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# Synthesis of *meso*-tetra(4-azidocarbonylphenyl)porphyrin

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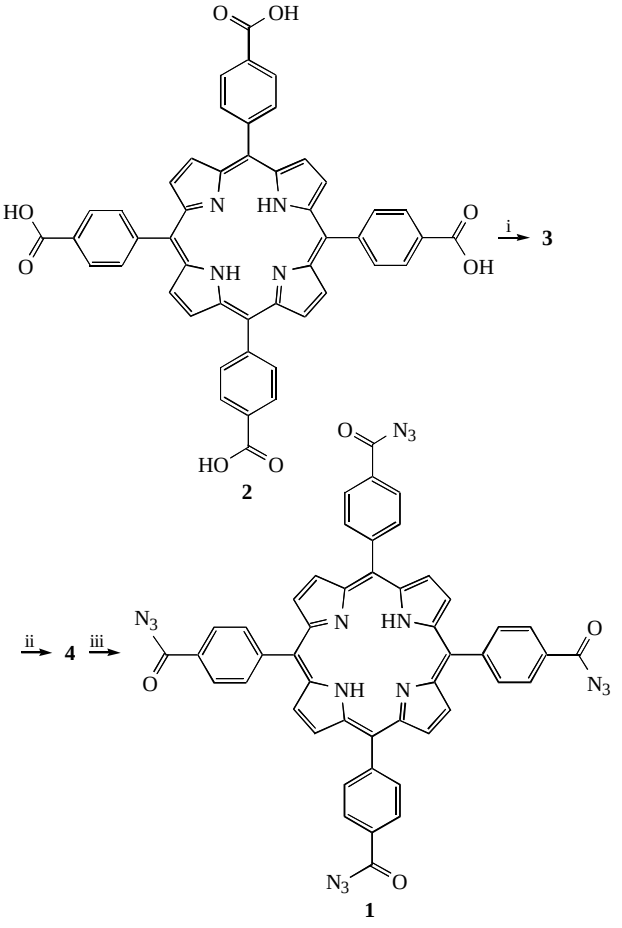
The title compound has been synthesised in three steps starting from *meso*-tetra(4-carboxyphenyl)porphyrin.

Presently, supramolecular donor–acceptor systems are being extensively investigated as models of the photosynthetic centre. The nucleus of porphyrin, free or in a complex with a metal ion, frequently serves as one of the participants of a transfer chain.[1–3] Porphyrins containing labile functional groups can be used for the construction of supramolecular systems with several donor–acceptor sub-units.[4–6] The azido group is one such labile group, which allows a supermolecule to be built both thermally and photochemically. However, until now, no method has been reported for the construction of covalently linked azidoporphyrins.

In this communication, we report the synthesis of *meso*-tetra(4-azidocarbonylphenyl)porphyrin **1**, which appears to be the first example of an acylazidophenylporphyrin. Besides its potential as a sub-unit for the construction of donor–acceptor systems, azidoporphyrins can be considered as very promising compounds for molecular biology and medicine.[7,8] For example, it can be locally linked to a biomacromolecule under mild conditions upon irradiation, *i.e.*, can be used as a photoaffinity label.

The title compound was synthesised in three steps starting from *meso*-tetra(4-carboxyphenyl)porphyrin **2** (Scheme 1).




**Scheme 1** *Reagents and conditions*: i, $P_2O_5$, MeOH (saturated with HCl), $CHCl_3$; ii, $N_2H_4 \cdot H_2O$, MeOH; iii, $NaNO_2$, AcOH.

The esterification of *meso*-tetra(4-carboxyphenyl)porphyrin **2** according to Smith[9] did not result in a quantitative yield of *meso*-tetra(4-methoxycarbonylphenyl)porphyrin **3**. We explored a modification of the original method and found that the use of MeOH saturated with gaseous HCl in the presence of $P_2O_5$ afforded compound **3** in 99% yield.

Our critical discovery was that hydrazine hydrate can be used to convert the four methoxy groups of **3** to hydrazido groups, the only compound isolated being *meso*-tetra(4-hydrazidocarbonylphenyl)porphyrin **4** (75%). Our attempts to selectively substitute one, two or three methoxy groups at various ratios between the starting reagents were unsuccessful. This is thought to be due to the low solubility of **4** in comparison with the mono-, di- and tri-substituted compounds. The reaction of **4** with $NaNO_2$ in the presence of acetic acid in chloroform at room temperature resulted in the formation of the desired tetraazidoporphyrin **1** in 50% yield, which showed the azido stretching absorption at 2140 $cm^{-1}$ in the IR spectrum.

