

Synthesis of β -Octasubstituted Sterically Bulky Porphyrins by Suzuki Cross Coupling

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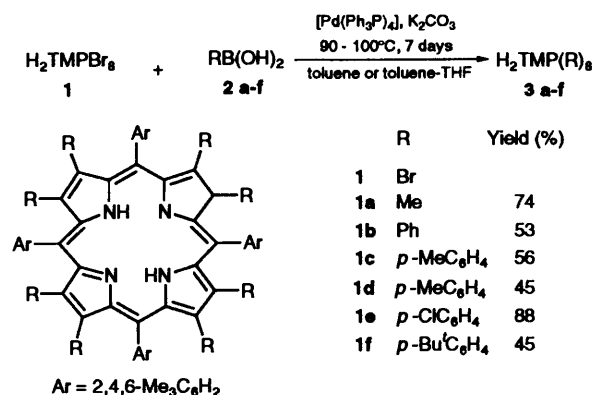
β -Octasubstituted tetramesitylporphyrins have been prepared in good yields by Suzuki cross coupling of β -octabromotetramesitylporphyrin with aryl- and alkyl-boronic acids. A single-crystal X-ray analysis of β -octamethyltetramesitylporphyrin **3a** shows a saddled non-planar structure.

Sterically encumbered porphyrins have been widely used as biomimetic models,¹ whilst tetramesitylporphyrin² (H_2TMP), such a compound, has been used in metalloporphyrin-catalysed oxygenations. Substituents on the β -positions of porphyrins seem to confer on them unusual optical properties, enhanced electrochemical redox stability,^{3,4} and increased catalytic efficiency of their metal complexes.⁵ Until now, syntheses of β -substituted porphyrins, especially those which are sterically bulky, have been hindered by the difficulty in preparing 3- and 3,4-di-substituted pyrroles,⁶ the low product yields and the tedious separation of reactants from products. Such limitations are particularly troublesome given that much of the cutting edge research in porphyrin chemistry depends critically on the synthesis of exotic porphyrins that are elaborated at the β -positions.⁷ We have recently described a facile synthesis of β -aryl substituted tetraphenylporphyrins⁸ by the Suzuki cross-coupling reaction⁹ and here we report the successful application of this method to the preparation of sterically hindered β -octasubstituted tetramesitylporphyrins [$H_2TMP(R)_8$] (R = Me, Ar).

Compounds $H_2TMP(R)_8$ **3a-f** were prepared by the reaction of aryl- and alkyl-boronic acids **2a-f** (20 equiv.) with $H_2TMP(Br)_8$ ^{3b} using a catalytic amount of $[Pd(PPh_3)_4]$ (10–20 mol%), and anhydrous K_2CO_3 (40 equiv.) (Scheme 1) in toluene or toluene-THF at 90–100 °C for 7 days; the isolated yields of products were in the range 45–88%. For arylboronic acids, the solvent used was toluene while for methylboronic acid THF-toluene was employed to enhance the solubility of the latter. It is unnecessary to protect the porphyrin as a zinc complex.⁶ Compound $H_2TMP(Br)_8$ which, compared to $H_2TPP(Br)_8$, is sterically more hindered and more electron donating did not seem to reduce the rate of the cross coupling,⁷ probably because the β -positions in non-planar porphyrins are less sterically crowded.³

The tetrahedral and non-planar saddled structure of **3a** was determined by a single-crystal X-ray analysis (Figs. 1 and 2).† The maximum deviation from the displacements of the atoms of **3a** from the mean plane of the macrocycle is between C(2) (0.103 Å) and C(2a) (–0.103 Å); the dihedral angle between the porphyrin mean plane and the phenyl plane was 122.6°.

† Crystal data: Dark-red prism, $C_{64}H_{70}N_4 \cdot 2(C_2H_5OH)$, **3a**, $M = 987.38$, tetragonal, space group $P4_2$, 1c (No. 114) with $a = 15.129(2)$, $b = 15.129(2)$, $c = 13.774(3)$ Å, 293 K, $Z = 2$, $F(000) = 1100$, Mo-K α radiation ($\lambda = 0.71073$ Å); $\mu = 0.06$ mm⁻¹, transmission factors 0.872 to 0.922. Refinement of 1148 reflections with $F > 4.0\sigma$ (F) and 164 parameters yield a final $R = 0.077$, $R_w = 0.089$ with $w^{-1} = \sigma^2(F) + 0.0010|F|^2$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1).



