Synthesis and Spectral Properties of *ms*-Tetrasubstituted *β*-Octaalkylporphyrins

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Abstract: Four new *ms*-tetrasubstituted *β*-octaalkylporphyrins are synthesized and their spectral properties are discussed.

Keywords: Porphyrin, dipyrrolylmethane, *ms*-substitution.

Introduction

Porphyrin synthesis variants are diverse, and the choice of a particular strategy is usually determined by the nature and relative position of the substituents desired in a given molecule. Simple porphyrins with identical substituents in *ms*- or *β*-positions are usually prepared by methods based on monopyrrole condensation, when four identical pyrrole molecules are condensed into a porphyrin in one step. More complicated structures are prepared through intermediate di- or tetrapyrrole compounds, in which the presence of the substituents leads to the possibility of formation of isomers around a substituent position. In the present work a method for synthesis of new *ms*-tetrasubstituted *β*-octaalkylporphyrins is reported. The advantage of the given method is that after condensation, not even insignificant amounts of isomeric porphyrins are detectable in the reaction mixture.

Results and Discussion

Condensation of *ms*-arylsubstituted dipyrrolylmethanes **1**-**3** [1] with aldehydes RCHO (R = CH_3,

C$_4$H$_9$) gives 5,15-diphenyl-3,7,10,13,17,20-hexamethyl-2,8,12,18-tetrabutylporphyrin (**4**), 5,15-diphenyl-3,7,13,17-tetramethyl-2,8,10,12,18,20-hexabutylporphyrin (**5**), 5,15-di-(4-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,10,12,18,20-hexabutylporphyrin (**6**) and 5,15-di-(4-nitrophenyl)-3,7,13,17-tetramethyl-2,8,10,12,18,20-hexabutylporphyrin (**7**) (*cf.* Scheme 1).

1-3   **4-7**

X = H (**1**, **4**, **5**), 4-OCH$_3$ (**2**, **6**), 4-NO$_2$ (**3**, **7**); R = CH$_3$ (**4**), C$_4$H$_9$ (**5-7**).
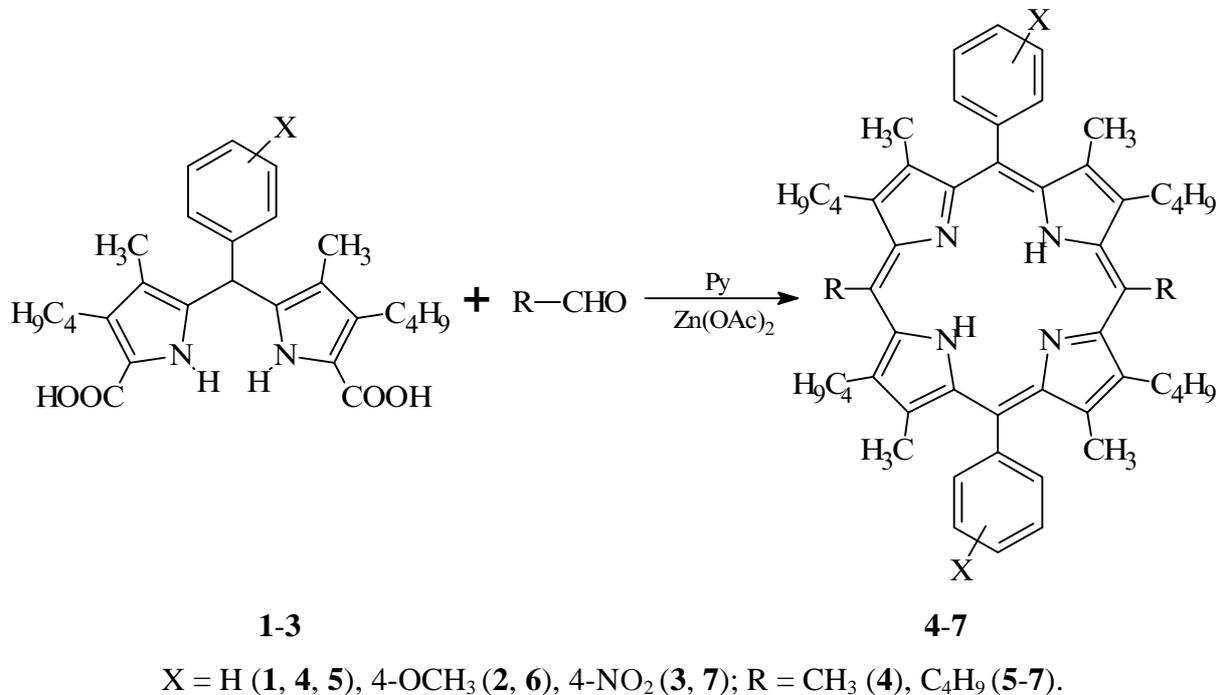
Scheme 1.

