiar electronic and redox properties, play a key role in many living nature processes such as oxygen activation and transfer, electron transfer, binding or transport of small molecules, light harvesting and photosynthesis.[1]

Chemical modification of natural and synthetic porphyrins has been an area of interest for a number of years. Development of new methodologies to functionalize Ps and their derivatives can provide a variety of novel compounds that otherwise could only be obtained by a total synthesis. Several investigations have shown that porphyrins and their metal complexes undergo electrophilic substitution reactions (nitration, formylation, deuteration and methylation)[2] as well as radical reactions (halogenations and oxidation)[3] in a similar manner like simple aromatic systems. Nitroporphyrins have proved to be versatile starting materials for the synthesis of porphyrins with other functionalities.[4] In addition, the number and position of introduced into the porphyrin core nitro-groups can influence dramatically on the acid-base properties of porphyrins and control the NH-tautomerism processes.

Here we present the synthesis of *meso*-mononitro- (**2a**, **2b**), *meso*-dinitro- (**3a**, **3b**) and *meso*-trinitro- (**4**) porphyrins by nitration of 5-phenyl-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**1**) using NaNO$_2$/trifluoroacetic acid (TFA) system, where the degree of nitration could be easily controlled by the reagents ratio (Scheme 1).

Experimental

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Analytical TLC was performed on Kieselgel F-254-percolated TLC plates. For flash chromatography, silica gel 60 (230 – 400 mesh) was used. ^{1}H NMR spectra were recorded on Bruker AC 250 and 400 spectrometers. The UV-visible spectra were taken in benzene with a Lambda 25 UV-visible spectrometer. Mass spectra were obtained on a Finnigan TSQ 70 MAT spectrometer.

5-Phenyl-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (1) was obtained as described earlier.[5] MS (EI) *m/z*: 526.2 (100) [M]$^+$. ^{1}H NMR (CDCl$_3$) δ ppm: 10.14 (s, 2H, H-20), 9.94 (s, 1H, H-15), 8.08-7.99 (m, 2H, H-Ph), 7.83-7.66 (m, 3H, H-Ph), 4.10 – 4.01 (m, 4H, -CH$_2$-), 3.62 (s, 6H, -CH$_3$), 3.51 (s, 6H, -CH$_3$), 2.43 (s, 6H, -CH$_3$), 1.87 (t, *J* = 7.50 Hz, 6H, -CH$_3$(Et)), -3.21 (br, 2H, NH). UV-Vis (C$_6$H$_6$) λ$_{max}$ nm (log ε): 405 (5.22), 502 (4.15), 534 (3.86), 573 (3,83), 626 (3.51).

5-Phenyl-10-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (2a) and *5-phenyl-15-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (2b)*. To a solution of **1** (105 mg, 0.2 mmol) in TFA (10 ml) was added sodium nitrite (13 mg, 0.19 mmol). After 10 min stirring at room temperature, the reaction mixture was quenched with ice water (50 ml) and neutralized with aqueous ammonia. Precipitate was filtrated and dried in vacuum. The resulting mixture of porphyrins was separated by column chromatography on silica gel, using chloroform as eluent. First zone was characterized as 5-phenyl-15-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**2b**) and second major zone – as 5-phenyl-10-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**2a**). Only traces of starting porphyrin **1** were separated as last zone.

5-Phenyl-10-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (2a). Yield: 76 mg (66%). MS (EI) *m/z*: 571.2 (68) [M]$^+$, 525.2 (100) [M-NO$_2$]$^+$. ^{1}H NMR (CDCl$_3$) δ ppm: 9.98 (s, 1H, H-20), 9.89 (s, 1H, H-15), 8.04–7.94 (m, 2H, H-Ph), 7.84–7.64 (m, 3H, H-Ph), 4.09 – 3.82 (m, 4H, -CH$_2$-), 3.51 (s, 3H, -CH$_3$), 3.38 (s, 3H, -CH$_3$), 3.27 (s, 3H, -CH$_3$), 3.15 (s, 3H, -CH$_3$), 2.29 (s, 3H, -CH$_3$), 2.26 (s, 3H, -CH$_3$), 1.85 – 1.75 (m, 6H, -CH$_3$(Et)), -3.54 (s, 2H, NH). UV-Vis (C$_6$H$_6$) λ$_{max}$ nm (lg ε): 405 (5.06), 508 (4.09), 538 (3.78), 581 (3.76), 633 (3.48).

