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Reaction of β-Amino-*meso*-Tetraphenylporphyrin with α,β-Unsaturated Carbonyl Compounds: An approach to fused pyridinoporphyrins

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Abstract: Fused pyridinoporphyrins (**3a** and **3b**) were obtained from the reaction of nickel (II) β-amino-*meso*-tetraphenylporphyrin with propenal or methyl vinyl ketone.
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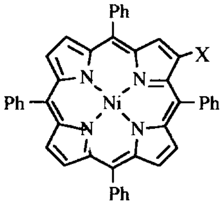
Highly conjugated porphyrins, such as benzoporphyrins, are considered to display certain properties, which might be of great significance in the fields of medicine and of new electronic materials.[1] Some of such conjugated systems have been obtained from pyrroles fused with various aromatic rings (isoindoles)[1] and others from Diels-Alder reactions of β-vinyl porphyrins with dienophiles.[2] Synthesis of extended heterocyclic porphyrin derivatives (e.g. pyrazinoporphyrin systems) have been recently described involving condensation of a porphyrin-2,3-dione with *o*-diaminoarenes[3] or coupling of a 2,3-diaminoporphyrin with α-diones.[4]

We report here our preliminary results from an unusual cyclization that occurs from the reaction of the nickel (II) complex of β-amino-*meso*-tetraphenylporphyrin (**2**) with propenal or methyl vinyl ketone resulting in novel fused pyridinoporphyrins.

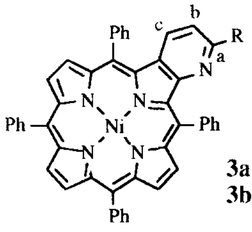
Porphyrin **2** was obtained via nitration of the nickel complex of *meso*-tetraphenylporphyrin **1** with $Cu(NO_3)_2$ in acetic anhydride, followed by reduction with Sn/HCl. Reaction of porphyrin **2** in tetrahydrofuran with propenal in the presence of H_2SO_4 and $Pd(AcO)_2$ afforded after work up and preparative chromatography a red bright compound in 40% yield. This new compound showed a parent ion at m/z=722 in the MS spectrum (FAB+) and the detailed analysis of the ^1H, 2D COSY ($^1H/^1H$) and ^{13}C NMR spectra has allowed us to establish the structure **3a** for this compound.[5] In particular from the ^1H and 2D COSY ($^1H/^1H$) NMR spectra in deuteriated acetone it was possible to assign the proton resonances of the extra ring Ha, Hb and Hc, which appear as double doublets, respectively, at δ 8.67 (J 1.6 and 4.4 Hz), 7.38 (J 4.4 and 8.3 Hz) and 7.28 ppm (J 1.6 and 8.3 Hz). From ^{13}C NMR spectra and HETCOR ($^1H/^{13}C$) experiments it was possible to assign the carbon resonances of Cc, Cb and Ca, respectively at δ 120.1, 130.9 and 148.0 ppm.

When this reaction was performed in the presence of methyl vinyl ketone, after the usual work up procedure, there was isolated a compound (30%) with a parent ion at m/z=736 in the MS spectrum (FAB+), to which structure **3b** has been assigned.[6] The ^1H NMR spectrum of this compound indicates the presence of only six β-pyrrolic protons at δ 8.70-8.77 ppm and of an AB spin system at δ 7.05 and 7.06 ppm (*J* 8.4 Hz). From one-dimensional selective INEPT[7,8] of the same compound, upon irradiation of the CH$_3$ protons resonance, enhancements were observed in the signals at δ 156.7 and 120.3 ppm. With an HETCOR (^{1}H/^{13}C) experiment, the signal at δ 120.3 ppm was assigned to Cb and the other one, at δ 156.7 ppm, was attributed to Ca carbon atom. Also based on the HETCOR (^{1}H/^{13}C) experiment it was possible to assign the resonance of Cc carbon at δ 130.9 ppm. These results are compatible with the structure **3b** and show that a Michael addition, imine formation and dehydrogenation have taken place.

Work is underway in our laboratories to extend these studies to other derivatives of *meso*-tetraphenylporphyrin and to other α,β-unsaturated carbonyl compounds.



1: X=H
2: X=NH$_2$



3a: R=H
3b: R=CH$_3$

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5. Spectroscopic data for **3a**: ^{1}H NMR (CD$_3$COCD$_3$) δ: 7.28 (dd, 1H, Hc, *J* = 1.6 and 8.3 Hz), 7.38 (dd, 1H, Hb, *J* = 4.4 and 8.3 Hz), 7.64-8.05 (m, 20H, phenyl-*o,m,p*-H), 8.67 (dd, 1H, Ha, *J* = 1.6 and 4.4 Hz), 8.70-8.77 (m, 6H, β-H); ^{13}C NMR (CDCl$_3$) δ: 115.6, 116.1, 120.1, 120.2, 126.8, 127.0, 127.2, 127.8, 128.0, 128.5, 130.9, 131.1, 131.7 131.7, 131.9, 132.6, 132.7, 132.7, 132.8, 133.2, 133.5, 134.9, 135.7, 140.3, 140.4, 140.8, 140.9, 141.7, 141.8, 143.1, 144.4, 148.0, 157.4; M. S (FAB+) *m/z* 722 (M+H)$^+$; UV-VIS optical absorption (chloroform) λmax (log ε), 425 (5.51), 542 (4.35), 578 (4.11)
6. Spectroscopic data for **3b**: ^{1}H NMR (CDCl$_3$) δ: 2.47 (s, 3H, CH$_3$), 7.05 and 7.06 (AB, 2H, Hb and Hc, *J* = 8.4 Hz), 7.59-8.00 (m, 20H, phenyl-*o,m,p*-H), 8.67-8.76 (m, 6H, β-H); ^{13}C NMR (CDCl3) δ: 24.9, 115.4, 116.2, 119.9, 120.1, 120.2, 126.6, 126.9, 127.0, 127.8, 127.9, 128.4, 130.9, 130.9, 131.5, 131.6, 131.6, 132.5, 132.6, 132.7, 132.9, 133.5, 135.4, 135.8, 140.4, 140.6, 140.7, 140.8, 141.0, 141.6, 141.7, 143.1, 144.2, 156.7, 157.2; M. S. (FAB+) *m/z* 736 (M+H)$^+$; UV-VIS optical absorption (chloroform) λmax (log ε), 424 (5.34), 539 (4.12), 578 (3.90)
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8. The one dimensional selective INEPT measurements give the connectivity of a selected proton, by irradiation of the corresponding resonance, to the carbons to which it is coupled and can be optimized for different long-range J (C/H) coupling. In this case we have choosen 7 Hz as the value of that coupling constant.

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