meso-Aryl tribenzosubporphyrin—a totally substituted subporphyrin species†

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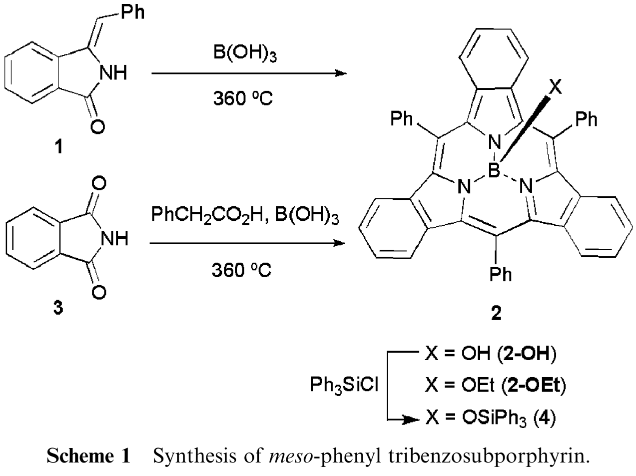
***meso*-Aryl tribenzosubporphyrin was synthesized by a self-condensation of 3-benzalphthalimidine and by a condensation of phthalimide with phenylacetic acid using boric acid as a template; the compounds derived were characterized based on a wide range of spectroscopic and electrochemical methods.**

Recently, there has been considerable interest in tripyrrole porphyrin analogues, inspired by the successful syntheses of tribenzosubporphine,[1] *meso*-aryl subpyriporphyrin,[2] and *meso*-aryl subporphyrin.[3,4] Subporphyrinoids have been much sought after as synthetic targets ever since subphthalocyanines[5] and subazaporphyrins[6] were synthesized in 1972 and 1995, respectively. Subphthalocyanines possess bowl-shaped triangular structures, intense fluorescence, and unusual second-order nonlinear optical properties.[7] Potential applications include use as pigments in industrial dyestuffs and as building blocks for supramolecular assemblies.[8] With the exception of *meso*-aryl subpyriporphyrin,[2] the subporphyrins that have been reported to date have exhibited bowl-shaped conformations and many of the characteristics of aromaticity based on 14 π-electron conjugation. Furthermore, these subporphyrins all exhibit intense green fluorescence as is observed for subphthalocyanines.[9] Since various substituents can be introduced at the *meso*-positions of subporphyrins, there is clearly greater scope for further modification of the electronic and optical properties than is the case with subphthalocyanines. However highly challenging synthetic procedures and low yields have hindered research in this area. In this communication, we report a synthesis and characterization of a new class of subporphyrinoids, *meso*-aryl tribenzosubporphyrin, which can be readily synthesized in moderate yield. Their electronic structure is elucidated based on an analysis of the magnetic circular dichroism spectrum and DFT calculations.

The synthesis of *meso*-phenyl tribenzosubporphyrin was initially achieved using a synthetic procedure that we developed previously for zinc *meso*-phenyl tetrabenzoporphyrin (Scheme 1).[10] For this reaction, boric acid was used in place of the zinc salt as a template to construct a triangular structure. 3-Benzalphthalimidine (**1**)[11] and boric acid were mixed, ground into a fine powder, and heated to 360 °C for 2 h under an argon atmosphere. The crude residue was washed with hot water and aqueous NaOH solution. A Soxhlet extraction was then carried out with toluene. The toluene solution was concentrated and purified on neutral alumina using toluene and diethyl ether (10 : 1, v/v) as an eluent followed by gel permeation chromatography. Recrystallization from acetone and water, provided *meso*-phenyl tribenzosubporphyrin (**2**) in 7.8% yield with a hydroxy axial ligand (**2-OH**). The synthesis of **2** can also be carried out with a similar yield using a second method based on phthalimide (**3**) and phenylacetic acid. The hydroxy axial ligand can be replaced with an ethoxy substituent (**2-OEt**) by using ethanol during the purification process.