5-Phenyl-15-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (2b). Yield: 27 mg (24%). MS (EI) *m/z*: 571.2 (100) [M]$^+$, 526.3 (44) [M-NO$_2$]$^+$. ^{1}H NMR (CDCl$_3$) δ ppm: 10.23 (s, 2H, H-20), 7.99 – 7.96 (m, 2H, H-Ph), 7.83 – 7.66 (m, 3H, H-Ph), 3.73 – 3.64 (m, 4H, -CH$_2$-), 3.60 (s, 6H, -CH$_3$), 3.47 (s, 6H, -CH$_3$), 2.41

(s, 6H, -CH$_3$), 1.65 (t, *J* = 7.50 Hz, 6H, -CH$_3$(Et)), -2.73 (s, 1H, NH), -3.15 (s, 1H, NH). UV-Vis (C$_6$H$_6$) λ_{max} nm (lg ε): 405 (5.07), 507 (4.08), 540 (3.78), 576 (3.76), 630 (3.56), 658 (3.27).

Mixture of 5-phenyl-10,20-dinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (3a) and *5-phenyl-10,15-dinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (3b)*. *Method A*. To a solution of **1** (105 mg, 0.2 mmol) in TFA (10 ml) was added sodium nitrite (28 mg, 0.4 mmol). After 1.5 h stirring at room temperature, the reaction mixture was quenched with ice water (50 ml) and neutralized with aqueous ammonia. Precipitate was filtrated and dried in vacuum. Column chromatography on silica gel with chloroform as eluent gives mixture no separable dinitroporphyrins **3a** and **3b**. Yield: 102 mg (83%). MS (EI) *m/z*: 616.2 (64) [M]$^+$, 571.3 (100) [M-NO$_2$]$^+$, 525.3 (100) [M-2NO$_2$]$^+$. ^{1}H NMR (CDCl$_3$) δ ppm: 9.94 (s, 1H), 9.77 (s, 1H), 8.06 – 8.02 (m, 2H, H-Ph), 7.97 – 7.93 (m, 2H, H-Ph), 7.85 – 7.66 (m, 6H, H-Ph), 3.89 – 3.79 (m, 4H, -CH$_2$-), 3.60 – 3.51 (m, 4H, -CH$_2$-), 3.43 (s, 3H, -CH$_3$), 3.27 (s, 3H, -CH$_3$), 3.17 (s, 3H, -CH$_3$), 3.15 (s, 6H, -CH$_3$), 3.00 (s, 3H, -CH$_3$), 2.98 (s, 6H, -CH$_3$), 2.21 (s, 3H, -CH$_3$), 2.19 (s, 3H, -CH$_3$), 2.07 (s, 6H, -CH$_3$), 1.72 (t, *J* = 7.50 Hz, 6H, -CH$_3$(Et)), 1.60 – 1.51 (m, 6H, -CH$_3$(Et)), -3.06 (s, 1H, NH), -3.26 (s, 2H, NH), -3.36 (s, 1H, NH). *Method B*. To a solution of **2a** (57 mg, 0.1 mmol) in TFA (5 ml) was added sodium nitrite (10 mg, 0.15 mmol). After 1.5 h stirring at room temperature, the reaction mixture was quenched with ice water (25 ml) and neutralized with aqueous ammonia. Precipitate was filtrated and dried in vacuum. Column chromatography on silica gel with chloroform as eluent gives mixture no separable dinitroporphyrins **3a** and **3b**. MS and UV-Vis data were similar to the data given in Method A. ^{1}H NMR (CDCl$_3$) δ ppm: 10.00 (s, 0.5H, H-20), 9.80 (s, 1H, H-15), 8.05 (d, *J* = 8 Hz, 2H, H-Ph), 7.98 (d, *J* = 8 Hz, 1H, H-Ph), 7.84 – 7.71 (m, 4.5H, H-Ph), 3.94 – 3.80 (m, 4H, -CH$_2$-), 3.60 – 3.51 (m, 2H, -CH$_2$-), 3.46 (s, 1.5H, -CH$_3$), 3.31 (s, 1.5H, -CH$_3$), 3.16 (s, 7.5H, -CH$_3$), 2.99 (s, 1.5H, -CH$_3$), 2.97 (s, 6H, -CH$_3$), 2.24 (s, 1.5H, -CH$_3$), 2.20 (s, 1.5H, -CH$_3$), 2.07 (s, 6H, -CH$_3$), 1.72 (t, *J* = 6.04 Hz, 6H, -CH$_3$(Et)), 1.54 – 1.49 (m, 3H, -CH$_3$(Et)), -3.06 (s, 0.5H, NH), -3.27 (s, 2H, NH), -3.36 (s, 0.5 H, NH).

