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Chemistry of Dimethylaminomethylporphyrins. 2. Porphyrin Dimers Linked by Pyrrolylmethylene Units[1]

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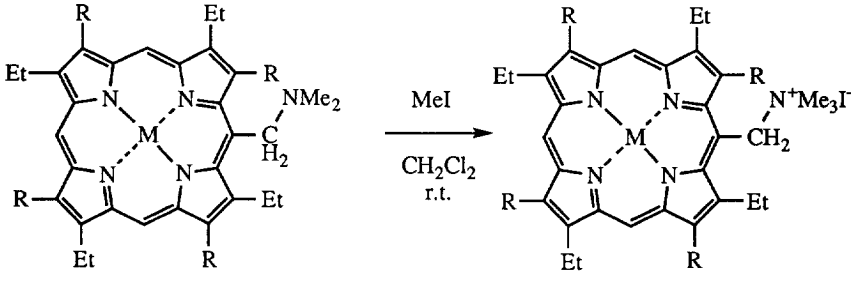
Abstract: Reaction of various α-unsubstituted pyrrole derivatives with trimethyl(porphyrinylmethyl)-ammonium iodides (generated *in situ* from the corresponding *meso*-dimethylaminomethylporphyrins and iodomethane) afforded a number of symmetrical and unsymmetrical porphyrinylmethylpyrrole adducts, including dimers linked by one and two pyrrolylmethylene units. The NMR spectra of the monopyrrole-linked dimers indicate a preference for a face-to-face conformation. Copyright © 1996 Elsevier Science Ltd

The search for new multi-porphyrin arrays with novel conformational, spectroscopic, and electron- and energy-transfer properties continues undiminished.[3] In this paper we report a facile method of preparation of porphyrin dimers linked in the *meso*-positions by one or two pyrrolylmethylene units, and describe briefly their interesting NMR properties.

This work stems from the recent discovery that dimethylaminomethyl (DMAM) porphyrin derivatives can be used as a precursor for porphyrinylmethyl cation formation. The former are readily prepared from Ni or Cu porphyrins by $NaBH_4$ reduction of the iminium salts from Vilsmeier substitutions.[4] Thus the free base derivatives of DMAM-porphyrins were found to be activated with $Zn(OAc)_2$ to give in the presence of alcohols or CH-acids (acetone, nitromethane, etc.), the corresponding alkylated products.[5] An alternative method to activate DMAM-porphyrins in reactions with nucleophiles is the formation of trimethylporphyrinylmethylammonium iodide. Thus treatment of **1** with MeI in dichloromethane at room temperature gave the salt **4** which is stable enough to be purified and characterised by UV/visible and NMR spectroscopy. It was found that this derivative can be easily transformed with alcohols into the corresponding ethers,[5] and via the triphenylphosphonium salt into *meso*-methylporphyrins.[1] In the absence of any nucleophiles, salt **4** underwent oxidative dimerisation to give *meso*-bis(porphyrinyl)ethane.[6]

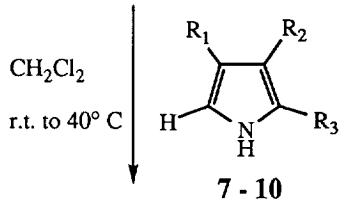
We now report a new reaction of DMAM-porphyrins **1**-**3** (*via* salts **4**-**6**) with a number of α-unsubstituted pyrrole derivatives. The simple treatment of **1** (or **2**, or **3**) with a 10-fold excess of MeI followed by addition of a 3- to 5-fold excess of pyrroles **7** - **10** in methylene chloride at room temperature for 0.5 - 2 h afforded the

adducts **11** - **16**[7] in high yields. The reverse ratio of the reagents (i.e. **1** : **9** ~ 2 : 1) led to the formation of the symmetrical dimer **17**.[7] Moreover the same compound could be obtained by using an excess of DMAM-porphyrin **1** over the pyrrolylmethylporphyrin **15** in the coupling process. The use of **15** as a nucleophile in the reaction with DMAM-porphyrin **3** afforded unsymmetrical adduct **18** in good yield.