Evidence for the isolation of *meso*-phenyl tribenzosubporphyrin was initially obtained from high-resolution ESI mass spectra (m/z = 660.2219 for **2-OH** ($[M^+ + \text{Na}]$; calcd for $C_{45}H_{28}N_3O_1B_1Na_1$: 660.2218) and 688.2527 for **2-OEt** ($[M^+ + \text{Na}]$; calcd for $C_{47}H_{32}N_3O_1B_1Na_1$: 688.2531)). The ^{1}H NMR spectrum of **2-OH** exhibits a triplet signal at 7.86 ppm and six broad peaks between 8.6 and 7.3 ppm at room temperature which sharpen considerably when the temperature is lowered. The ^{1}H NMR spectrum of **2-OH** measured at −60 °C contains five well-resolved proton signals for the *meso*-phenyl groups at 8.50 (*ortho*), 7.92 (*meta*), 7.79 (*para*), 7.58 (*meta*), and 7.24 (*ortho*) ppm, and two peaks due to the fused benzene rings at



Scheme 1 Synthesis of *meso*-phenyl tribenzosubporphyrin.

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† Electronic supplementary information (ESI) available: Experimental details, ^{1}H NMR and ^{13}C NMR spectra, 2D ^{1}H–^{1}H COSY, HMQC, and HMBC spectra, and electrochemical analyses. Crystallographic data: CCDC 676629. See DOI: 10.1039/b801712c

7.54 (benzo) and 7.41 (benzo) ppm. A broad signal at −2.33 ppm can be assigned to the hydroxy group. These results are consistent with a conformation with C_3 symmetry, which is supported by an analysis of the ^{13}C NMR spectrum based on HMQC and HMBC experiments (see ESI†). Free rotation of the phenyl groups is inhibited by the benzo moieties, since the peaks arising from the *ortho*- and *meta*-protons still appear as broad signals at different chemical shifts even at room temperature. The ^{1}H NMR spectrum of **2-OEt** is comprised of broad peaks at room temperature, which sharpen considerably when the temperature is reduced in a similar manner to what is observed with **2-OH**. The peaks due to the ethoxy group appear at 0.77 and −0.23 ppm. The marked upfield shifts of the axial hydroxy or ethoxy ligand peaks are consistent with a large paratropic ring current effect based on the 14 π-electron aromatic conjugation.

Single crystals for X-ray diffraction analysis were initially prepared by slow diffusion of methanol into a dichloromethane solution of **2-OH**, resulting in a replacement of the hydroxy axial ligand with a methoxy group. Unfortunately, the subporphine moiety was found to be severely disordered, even though measured at low temperature (173 K). Since complex crystal packing patterns were believed to be the problem, a bulky substituent was then introduced at the axial position. Triphenylchlorosilane was reacted with **2-OH** in pyridine at room temperature to provide a complex of **2** with a triphenylsiloxy substituent at the axial position (**4**) (Scheme 1) in an almost quantitative yield. A crystal structure was successfully determined by X-ray diffraction analysis,‡ which contained no structural disorder (Fig. 1). **4** was found to adopt a bowl-shaped triangular structure similar to those observed for tribenzosubporphine[1] and *meso*-aryl subporphyrins.[3,4] The phenyl substituents at the *meso*-positions lie almost perpendicular to the subporphyrin ligand. The dihedral angles of 80.0°, 81.3°, and 84.1° are the largest of those reported to date for subporphyrins. The boron atom is displaced 1.18 Å from the mean plane defined by the six β-position carbon atoms of pyrrole moieties. The large B–O–Si angle of 161° is accounted for in terms of steric congestion between the triphenylsiloxy group and the phenyl rings at the *meso*-positions.