5-Phenyl-10,15-dinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (3b). To a solution of **2b** (57 mg, 0.1 mmol) in TFA (5 ml) sodium nitrite (10 mg, 0.15 mmol) was added. After 1.5 h stirring at room temperature, the reaction mixture was quenched with ice water (25 ml) and neutralized with aqueous ammonia. Precipitate was filtrated and dried in vacuum. Column chromatography on silica gel with chloroform as eluent gives porphyrin **3b**. Yield: 56 mg (91%). MS (EI) *m/z*: 571.3 (100) [M-NO$_2$]$^+$, 526.3 (95) [M-2NO$_2$]$^+$. ^{1}H NMR (CDCl$_3$) δ ppm: 10.00 (s, 1H, H-20), 8.02 – 7.94 (m, 2H, H-Ph), 7.81 – 7.69 (m, 3H, H-Ph), 3.63 – 3.49 (m, 4H, -CH$_2$-), 3.46 (s, 3H, -CH$_3$), 3.32 (s, 3H, -CH$_3$), 3.16 (s, 3H, -CH$_3$), 3.00 (s, 3H, -CH$_3$), 2.25 (s, 3H, -CH$_3$), 2.20 (s, 3H, -CH$_3$), 1.62 – 1.45 (m, 6H, -CH$_3$(Et)), -3.03 (s, 1H, NH), -3.34 (s, 1H, NH). UV-Vis (C$_6$H$_6$) λ_{max} nm (lg ε): 410 (5.04), 508 (4.07), 540 (3.92), 579 (3.89), 630 (3.57).

5-Phenyl-10,15,20-trinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (4). To a solution of **1** (53 mg, 0.1 mmol) in TFA (5 ml) sodium nitrite (69 mg, 1.0 mmol) was added. After 2 days stirring at room temperature, the reaction mixture was quenched with ice water (100 ml) and neutralized with aqueous ammonia. Precipitate was filtrated and dried in vacuum. Column chromatography on silica gel with chloroform as eluent gives porphyrin **4**. Yield: 52 mg (78 %). MS (EI) *m/z*: 662.4 (35) [M]$^+$, 647.4 (100) [M-CH$_3$]$^+$. ^{1}H NMR (CDCl$_3$) δ ppm: 8.11 – 8.01 (m, 2H, H-Ph), 7.85 – 7.74 (m, 3H, H-Ph), 3.43 – 3.27 (m, 4H, -CH$_2$-), 2.97 (s, 3H, -CH$_3$), 2.80 (s, 3H, -CH$_3$), 1.98 (s, 3H, -CH$_3$), 1.38 (t, *J* = 7.50 Hz, 6H, -CH$_3$(Et)), -2.45 - -3.24 (m, 2H, NH). UV-Vis (C$_6$H$_6$) λ_{max} nm (lg ε): 433 (4.77), 532 (3.94), 609 (3.65), 679 (3.44).

The same product was obtained by reaction of mixture **3a** and **3b** with excess of sodium nitrite in TFA for 2 days at room temperature.

Results and Discussion

Synthesis

Nitration of porphyrin **1** could be carried out using different nitrating systems such as nitric acid or acetyl nitrate in acetic acid, nitric acid in dichloromethane, sodium nitrate in TFA as well as sodium nitrite in TFA, all leading to the same products. However, the best yields were achieved with the latter system. Thus, reaction of **1** with 0.95 equivalents of NaNO$_2$ in TFA leads in 15 min to a mixture of two mono-nitrated products **2a** and **2b** in 3:1 ratio (Scheme 1), which were separated by column chromatography on silica gel using chloroform as eluent. The ratio of isomers differs from the statistically expected due to the steric hindrance of attack in position 15 of the porphyrin core.

Increase of the NaNO$_2$ amount up to 2 equivalents to porphyrin **1** allows to obtain a mixture of *meso*-dinitroporphyrins **3a** and **3b** in an approximately 1:1 ratio, when conducting the reaction for 1.5 h.