The reactions of 5,5'-dicarboxydipyrrolylmethanes (**1-3**) with appropriate aldehydes was carried out in pyridine at elevated temperatures and pressures. Maximum yields were obtained by the reaction of 1 mole *ms*-phenyl-5,5'-dicarboxy-4,4'-dibutyl-3,3'-dimethyl-2,2'-dipyrrolylmethane (**1**) with 3.6 moles of aldehyde in the presence of 3.6 moles of nitrobenzene. The increased yield observed in the presence of nitrobenzene is probably related to the oxidizing ability of nitro-group. The rather low yields of *ms*-tetrasubstituted porphyrins (**4**-**7**) is probably caused by unfavourable spatial factors affecting the cyclo-condensation process. Similar results were obtained for condensation of 2,5-unsubstituted 3,4-dimethyl-pyrroles with aldehydes [2]. The porphyrin yield was 5-6% and did not depend on the nature of the aldehyde.

^{1}H-NMR-spectra are in complete accord with the proposed structures **4**-**7**. The signals of the *ms*-phenyl group protons appear in the range of 7.7-8.0 ppm. The chemical shifts of the *β*-alkyl protons are located between 0,8-4,0 ppm. The magnetic field of the porphyrin ring *π*-electron current influences the position of signals of the hydrocarbon fragments of the *ms*-substituents, a fact reflected in the NMR spectrum by the separate, non-overlapping, signals of the CH$_2$ and CH$_3$ fragments of the alkyl substituents. Thus, in porphyrins **5**-**7** the protons of the CH$_2$ groups of the butyl substituents directly connected

to the macroheterocyle appear as a triplet at 4.5 ppm., the adjacent CH_2 group gives a pentet at 2.5 ppm., the following CH_2 group gives a sextet located at 1.55 ppm. Finally, the terminal CH_3 group appears as a triplet at 0.85 ppm. Substitution in the phenyl rings of 5,15-diphenylporphyrins (X = 4-OCH_3 in compound **6**, 4-NO_2 in **7**) has no significant effects on the position of *β*-alkyl and *ms*-substituent proton signals. The disappearance of N-H proton bands is unclear. Similar effects have been observed for *ms*-tetraphenylsubstituted *β*-octamethylporphyrin [3].

ms-Tetrasubstituted octaalkylporphyrins **4**-**7** have a deformed porphyrin cycle structure, that causes a red shift and broadening of the absorption in the UV-vis. spectra in a comparison with tetraphenylporphyrin and *ms*-unsubstituted octaalkylporphyrins [3]. To confirm the molecular structures the IR spectra of the synthesized porphyrins were investigated. Together with the NMR data they reliably prove the proposed structures **4**-**7** in most cases.

Experimental

General

^{1}H NMR spectra were recorded on a Bruker AC-500 spectrometer operating at 600 MHz with HMDS as internal standard in $CDCl_3$. UV-vis. spectra were obtained on a Specord M400 spectrophotometer in $CHCl_3$. IR spectra (KBr disks) were obtained on a Specord M80 spectrophotometer.