Scheme 1

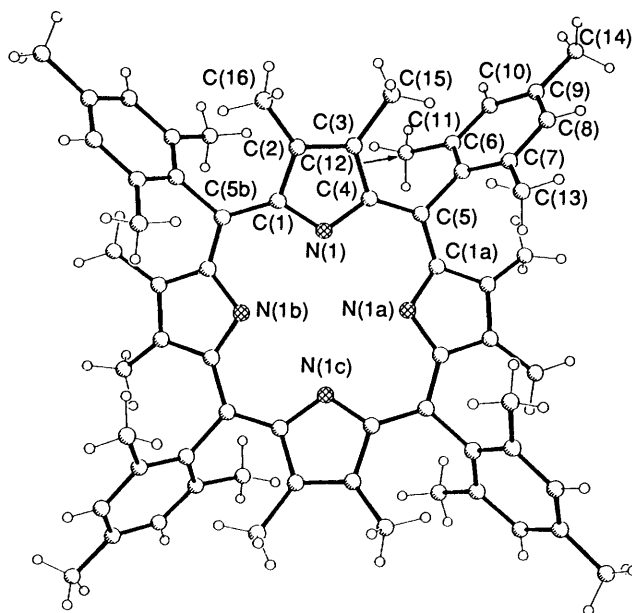


Fig. 1 Perspective view of $H_2TMP(Me)_8$ **3a** normal to the porphyrin plane

Experimental

Typical procedure.—A Teflon-stoppered flask (50 cm³) was charged with H_2TMPBr_8 **1** (125 mg, 1 equiv.), $[Pd(PPh_3)_4]$ (15 mg, 15 mol%), toluene (18 cm³)–THF (12 cm³), anhydrous K_2CO_3 (483 mg, 40 equiv.), and methylboronic acid **2a** (105 mg, 20 equiv.). The green suspension was degassed by the freeze–pump–thaw method (3 cycles), and then was heated at 90–100 °C under N_2 for 7 days. The reaction mixture was then

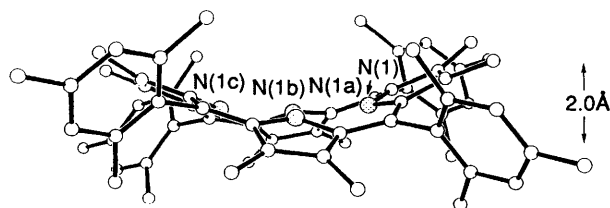


Fig. 2 Edge-on view of $H_2TMP(Me)_8$ **3a**

diluted with CH_2Cl_2 (30 cm^3) and washed with aqueous $NaHCO_3$ (40 cm^3), water ($2 \times 40\text{ cm}^3$), and brine. The organic layer was then dried ($MgSO_4$) and evaporated to afford the crude product which was purified by column chromatography on silica gel using $CHCl_3$ as the eluent. The slowest-moving green band was collected and evaporated to give a green solid, which was recrystallised from CH_2Cl_2 -EtOH to yield pure green crystals of $H_2TMP(Me)_8$ 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetramesitylporphyrin **3a** (74%); $R_f = 0.11$; δ_H (250 MHz, $CDCl_3$) 1.90 (s, 24 H), 2.18 (s, 24 H), 2.55 (s, 12 H) and 7.24 (s, 8 H); λ_{max}/nm (log ϵ) 458.5 (5.17), 614.5 (4.11) and 666.0 (4.09); m/z (FAB) 896 (M^+) (Found: C, 79.1; H, 8.0; N, 5.4. $C_{64}H_{70}N_4 \cdot 4H_2O$ requires C, 79.49; H, 8.13; N, 5.79%).*

* All new compounds have satisfactory spectral and elemental analysis.

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