Unfortunately, the mixture could not be separated by column chromatography. The mixture of the same products in 2:1 ratio was also formed upon nitration of 5-phenyl-10-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphin (**2a**) with 1.5 molar excess of NaNO$_2$. Nevertheless, pure 5-phenyl-10,15-dinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphin (**3b**) could be prepared by nitration of **2b** using 1.5 equivalents of NaNO$_2$, thus allowing a reliable assignment of signals in the ^{1}H NMR spectrum of **3a** and **3b** products mixture.

Both porphyrin **1** and the mixture of porphyrins **3a** and **3b** give 5-phenyl-10,15,20-trinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphin (**4**) upon nitration with 10 equivalents of NaNO$_2$ for 2 days. Neither longer reaction time (up to 8 days) nor increase of the reaction temperature to 70 °C lead to nitration of phenyl ring in **1**, thus excluding the formation of tetranitro derivative.

UV-Vis and MS Spectra

The UV-Vis spectra of mono-nitroporphyrins **2a** and **2b** (Figure 1) in benzene are very similar with the spectrum of **1**. The only observed difference is a slight bathochromic shift of all absorption bands and a negligible decrease of their intensity for the nitrated species compared to the initial porphyrin.
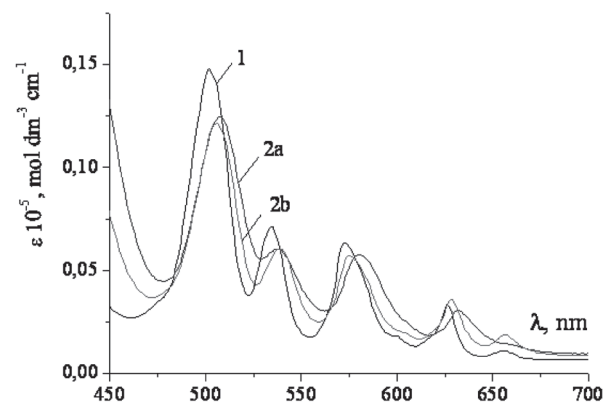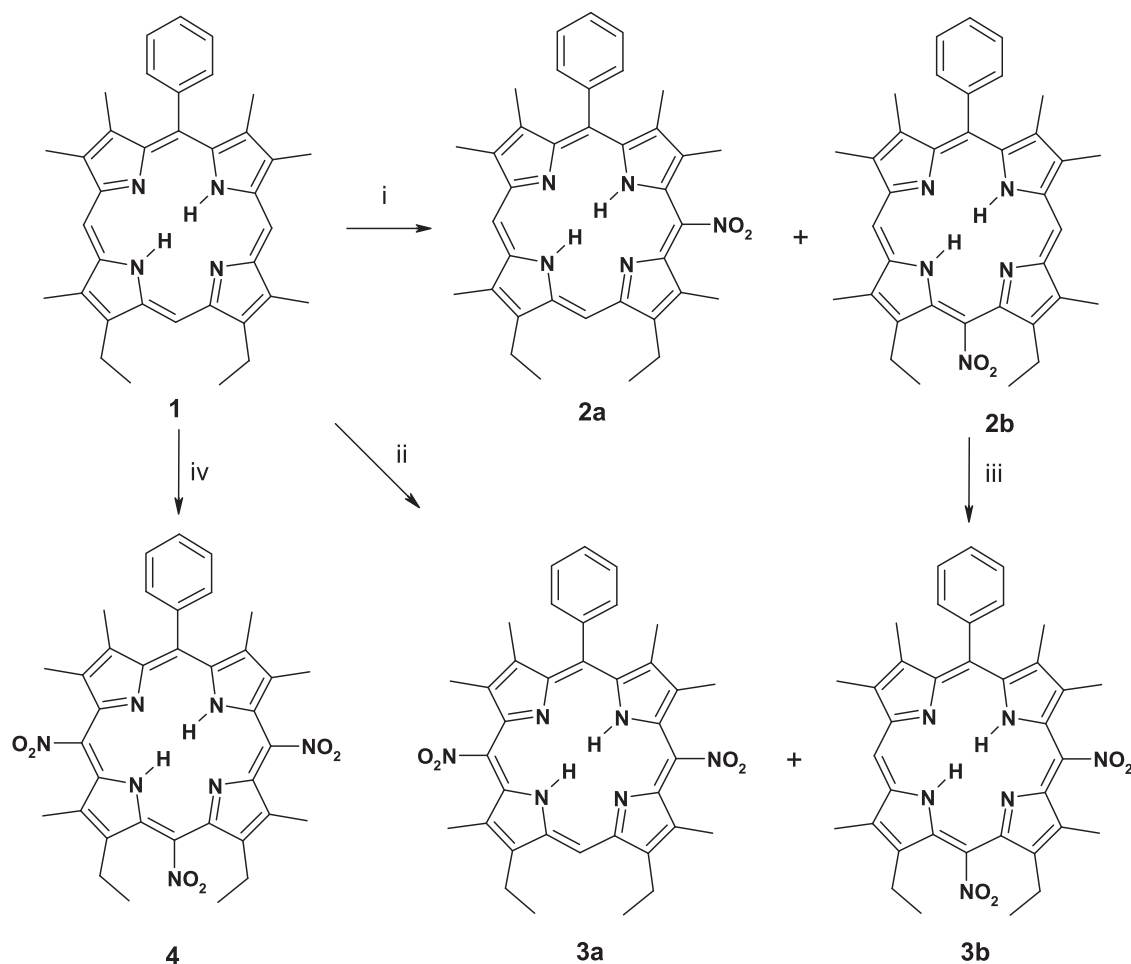