*5,15-Diphenyl-3,7,10,13,17,20-hexamethyl-2,8,12,18-tetrabutylporphyrin (**4**)*

A mixture of *ms*-phenyl-5,5$^/$-dicarboxy-4,4$^/$-dibutyl-3,3$^/$-dimethyl-2,2$^/$-dipyrrolylmethane (**1**, 0.50 g), anhydrous zinc acetate (0.63 g), nitrobenzene (0.48 mL), pyridine (8 mL) and acetaldehyde (0.20 mL) was heated at 180° C for 2 hours in a sealed ampule. The reaction mixture was cooled, diluted with water (50 mL) and heated at 100° for 30 minutes. The precipitate was isolated by filtration and kept into a solution of sulfuric acid (0.50 mL) in dimethylformamide (50 mL) for 1 hour. The product was extracted with 50 mL of chloroform and washed with water, then ammonia solution and water again. The product was purified by silica gel chromatography (benzene), followed by recrystallization ($CHCl_3$/methanol) to afford the title compound. Yield 32 mg (8%). R_f 0.30 (Silufol, benzene); UV-vis ($CHCl_3$): λ_{max}, nm (lg ε) 629.1(3.48); 547.5(3.62); 540.4(3.68); 507.1(4.01); 421.4(4.89). IR , cm^{-1}: ν_{NH} 3325; δ_{NH} 974; γ_{NH} 710; ν_{CH} 3060; δ_{CH} 1500. ^{1}H NMR ($CDCl_3$): phenyl protons - [7.97d (4H; o-H); 7.35 t (4H; m-H); 7.70 t (2H; p-H)]; 4.00 s (6H; *ms*-CH_3); 3.92 (t, 8H, $\underline{CH_2}CH_2CH_2CH_3$); 2,42 s (12H; β-$CH_3$); 2.13 (pentet, 8H, $CH_2\underline{CH_2}CH_2CH_3$), 1.64 (sextet, 8H, $CH_2CH_2\underline{CH_2}CH_3$), 1.11 (t, 12H, $CH_2CH_2CH_2\underline{CH_3}$). Anal. Calcd for $C_{57}H_{84}N_4$: C 83.01, H 10.19, N 6.80. Found: C 82.98, H 10.14, N 6.77.

The following substances were similarly prepared:

*5,15-Diphenyl-3,7,13,17-tetramethyl-2,8,10,12,18,20-hexabutylporphyrin (**5**)*

Yield 37,7 mg (9.5%). R_f 0.39 (Silufol, benzene); UV-vis (CHCl$_3$): λ_{max}, nm (lg ε) 629.9 (3.50); 548.1 (3.67); 540.9 (3.70); 507.7 (4.08); 422.1 (4.90). IR, cm^{-1}: ν_{NH} 3322; δ_{NH} 971; γ_{NH} 712; ν_{CH} 3067; δ_{CH} 1505. ^{1}H NMR (CDCl$_3$): phenyl protons: 7.92d (4H; o-H); 7.37 t (4H; m-H); 7.68 t (2H; p-H)]; 4.50 t (4H; *ms*-C<u>H$_2$</u>CH$_2$CH$_2$CH$_3$); 4.07 s (6H; *ms*-CH$_3$); 3.90 (t, 8H, C<u>H$_2$</u>CH$_2$CH$_2$CH$_3$); 2.50 pentet (4H; *ms*-CH$_2$C<u>H$_2$</u>CH$_2$CH$_3$); 2.42 s (12H; β-CH$_3$); 2.10 (pentet, 8H, CH$_2$C<u>H$_2$</u>CH$_2$CH$_3$); 1.62 (sextet, 8H, CH$_2$CH$_2$C<u>H$_2$</u>CH$_3$); 1.55 sextet (4H; ms-CH$_2$CH$_2$C<u>H$_2$</u>CH$_3$); 1.08 (t, 12H, CH$_2$CH$_2$CH$_2$C<u>H$_3$</u>); 0.85 t (6H; *ms*-CH$_2$CH$_2$CH$_2$C<u>H$_3$</u>). Anal. Calcd for C$_{63}$H$_{96}$N$_4$: C 83.26, H 10.57, N 6.17. Found: C 83.21, H 10.52, N 6.12.

