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NEW TETRAPYRROLIC MACROCYCLES. 18 AND 20π ELECTRONS HOMOPORPHYRINS AND RELATED COMPOUNDS

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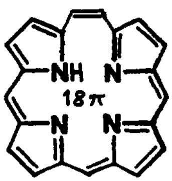
Macrocyclic conjugated systems A and B, possessing 18 and 20π electrons, should formally be aromatic and non aromatic homologs of porphyrins (1). We earlier prepared a series of nickel-homoporphyrins 1 to 4 lacking a fully conjugated system (2). In this paper we describe the preparation of a substituted system B and the reactions of the nickel complexes of substituted A and B. Furthermore this study enabled us to characterize a series of nickel-homoporphyrins possessing an sp3 carbon at C-10.

A



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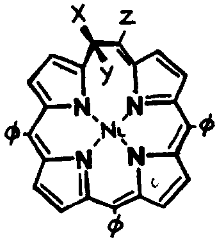
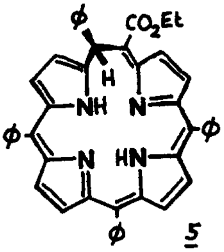


	X	Y	Z
1	CO_2Et	H	C_6H_5
2	H	CO_2Et	C_6H_5
3	C_6H_5	H	CO_2Et
4	H	C_6H_5	CO_2Et

Acid treatment (3×10^{-2} M CF_3COOH in CH_2Cl_2) of 1, 2, 3 or 4 initially yielded a mixture of the four nickel complexes in equilibrium (3) (ratio ca 25.65.5 10). More drastic conditions (1 M CF_3COOH or conc HCl) caused demetalation and formation of bases 5 and 6 (resp. 20 and 80 % ; acid catalyzed equilibrium ratio)



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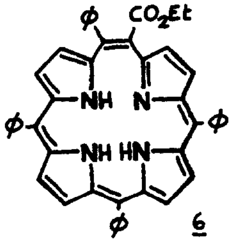
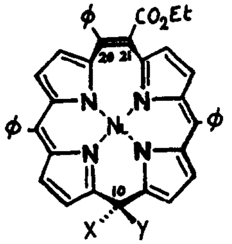


6

The structure of base 5 was easily determined by comparison with the known homoporphyrins and by quantitative remetalation [Ni(OAc)$_2$ in MeOH] to complex 3. Base 6 - the first fully conjugated homoporphyrin base known - is rather unstable as could be expected. Its ^{13}C n.m.r. spectrum showed that all carbon atoms of the macrocycle are sp2 hybridized, thus leaving only one possible structure. Moreover its visible and ^{1}H n.m.r. spectra are extremely different from those of porphyrins [6 (C_6H_6) λ_{max} = 472 nm (ε = 38000), 692 (13400) ; n.m.r. δ($CDCl_3$, TMS) = 6.2 to 7.5 ppm for 8 pyrrolic protons].

Metalation [Ni(OAc)$_2$, AcOH, 60°] of base 6, under an inert atmosphere (purified N_2) led to a mixture of 1 to 4 (30 %), resulting from an acid catalyzed equilibrium. The same experiment performed at 25°C, allowed us to observe the exclusive formation of 1, but the longer reaction time required caused 6 to decompose.

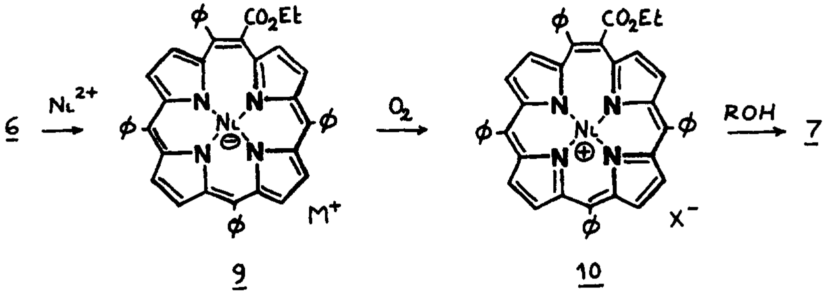
However, when treated with Ni(OAc)$_2$ in MeOH or H_2O, in the presence of oxygen, base 6 gave 10-H homoporphyrin 7 ("axial" OH or OCH_3). Heating 7 in refluxing toluene yielded 8 ("equatorial" OH or OCH_3). The X-rays structure determination of 8 (X = OH) (4) showed a large folding of the macrocycle along the Ni—C-10 axis, the C-20—C-21 and C-10 bridges beeing pushed upwards with respect to the pyrrole rings, thus discriminating "axial" and "equatorial" substituents at C-10. This structure inhibits the conjugation of the C-21—C-20 double bond with the neighbouring pyrrole rings.



	X	Y
7	C_6H_5	OH or OCH_3
8	OH or OCH_3	C_6H_5

These data explain the dipyrromethene-like visible spectra or compounds 7 and 8 [λ_{max} = 420 to 500 nm ; ε<35000] and the shielding of the pyrrolic protons [δ 6 0 to 7 0 ppm]

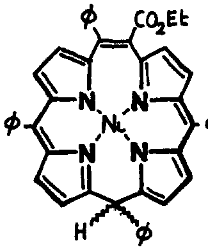
The formation of the kinetically favoured product 7 from 6 could be interpreted by initial complexation of nickel followed by oxydation of the anionic 20π species produced to a 18π cation, solvolyzed to 7 A similar oxydation is involved in the formation of nickel-tetradehydrocorrines (5).



The isomerisation 7 → 8 operates via heterolytic dissociation to cation 10 followed by addition of the nucleophile at the thermodynamically favoured "equatorial" position. This reaction pathway was confirmed by the solvent effect observed (rate CH_3CN/C_6H_6 = 50).

We generated cation 10 by acid treatment (CF_3COOH/CH_2Cl_2) of either 7 or 8 The product was stable in acid solution but isolation of a pure solid (X^- = ClO_4 or $B\phi_4$) failed. Although this cation possessed 18π electrons its spectral data [visible spectrum λ_{max} = 457 nm (ε = 55000), 594 (6800), 786 (10600) , n m.r pyrrolic proton δ = 7 3 to 8 1 ppm] differed from those of porphyrins and compared better with those of unconjugated homoporphyrins 1 to 4 Actually the coordination requirements of the nickel atom must force cation 10 into a conformation similar to that of compounds 7 and 8, thus breaking conjugation next to the C-20 and C-21 carbon atoms

Reduction of cation 10 (X = CF_3COO , Zn, AcOH) gave a mixture of 1 + 2 + 11 This last compound was very similar to 7, but the stereochemistry at C-10 is still to be proved Selective basic isomerization (NEt_3) of 11 to 1 proceeded within a few minutes



11

The same products (1 + 2 + 11) could be easily prepared by protonation of the 20π electrons anion 9 obtained from 1 or 2 [$\mathrm{LiN(iPr)_2}$, THF, 0°C, purified $\mathrm{N_2}$]. The ratio of 1, 2 and 11 was found to be extremely sensitive to the protonating agent (H_2O, AcOH), the rate of addition and the temperature.

As expected, solutions of the anion 9 react rapidly with oxygen to yield 7 (Y = OH) upon hydrolysis

All isolated compounds (1 to 4, 5, 6, 7, 8, 11) gave satisfactory spectral and analytical data. All are racemic mixtures

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