Figure 1. UV-Vis spectra of porphyrins **1**, **2a** and **2b** in benzene.

Scheme 1. Nitration of 5-phenyl-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**1**) with NaNO$_2$-TFA: i – 0.95 equv. NaNO$_2$, 15 min, r.t.; ii – 2.0 equv. NaNO$_2$, 2 h, r.t.; iii – 1.5 equv. NaNO$_2$, 2 h, r.t.; iv – 10.0 equv. NaNO$_2$, 2 d, r.t. (see experimental part for details).

Presence of two nitro-groups in positions 10 and 15 of dinitro-derivative **3b** do not change the spectral pattern compared to the mono-nitro products **2a** and **2b**, whereas trinitroporphyrin **4** features a three-band spectrum in the visible region with all bands including Soret-band being pronouncedly red-shifted (Figure 2).
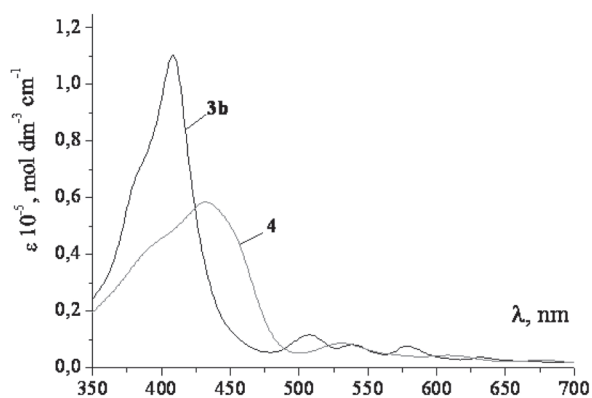

Figure 2. UV-Vis spectra (benzene) of porphyrins **3b** and **4**.

Mass-spectra of all synthesized nitro-porphyrins display the peak of corresponding molecular ion as well as the fragmentation peaks, which are mainly due to the loss of nitro-groups.

^{1}H NMR Spectra

Signals of three *meso*-protons in the ^{1}H NMR spectrum (Figure 3) of porphyrin **1** in CDCl$_3$ appear as two singlets at 10.14 (2H-20) and 9.94 (H-15) ppm. Five protons of phenyl ring give two multiplets in the range of 8.08 - 7.66 ppm. Three singlets at 3.62, 3.51 and 2.43 ppm correspond to 18 protons of β-methyl groups, whereas a multiplet at 4 ppm and a triplet at 1.87 ppm are due to four and six protons respectively of the ethyl substituents. Resonances of two transannular imine protons appear as a broad singlet at -3.21 ppm.

Interestingly, in an acidic deuterated chloroform due to the traces of HCl or DCl a subset of low intensity peaks arises. These peaks are shifted either down or high field compared to the main signals of the above described pattern, maintaining their multiplicity. In the high field area of the spectrum, however, two new sharp signals appear at -0.90 and -1.95 ppm in addition to the broad singlet (Figure 3a). This new set of signals was ascribed to a double-protonated form of **1** considering the integration values and the number of imine proton resonances.