*5,15-Di-(4-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,10,12,18,20-hexabutylporphyrin (**6**)*

Yield 39 mg (10%). R_f 0.47 (Silufol, benzene); UV-vis (CHCl$_3$): λ_{max}, nm (lg ε) 626.8 (3.43); 548.9 (3.61); 542.3 (3.78); 508.7 (4.11); 425.1(4.99). IR, cm^{-1}: ν_{NH} 3326; δ_{NH} 978; γ_{NH} 717; ν_{CH} 3072; δ_{CH} 1510. ^{1}H NMR (CDCl$_3$): phenyl protons: 7,90 d (4H; o-H); 7,33 t (4H; m-H); 4,52 t (4H; *ms*-C<u>H$_2$</u>CH$_2$CH$_2$CH$_3$); 4,11 s (6H; *ms*-CH$_3$); 4.00c(6H; CH$_3$O); 3.90 (t, 8H, C<u>H$_2$</u>CH$_2$CH$_2$CH$_3$); 2.55 pentet (4H; *ms*-CH$_2$C<u>H$_2$</u>CH$_2$CH$_3$); 2.40 s (12H; β-CH$_3$); 2.16 (pentet, 8H, CH$_2$C<u>H$_2$</u>CH$_2$CH$_3$); 1.69 (sextet, 8H, CH$_2$CH$_2$C<u>H$_2$</u>CH$_3$); 1.53 sextet (4H; ms-CH$_2$CH$_2$C<u>H$_2$</u>CH$_3$); 1.12 (t, 12H, CH$_2$CH$_2$CH$_2$C<u>H$_3$</u>); 0.80 t (6H; *ms*-CH$_2$CH$_2$CH$_2$C<u>H$_3$</u>). Anal. Calcd for C$_{65}$H$_{100}$N$_4$O$_2$: C 80.58, H 10.33, N 5.78. Found: C 80.52, H 10.30, N 5.72.

*5,15-Di-(4-nitrophenyl)-3,7,13,17-tetramethyl-2,8,10,12,18,20-hexabutylporphyrin (**7**)*

Yield 40 mg (10%). R_f 0.17 (Silufol, benzene); UV-vis (CHCl$_3$): λ_{max}, nm (lg ε) 631.1(3.53); 549.2(3.71); 541.2 (3.71); 508.7(4.11); 424.7(4.94). IR (KBr), cm^{-1}: ν_{NH} 3328; δ_{NH} 976; γ_{NH} 723; ν_{CH} 3070; δ_{CH} 1511. ^{1}H NMR (CDCl$_3$): phenyl protons: 7.92d (4H; o-H); 7,37 t (4H; m-H)]; 4.50 t (4H; *ms*-C<u>H$_2$</u>CH$_2$CH$_2$CH$_3$); 4.07 s (6H; *ms*-CH$_3$); 3.90 (t, 8H, C<u>H$_2$</u>CH$_2$CH$_2$CH$_3$); 2.50 pentet (4H; *ms*-CH$_2$C<u>H$_2$</u>CH$_2$CH$_3$); 2.42 s (12H; β-CH$_3$); 2.10 (pentet, 8H, CH$_2$C<u>H$_2$</u>CH$_2$CH$_3$); 1.62 (sextet, 8H, CH$_2$CH$_2$C<u>H$_2$</u>CH$_3$); 1.55 sextet (4H; ms-CH$_2$CH$_2$C<u>H$_2$</u>CH$_3$); 1.08 (t, 12H, CH$_2$CH$_2$CH$_2$C<u>H$_3$</u>); 0.85 t (6H; *ms*-CH$_2$CH$_2$CH$_2$C<u>H$_3$</u>). Anal. Calcd for C$_{63}$H$_{94}$N$_6$O$_4$: C 75.75, H 9.42, N 8.42. Found: C 75.72, H 9.38, N 8.37.

References and Notes

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Samples Availability: Available from the authors.