1 - 3 **4 - 6**

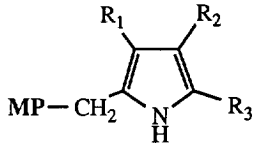
1,4: R = Et (OEP); M = Ni
2,5: R = Me (EtioP); M = Ni
3,6: R = Me (EtioP); M = H_2



7: R_1, R_2, R_3 = H
8: R_1, R_3 = Me; R_2 = CO_2Et
9: R_1, R_2 = Et; R_3 = H
10: R_1, R_2 = Et; R_3 = NiOEP-CH_2

7 - 10

11: **P** = EtioP; M = Ni; R_1, R_2, R_3 = H (89%)
12: **P** = EtioP; M = 2H; R_1, R_2, R_3 = H (82%)
13: **P** = EtioP; M = Ni; R_1, R_3 = Me; R_3 = CO_2Et (89%)
14: **P** = EtioP; M = 2H; R_1, R_3 = Me; R_3 = CO_2Et (94%)
15: **P** = OEP; M = Ni; R_1, R_2 = Et; R_3 = H (94%)
16: **P** = EtioP; M = 2H; R_1, R_2 = Et; R_3 = H (80%)



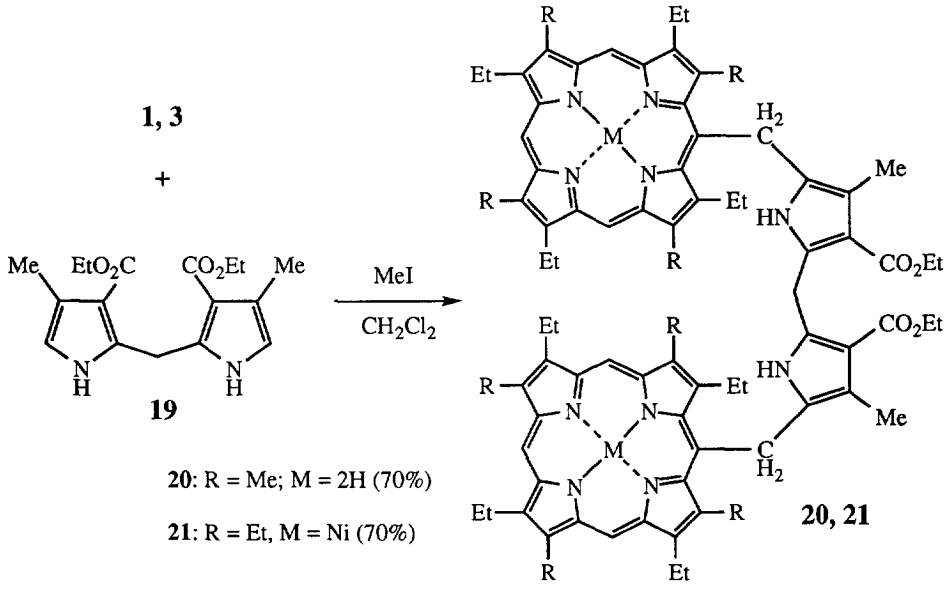
11 - 18

17: **P** = OEP; M = Ni; R_1, R_2 = Et; R_3 = NiOEP-CH_2 (78%)
18: **P** = EtioP; M = 2H; R_1, R_2 = Et; R_3 = NiOEP-CH_2 (71%)

The ^{1}H-NMR spectra of dimers **17** and **18** clearly indicate a tendency towards a face-to-face orientation of the macrocycles. The lateral 10,20-*meso*-protons of **17**, for example, appear at 8.58 ppm, shifted upfield from the typical monomer chemical shift, e.g. 9.40 ppm for **15**. The unsymmetrical dimer **18** shows a very broad *meso*-proton signal at *ca.* 8.5 ppm for the 10,20-*meso*-protons of the NiOEP ring. This is expected if rotation of the porphyrin rings causes partial averaging of these protons, which are non-equivalent due to the asymmetry of the neighbouring Etioporphyrin I ring.

The formation of analogous dimers **20** and **21** linked by two pyrrole units was achieved by reaction of DMAM-porphyrins **1** and **3** respectively, with dipyrrylmethane derivative **19** in the presence of methyl iodide. In contrast to **17** and **18**, it is now the protons of the ethyl ester groups which are shifted dramatically upfield.