A threefold dilution of the porphyrin solution in CDCl$_3$ increases the fraction of the protonated species from ca. 10% to 30%, suggesting a large equilibrium constant of the protonation (Figure 3b). The signals of protonated form
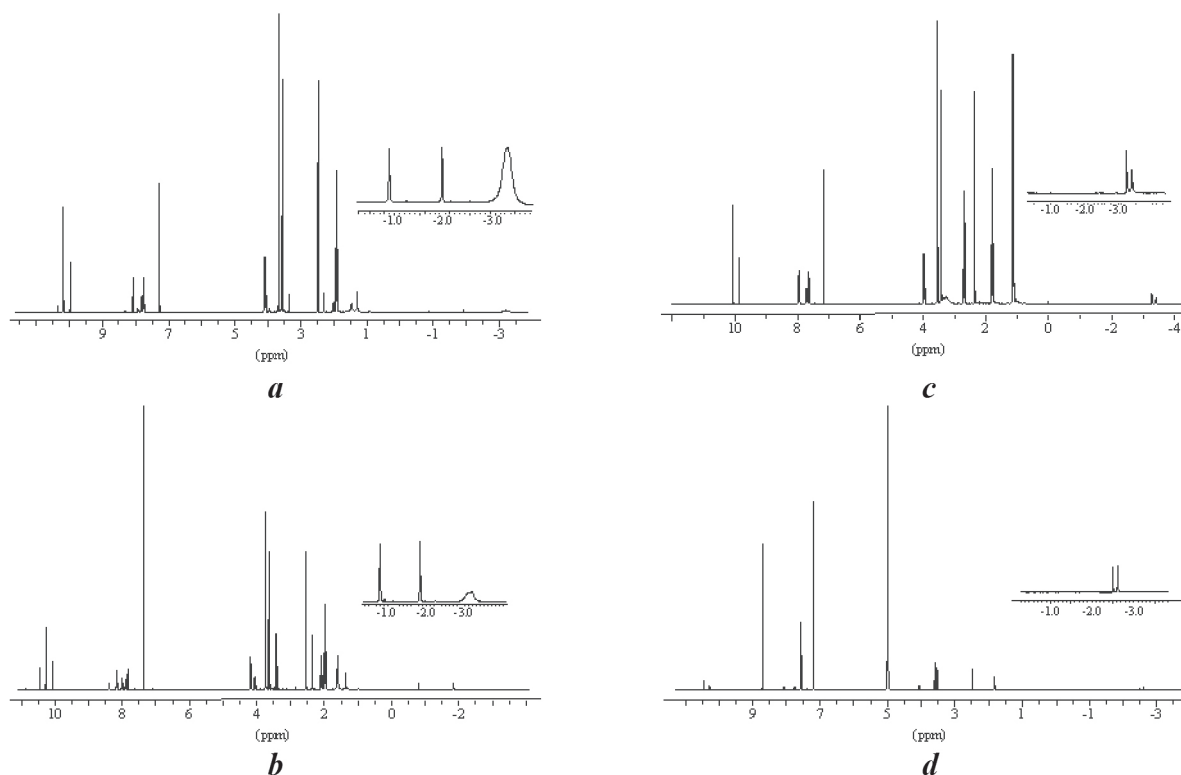
a

c

b

d

Figure 3. ¹H NMR spectra of 5-phenyl-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**1**): *a* – in CDCl₃; *b* – in CDCl₃ after dilution; *c* – in CDCl₃ with two drops DEA; *d* – in pyridine-*d*₅.
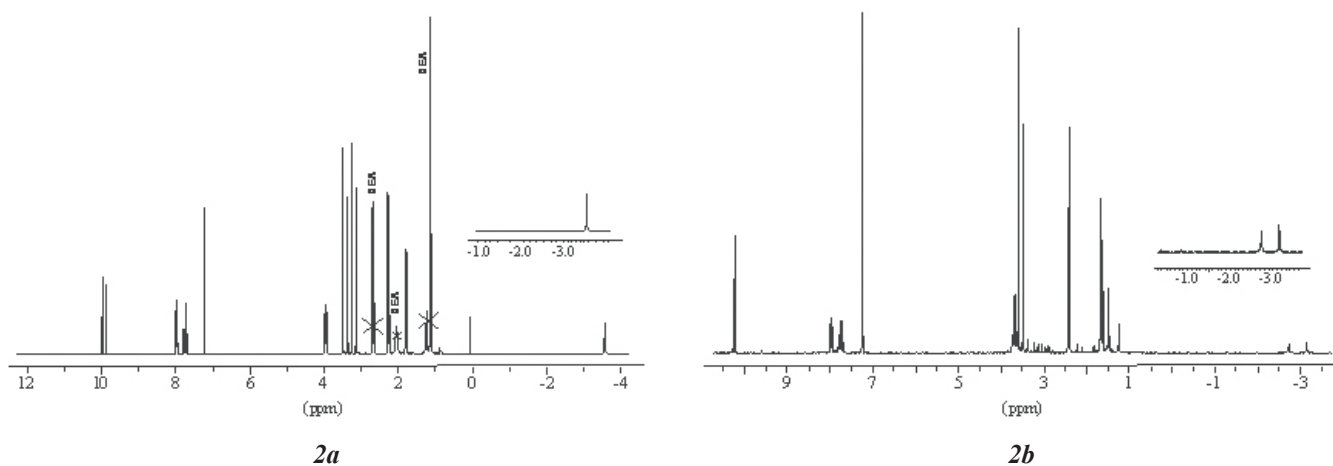