The absorption spectrum of **2-OH** in CH_2Cl_2 contains a Soret band at 372 nm with a shoulder peak at 353 nm, and a Q band at 517 nm with a vibrational band at 485 nm (Fig. 2). The Soret band is shifted to a lower energy by 1530 cm^{-1} relative to the analogous band in the spectrum of tribenzosubporphine,[1] while the red shift for the Q band is only 113 cm^{-1}. **2-OH** was found to exhibit green fluorescence at 524 nm upon excitation at 480 nm. The Stokes shift of 258 cm^{-1} is smaller than the shifts observed for *meso*-aryl subporphyrins,[3,4] but larger than that reported for tribenzosubporphine.[1]

Further insight into the electronic structure of *meso*-phenyl tribenzosubporphyrin was derived from a comparison of the experimental UV/Vis absorption and magnetic circular dichroism (MCD) spectra with the results of time-dependent density functional theory (TDDFT) calculations. A geometry optimization was performed for **2-OH** by using the B3LYP hybrid functional with 6-31G(d) basis sets. Transition energies and oscillator strengths were then calculated using the TDDFT method. The four frontier π-molecular orbitals predicted for **2-OH** are similar to those reported for tribenzosubporphine. The LUMO is orbitally degenerate, while the 1st and 2nd HOMOs are non-degenerate (Fig. 3). The TDDFT calculation reveals that the absorption spectrum of **2** can be successfully described using Gouterman's four-orbital model[12] as a theoretical framework based on forbidden Q and allowed Soret (or B) bands arising from transitions with $\Delta M_L = \pm 7$ and $\Delta M_L = \pm 1$ orbital angular momentum properties, respectively.

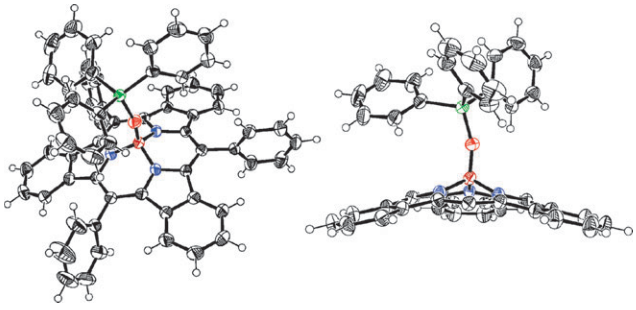

Fig. 1 Crystal structure of **4**, top view (left) and side view (right). The thermal ellipsoids are scaled to the 50% probability level. Phenyl groups at *meso*-positions are omitted for clarity in the side view.

The MCD spectrum (Fig. 2) is similar to the spectra reported previously for standard porphyrins. The positive Faraday *A* terms observed for both Q and Soret bands are consistent with transitions to orbitally degenerate excited states. These results are in marked contrast with those reported for the Soret bands of *meso*-aryl subporphyrins where the sign of the Faraday *A* term varies depending on the nature

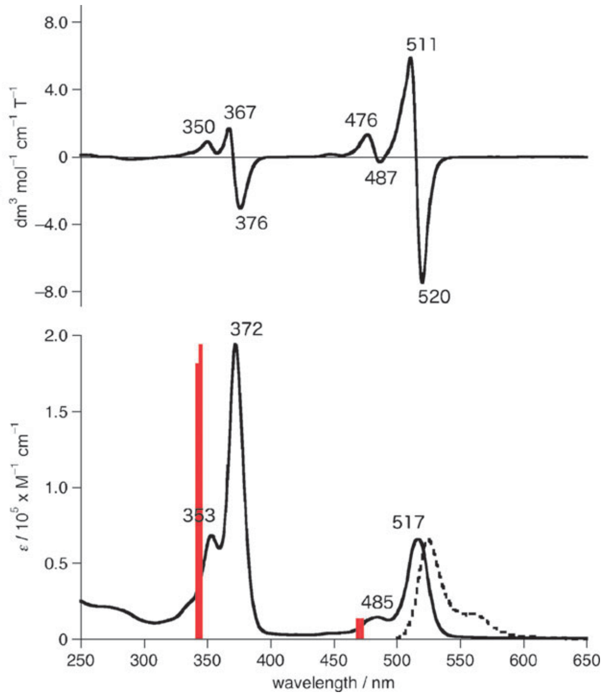

Fig. 2 MCD (top), and electronic absorption (solid line) and fluorescence (dashed line) spectra (bottom) of **2-OH** in CH_2Cl_2 and theoretical (TDDFT) absorption bands (red bars). The fluorescence spectrum was measured upon excitation at 480 nm.