Thus the signal of the CH_3 group is shifted upfield to -0.91 ppm (**20**) and -0.66 ppm (**21**) from 1.37 ppm for a reference monomer (e.g. **13**). Even more difference was observed for the CH_2 groups of the ester functions, which are shifted upfield to 1.2 ppm (**20**) and 1.65 (**21**) ppm from 4.30 ppm for **13**. Thus these dipyrrole-linked dimers exhibit conformations in which the ester groups lie within the shielding zone of the porphyrins.



The possible transformation of the dimers into conjugated systems is now being studied. We expect these multiunit adducts to lead to further novel porphyrin structures with interesting redox and spectroscopic properties.

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7. All compounds described were purified by chromatography on silica gel, and were characterized by TLC and NMR and mass spectra. Data for representative compounds follow. **11**: ^{1}H NMR ($CDCl_3$, 250 MHz): 9.45 (s, 1 H, *meso*-15-H), 9.44 (s, 2 H, *meso*-10,20-H), 6.55 (bs, 1 H, NH-Pyr), 6.05 - 5.90 (m, 5 H, Por*CH*$_2$Pyr and PyrH), 3.95 - 3.75 (overlapping q, 8 H, CH_2 of peripheral Et), 3.39, 3.38, 3.35, and 3.34 (s, 12 H, Por*CH*$_3$), 1.76, 1.75, 1.70, and 1.67 (overlapping t, 12 H, CH_3 of peripheral Et); UV/vis ($CHCl_3$) λ_{max} (ε_{rel}) 406 (10.0), 530 (1.0), 564 (1.4) nm. **14**: ^{1}H NMR ($CDCl_3$, 250 MHz): 10.19 (s, 2 H, *meso*-10,20-H), 9.94 (s, 1 H, *meso*-15-H), 7.10 (bs, 1 H, NH-Pyr), 6.22 (m, 2 H, Por*CH*$_2$Pyr), 4.30 (q, 2 H, J = 7.5 Hz, CH_3*CH*$_2$O), 4.15 - 3.95 (overlapping q, 8 H, CH_2 of peripheral Et), 3.64, 3.63, 3.61, and 3.34 (s, 12 H, Por*CH*$_3$), 2.70 and 1.90 (s, 6 H, Pyr*CH*$_3$), 1.75 - 1.65 (overlapping t, 12 H, CH_3 of peripheral Et), 1.36 (t, 3 H, J = 7.5 Hz, *CH*$_3$$CH_2$O), -2.95 and -3.15 (bs, 2 H, NH of Por); UV/vis ($CHCl_3$) λ_{max} (ε_{rel}) 406 (7.1), 504 (1.0), 540 (0.6), 575 (0.5), 624 (0.4) nm. **17**: ^{1}H NMR ($CDCl_3$, 300 MHz): 9.29 (s, 2 H, *meso*-15-H), 8.58 (s, 4 H, *meso*-10,20-H), 6.73 (bs, 1 H, NH-Pyr), 5.20 (s, 4 H, Por*CH*$_2$Pyr), 3.80 - 2.60 (overlapping q, 32 H, CH_2 of peripheral Et), 2.32 (q, 4 H, J = 7.5 Hz, Pyr*CH*$_2$$CH_3$), 1.80-1.10 (overlapping t, 48 H, CH_3 of peripheral Et), 0.93 (t, 6 H, J = 7.5 Hz, PyrCH_2*CH*$_3$); UV/vis ($CHCl_3$) λ_{max} (ε x 10^{-3}) 402 (438), 532 (39.6), 565 (54.5) nm. **21**: ^{1}H NMR ($CDCl_3$, 300 MHz): 9.47 (s, 4 H, *meso*-10,20-H), 9.46 (s, 2 H, *meso*-15-H), 8.38 (s, 2 H, NH-Pyr), 5.52 (s, 4 H, Por*CH*$_2$Pyr), 3.90 - 3.40 (overlapping q, 16 H, CH_2 of peripheral Et), 3.57 (s, 2 H, Pyr*CH*$_2$Pyr), 2.37 (s, 6 H, Pyr*CH*$_3$), 1.90-1.50 (overlapping t and q, 28 H, CH_3 of peripheral Et and CH_3*CH*$_2$O), -0.66 (t, 6 H, J = 7.5 Hz, *CH*$_3$$CH_2$O); UV/vis ($CHCl_3$) λ_{max} (ε x 10^{-3}) 407 (439), 529 (29.7), 564 (45.7) nm.

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