2a

2b

Figure 4. ¹H NMR spectra (CDCl₃) 5-phenyl-10-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**2a**) and 5-phenyl-15-nitro -2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**2b**).

disappear upon addition of strong base like diethylamine (Figure 3c) as well as when deuterated pyridine or THF is used as a solvent for the ¹H-NMR-experiments (Figure 3d). Moreover, the broad signal of imine protons of **1** split in this case into two resolved singlets with good matching in integration, which is consistent with the symmetry of the macrocyclic tautomer of lowest energy depicted in Scheme 1. Obviously, the broadening of imine resonance in CDCl₃ is caused by a relatively fast tautomerism, being catalyzed by the traces of acid. Such feature was also noticed previously for a range of other mono-phenylporphyrins.[5]

¹H NMR spectra of mono-nitro derivatives **2a** and **2b** are also very characteristic. Thus, **2b** having a C_{2v}-symmetric core

exhibits only one signal of *meso*-protons (positions 10 and 20) at 10.23 ppm, whereas in the spectrum of C_s-symmetric **2a** two singlets (*meso*-protons in positions 15 and 20) are observed in this region (Figure 4). The lowered symmetry of **2a** due to the nitro-group in position 10 is also a reason for the non-equivalence of β-methyl as well as β-ethyl groups in the ¹H NMR spectrum. In the case of porphyrin **2b**, the signals pattern of β-methyl and β-ethyl protons remains as that of **1**.

In the high field two imine protons of 5-phenyl-10-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**2a**) appear as a singlet at -3.54 ppm, splitting into two signals at lower temperature (Figure 4). Similar behavior was observed also for the imine protons of **1** and is to assign to a high

tautomerism rate at room temperature, which decreases upon cooling down. In the case of **2b** the imine protons give two singlets at -3.15 and -2.73 ppm as is also to expect from the symmetry of the macrocycle. The shape and position of these signals are temperature independent in the range of 313-233 K. This indicates a relatively slow tautomerism even at room temperature due to the higher energy barrier between different tautomeric forms caused by a strong polarizing effect of phenyl and nitro substituents situated opposite to each other in the porphyrin macrocycle. Additionally, the change of acid-base properties of **2b** compared to **1** can also influence the dynamics of tautomers interconversion. To be precise, introduction of nitro-groups into mono-phenylporphyrin decreases the basicity of the pyrrolic *N*-atoms, since only traces of the corresponding protonation products were observed in the ^{1}H NMR spectra recorded in acidic $CDCl_3$.

Conclusions

Selective nitration of **5**-phenyl-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**1**) was carried out using sodium nitrite/trifluoroacetic acid system. Depending on the reagents ratios and reaction time the following porphyrins could be obtained either as individual compounds or as mixtures: 5-phenyl-10-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**2a**), 5-phenyl-15-nitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**2b**), 5-phenyl-10,15-dinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**3b**), 5-phenyl-10,20-dinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**3a**) and 5-phenyl-10,15,20-trinitro-2,3,7,8,12,18-hexamethyl-13,17-diethylporphine (**4**). Formation of tetranitro derivative using this reaction protocol is prohibited: neither high excess of sodium nitrite nor increasing the reaction time and temperature lead to such product. As found from ^{1}H NMR experiments, nitration of porphyrin **1** decreases the basicity of pyrrolidinic nitrogen atoms of the porphyrin moiety.

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