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Polypyrroles in Three Dimensions. The Synthesis of Tripyrrane-strapped 2-Aminophenylporphyrins

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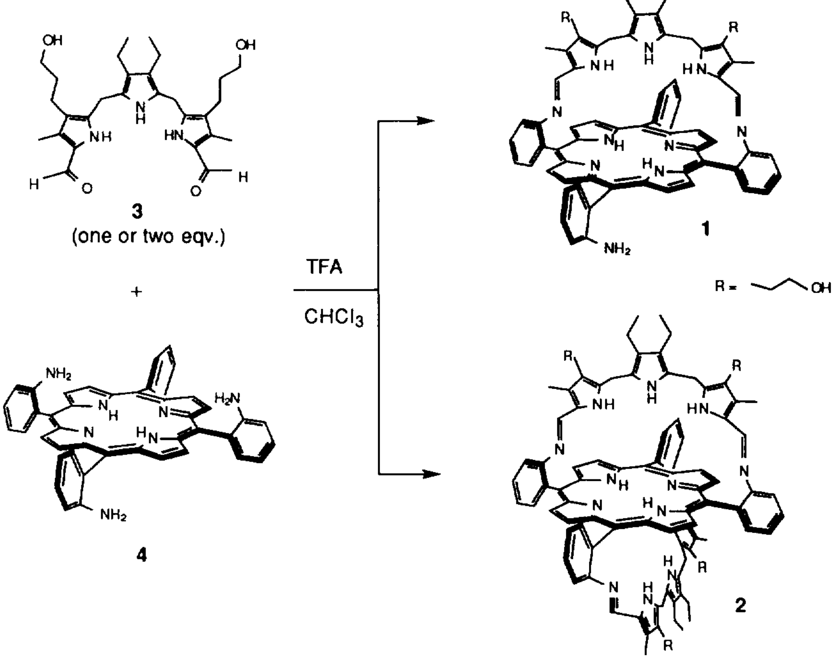
Abstract: The synthesis of two "three dimensional expanded porphyrins", namely the singly and doubly bridged, tripyrrane-strapped tetrakis(2-aminophenyl)porphyrins, **1** and **2**, is described.

Recent developments in the expanded porphyrin area[1] have served to show that if polypyrrolic macrocycles are made sufficiently large, they can adopt conformations that are far from planar.[2-4] These findings have added a new dimension (literally) to the chemistry of expanded porphyrin chemistry and have inspired us *inter alia* to try making "three dimensional expanded porphyrins" *via* more rational means. As a first step towards realizing this challenging topological goal we wish to report the synthesis of the three dimensional macrobi- and macrotricycles **1** and **2**; in these systems, non-conjugated tripyrrane "straps" are used to bridge facially the top and/or bottom of a central porphyrin core.

Unlike the chemistry of three dimensional expanded porphyrins, the science of strapped, or cyclophane-type, porphyrins is exceedingly well developed.[5] Such systems have been studied as mimics of hemoglobin, cytochrome P-450, and cytochrome c oxidase, as models for the study of electron transfer processes, as reaction catalysts, and as molecular recognition units among other things. Not surprisingly, therefore, a large number of "capping", "strapping" and metal-coordinating subunits have been used to create these so-called superstructured porphyrins. Interestingly, in no cases have polypyrrolic bridging entities been employed. Were such bridging units to be used, however, it would provide an easy entry into the chemistry of three dimensional expanded porphyrins and allow this area to interface with that of the better-studied porphyrins.

In the case of the αβαβ atropisomer of 5,10,15,20-tetrakis(2-aminophenyl)porphyrin,[6] **4**, a key precursor often used to prepare superstructured porphyrins,[7] inspection of CPK space filling molecular models led us to consider that doubly formylated tripyrrane subunits, such as **3**,[8] would fit as "straps" above and below the porphyrin plane. Specifically, it was expected that standard imine-producing condensations would give rise to

Scheme 1



the three dimensional expanded porphyrins **1** and **2**. System **1** would define an example of a tetrakis(2-aminophenyl)porphyrin bridged by a single tripyrrane subunit and compound **2** a congener with two straps.

Under conditions of high dilution (chloroform, Dean-Stark trap, reflux), compounds **1** and **2** were prepared in moderate yield (30-45% after aqueous NaOH wash and recrystallization from CH_2Cl_2-hexanes) *via* the acid catalyzed condensation of αβαβ-5,10,15,20-tetrakis(2-aminophenyl)porphyrin (**4**)[6] with one or two equivalents, respectively, of the diformyltripyrrane[8] **3** (Scheme 1). The porphyrin-centered Cu(II) and Ni(II) complexes of **1** were also prepared in a like way starting from **3** and the Cu(II) and Ni(II) adducts of **4**.

While sensitive to acid, the above products proved stable under normal laboratory conditions. Characterization could thus be effected *via* standard means.[9] Here, in general, ^1H NMR spectroscopy proved most informative; it provided evidence that the proposed strapped structures were in fact being formed. For instance, in **1** and **2** the signals corresponding to the condensed tripyrrane unit were found to be shifted upfield substantially (by up to 3.2 ppm) as compared to those of the starting diformyl precursor **3**. Such ring current-derived upfield shifts are characteristic of strapped porphyrins[7] and are generally taken as an indication that the strap lies above the plane of the porphyrin.[7]

Based on analogy with other nonaromatic expanded porphyrin systems,[1-3] it is expected that the polypyrrole portion of these new materials should act as effective complexing agents for both neutral and anionic substrates. Preliminary mass spectrometric analyses are consistent with such suggestions; ion peaks corresponding to the formation of 1:1 methanol-*d*$_4$ and acetonitrile-*d*$_3$ adducts were explicitly obtained in the case of the doubly strapped system **2** (m/z = 1598 and 1608 amu, respectively) It is thus proposed that "three dimensional expanded porphyrins" such as **1** and **2** could emerge as interesting polytopic receptors wherein the metal coordinating ability of the porphyrin is used in concert with the neutral/anion binding capabilities of the polypyrroles to effect the recognition of multifunctional substrates of well defined geometry and structure.