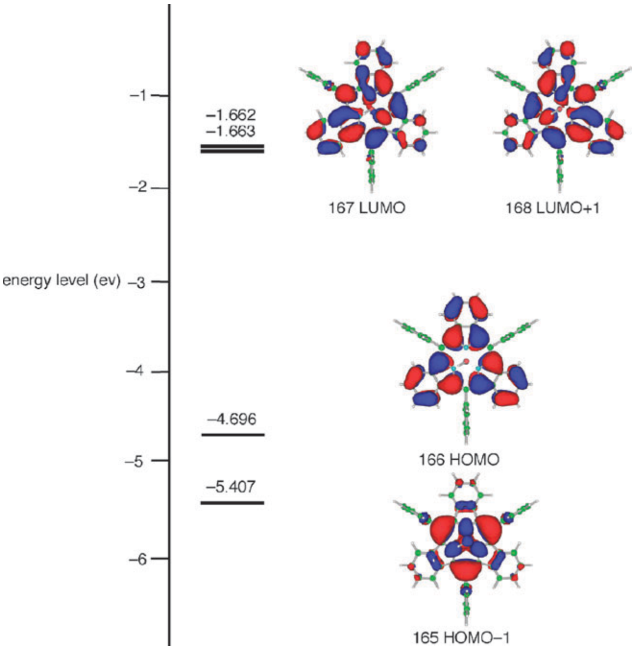

Fig. 3 Calculated frontier MOs and MO energies of **2-OH**.

of the substituents at the *meso*-positions.[3] As would be anticipated based on the orbital angular momentum properties predicted by Gouterman's four-orbital model, the MCD intensity (peak-to-trough) of the Q band is much stronger than that of the Soret band despite the fact that in the UV/Vis absorption spectrum the Q band is weaker than the Soret band.[13]

The cyclic and differential pulse voltammograms of **2-OH** reveal a reversible first oxidation wave at 0.27 V and an irreversible reduction wave at −2.22 V *vs.* ferrocene/ferrocenium. The potential difference of 2.49 V is similar to that reported for *meso*-aryl subporphyrins (*ca.* 2.58 V)[3,4] and tribenzosubporphine,[1] and significantly larger than those reported for normal porphyrins (*ca.* 2.25 V).[14] The electrochemical data for **2** are, therefore, fully consistent with a contraction of the π-conjugation system.

In summary, we have succeeded in synthesizing *meso*-phenyl tribenzosubporphyrin. The triangular and bowl-shaped structure is broadly similar to that of the subphthalocyanines. The optical properties are similar to those of *meso*-aryl subporphyrins and tribenzosubporphine. The two synthetic methods result in yields, which although moderate, are higher than those reported previously for any other subporphyrins. Since the second reaction method can potentially be used to synthesize *meso*-aryl subporphyrins containing a wide range of substituents through the use of substituted phthalimide and phenylacetic acid precursors, it should be possible to tune many of the optical and electronic properties. We are currently carrying out additional experiments to investigate the extent to which the properties can be modified in this manner.

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Notes and references

‡ Crystallographic data for **4**: $C_{64}H_{44}B_1N_3O_1Si_1Cl_2$, $M_W = 980.82$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.127(3)$, $b = 36.058(8)$, $c = 14.055(3)$ Å, $\beta = 101.8532(9)^\circ$, $V = 5023(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.297$ g cm^{-3}, $T = -100$ °C, 35 656 measured reflections, 11 352 unique reflections ($R_{int} = 0.0496$), $R = 0.0861$, w$R = 0.2333$ (all data), GOF = 1.130.

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