The new compounds prepared here have satisfactory elemental analysis (C, H) data, and the NMR and IR spectra accord with the assigned structures.†

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† *Experimental*. Solvents were dried using standard techniques. TLC was performed on Silufol UV-254 plates. Column chromatography was done on Silpearl. NMR spectra were recorded on a Bruker AM-300 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were determined in potassium bromide pellets using a Specord-80 instrument.

*Synthesis*. meso-*Tetra(4-methoxycarbonylphenyl)porphyrin* **3**. Methanol (25 ml) was added dropwise to a suspension of $P_2O_5$ (5 g) in chloroform (5 ml) at 0 °C with stirring. *meso*-Tetra(4-carboxyphenyl)porphyrin (50 mg) was added to the mixture followed by the addition of methanol (25 ml) saturated with gaseous HCl. After stirring for 24 h at room temperature, water (100 ml) and chloroform (400 ml) were added to the reaction mixture. The organic layer was washed with water and saturated aqueous $Na_2CO_3$ and evaporated to dryness. The residue was chromatographed twice on Silpearl (200 g) with chloroform. Crystals of tetra-(4-methoxycarbonylphenyl)porphyrin **3** were obtained (53 mg, 99%). $^1$H NMR ($CDCl_3$) $\delta$: –2.80 (br. s, 2H, NH), 4.10 (s, 12H, OMe), 8.30 (d, 8H, C-3,5, *J* 8 Hz), 8.43 (d, 8H, C-2,6, *J* 8 Hz), 8.82 (s, 8H, β-CH). The IR and UV spectra of **3** are consistent with published data.[10]

meso-*Tetra(4-hydrazidocarbonylphenyl)porphyrin* **4**. Hydrazine hydrate (9 ml) was added to a solution of **3** (24 mg) in THF (90 ml) and methanol (90 ml). The mixture was refluxed for 48 h and then cooled to room temperature. The solvent was removed on a rotary evaporator, and the residue was washed with hot isopropanol (2×20 ml). Crystals of *meso*-tetra(4-hydrazidocarbonylphenyl)porphyrin **4** were obtained (18 mg, 75%), mp > 250 °C. $^1$H NMR ([$^2H_6$]DMSO) $\delta$: –1.52 (m, 2H, NH), 4.05 (m, 8H, $NH_2$), 8.30 (m, 16H, CH=), 8.75 (m, 8H, β-CH), 10.00 (m, 4H, NH). IR (KBr, $\nu$/$cm^{-1}$): 3423, 3376, 3274 (NH), 2935 (CH), 1717 (C=O), 1609, 1581, 1401, 817 (Ar). Found (%): C, 68.01; H, 4.68. Calc. for $C_{48}H_{38}N_{12}O_4$ (%): C, 68.07; H, 4.53.

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meso-*Tetra(4-azidocarbonylphenyl)porphyrin* **1**. Compound **4** (3 mg) was dissolved in chloroform (3 ml) and acetic acid (1 ml). $NaNO_2$ (20 mg) was added to the solution. After stirring for 20 min at room temperature, the reaction mixture was poured into water (100 ml) and extracted twice with chloroform (40 ml). The organic layer was separated, washed twice with water and a saturated aqueous $NaHCO_3$ solution, and evaporated to dryness at 40 °C. The residue was chromatographed twice on Silpearl (50 g) with chloroform. Crystals of tetraazidoporphyrin **1** were obtained (1.6 mg, 50%), mp > 250 °C (decomp.). $^1$H NMR ($CDCl_3$) $\delta$: –2.80 (br. s, 2H, NH), 8.31 (d, 8H, C-3,5, *J* 8 Hz), 8.42 (d, 8H, C-2,6, *J* 8 Hz), 8.80 (s, 8H, β-CH). IR (KBr, $\nu$/cm$^{-1}$): 3259 (NH), 2930 (CH), 2140 ($N_3$), 1717 (C=O), 1606, 1560, 1492, 1404, 807 (Ar). Found (%): C, 64.58; H, 3.11. Calc. for $C_{48}H_{26}N_{16}O_4$ (%): C, 64.72; H, 2.94.

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