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6. Obtained as per: Sorrell, T.N.; Bump, C.M.; Jordan, J. *Inorg. Syn.* Busch, D. H. Ed.; J. Wiley: New York, 1980; pp. 161-165.
7. See for example: Momenteau, M.; Lavalette, D. *J. Chem. Soc., Chem. Commun.*, **1982**, 341; see also ref. 5.
8. The synthesis of **3** is described in: Sessler, J.L.; Mody, T.D.; Hemmi, G.W.; Lynch, V. *Inorg. Chem.* **1993**, *32*, 3175.
9. Characterization data: For **1**, HR-MS: m/e 1119.562270 for $C_{72}H_{69}N_{11}O_2$; UV-Vis (CH_2Cl_2): 422 (Soret), 518, 552, 592, 648; ^{1}H NMR (CD_2Cl_2) δ -2.71 (2H, s, NH), -0.30 (6H, bt, $CH_2\mathbf{CH_3}$), -0.10 (4 H, m, $CH_2\mathbf{CH_2}CH_2OH$), 0.85 (6H, s, CH_3), 1.10 (4H, m, $\mathbf{CH_2}CH_3$), 1.30 (4H, m, $\mathbf{CH_2}CH_2CH_2OH$),

1.93 (4H, s, $-CH_2-$), 2.00 (4H, m, $CH_2CH_2\mathbf{CH_2}OH$), 7.05 - 8.90 (24H, m, aromatic), 8.34 (2H, s, $\mathbf{CH}=N$); ^{13}C NMR (CD_2Cl_2) δ 7.60, 7.83, 13.09, 14.82, 16.02, 18.83, 21.29, 21.88, 28.93, 30.82, 31.95, 60.67, 76.79, 114.36, 116.46, 119.49, 122.17, 123.91, 125.96, 128.87, 133.93, 134.84, 146.37, 147.02, 147.66, 153.0. For Cu•**1**, HR-MS: m/e 1181.479897 for $C_{72}H_{68}N_{11}O_2Cu$ ($[M + 1]^+$); UV-Vis (CH_2Cl_2) 421 (Soret), 542. For Ni•**1**, HR-MS: m/e 1176.488800 for $C_{72}H_{68}N_{11}O_2Ni$ ($[M + 1]^+$); UV-Vis (CH_2Cl_2) 419 (Soret), 529; ^1H NMR (CD_2Cl_2) δ 0.13 (6H, t, CH_2CH_3), 0.25 (4H, m, $CH_2\mathbf{CH_2}CH_2OH$), 1.35 (6H, s, CH_3), 1.58 (4H, bq, $\mathbf{CH}_2CH_3$), 1.7 (4H, m, $\mathbf{CH_2}CH_2CH_2OH$), 2.35 (4H, m, $CH_2CH_2\mathbf{CH_2}OH$), 2.12 (4H, s, $-CH_2-$), 7.00 - 8.80 (24H, m, aromatic), 8.30 (2H, s, $\mathbf{CH}=CN$); ^{13}C NMR (CD_2Cl_2) δ 7.72, 13.05, 14.75, 16.11, 18.95, 21.39, 21.90, 28.95, 30.86, 32.15, 60.50, 76.95, 114.58, 116.65, 118.31, 118.98, 120.59, 122.34, 125.36, 128.89, 131.46, 132.75, 142.29, 146.09, 148.35, 153.30. For **2**, HR-MS: m/e 1564.839259 for $C_{100}H_{104}N_{14}O_4$; UV-Vis (CH_2Cl_2) 427 (Soret), 516, 562, 594, 651; ^1H NMR (CD_2Cl_2) δ -2.803 (2H, s, **NH**), -0.06 (12H, t, $CH_2\mathbf{CH_3}$), 0.48 (4H, m, $CH_2\mathbf{CH_2}CH_2OH$), 0.59 (4H, m, $CH_2\mathbf{CH_2}CH_2OH$), 1.13 (8H, m, $\mathbf{CH_2}CH_3$), 1.22 (12H, s, CH_3), 1.80 (12H, s, CH_3), 1.95 (8H, m, $\mathbf{CH_2}CH_2CH_2OH$), 2.90 (8H, s, $-CH_2$), 3.08 (8H, bt, $CH_2CH_2\mathbf{CH_2}OH$), 7.30 (4H, m, aromatic), 7.50 (4H, m, aromatic), 7.78 (4H, m, aromatic) 8.12 (4H, s, $\mathbf{CH}=N$), 8.22 (4H, m, aromatic), 8.67 (8H, s, ß pyrr); ^{13}C NMR (CD_2Cl_2) δ 1.26, 8.70, 15.70, 17.10, 19.76, 22.71, 30.09, 33.18, 61.71, 77.92, 117.75, 118.71, 120.22, 121.29, 123.01, 125.58, 126.40, 129.86, 131.81, 147.89, 147.90, 155.10.

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