The first stable monocyclic phlorin free base. Preparation and X-ray structure determination of 5,21-dihydro-5,10,15,20,22-pentaphenylporphyrin (*N*-phenyl-*meso*-tetraphenylphlorin)

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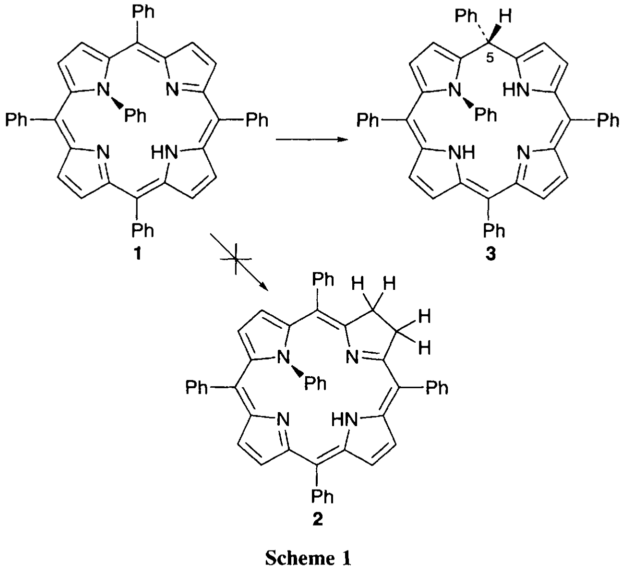
Reduction of *N*-phenyl-*meso*-tetraphenylporphyrin with tosylhydrazine gives air-stable *N*-phenyl-*meso*-tetraphenylphlorin.

Phlorins[1–6] are non-aromatic isomers of chlorins (dihydroporphyrins), the macrocycles present in chlorophyll *a* and related pigments. The additional hydrogen atoms are located at the *meso* and *N*-positions instead of vicinal pyrrolic carbons. The visible chromophore of phlorins is of potential interest as a photosensitizer for biological applications since it shows a strong absorption in the 600–800 nm range. However, phlorins are unstable towards oxidation and transform into the corresponding porphyrins. This process is slowed down by steric hindrance and the only simple phlorin free bases that could be observed bear a *meso* group flanked by two pyrrolic substituents in a peri position, their longest half-life being in the order of days.[3,5] On the other hand, two gold(III) phlorin complexes,[7,8] a series of highly distorted *N,N′*-bridged phlorins,[9] a tetra-*N*-substituted phlorin cation,[10] as well as several dehydrophlorins (isoporphyrins)[11] were found to be stable. Here we report the full structural characterisation of a stable monocyclic phlorin free base unsubstituted at the pyrrolic positions.

The reduction of porphyrins using diimide (from tosylhydrazine and potassium carbonate in refluxing pyridine) gives chlorins, bacteriochlorins, depending on the amount of reducing agent used.[12] While trying to prepare *N*-phenyl-*meso*-tetraphenylchlorin **2** from the corresponding *N*-phenyl-*meso*-tetraphenylporphyrin **1** (*N*-phenylTPP) we observed the rapid and specific formation of an unexpected green pigment **3** instead of chlorin **2** (Scheme 1). Isolation using classical work-up procedures including silica gel chromatography under air, allowed the isolation of dark-green air-stable crystals in good yield (45%, recrystallised). The NMR spectrum of **3** demonstrated the absence of pyrrole reduction as well as the lack of aromaticity of the product: the *N*-phenyl group signals are found between δ 7.1 and 6.9 and not spread at high field as in **1**, pyrrolic protons appear as 8 doublets between δ 6.16 and 6.98 while the *meso* phenyl groups did not show the large splitting typical for porphyrin-like compounds. A singlet at δ 4.34 suggested the presence of a *meso* proton, while a broad signal at δ 8.83 confirmed that the N–H protons did not experience any shielding. The UV–VIS spectrum is dramatically different from the one expected and shows three broad bands at 392, 422 and 686 nm (ε 26 800, 26 900 and 23 200). All spectral data are in good agreement with those of the few known phlorins and structure **3** could reasonably be proposed.

Our structural hypothesis was confirmed by an X-ray diffraction study.† Suitable crystals of the chlorobenzene solvate of **3** were obtained by slow diffusion (7 d) of hexanes into a solution of **3** in chlorobenzene under air. The structure (Figs. 1 and 2) is highly distorted with the *N*-substituted pyrrole almost perpendicular [73.35(1) °] to the plane defined by the N(21)–N(22)–N(24) atoms. This rotation of the *N*-substituted pyrrole is a general trend[13] for mono-*N*-substituted porphyrins and the angles are generally in the 20–40 ° range, except for the *N*-aryl series,[14–16] the maximum being reached for *N*-*o*-tolylTPP[17] (57 °, to be compared with 28 ° for *N*-methylTPP[18]). The conjugation in **3** is interrupted on both sides of the *N*-phenylpyrrole, at the sp^3 C(5) carbon, but also because of the rotation across C(1)–C(20) bond, whose length is closer to that of a single bond (1.454 Å). These large deviations from



Scheme 1

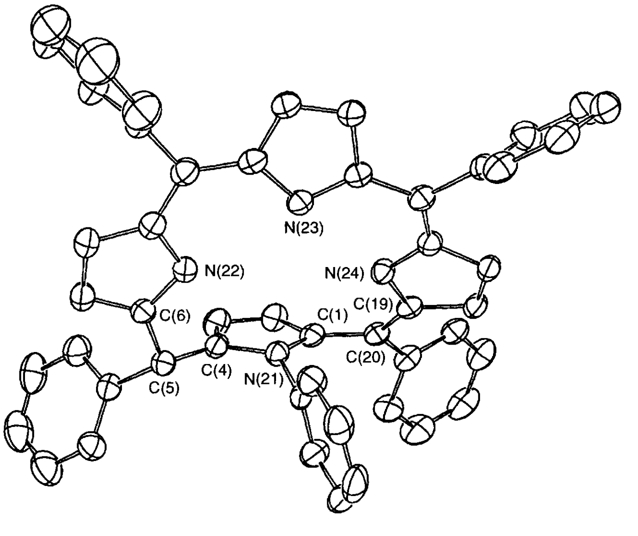


Fig. 1 Molecular structure of **3**. Selected distances (Å) and angles (°): C(1)–C(20) 1.454(4), C(4)–C(5) 1.515(4), C(5)–C(6) 1.514(4), C(19)–C(20) 1.377(4), C(1)–C(20)–C(19) 120.5(3) and C(4)–C(5)–C(6) 112.3(3).

planarity result in a juxtaposition of two independent units: an isolated *N*-phenylpyrrole and a fully unsaturated tripyrrene fragment, the NH groups being located on both lateral pyrroles.

The formation of **3** was rapid and stoichiometric. In addition, we found that both the base (K_2CO_3) and the basic solvent (pyridine) could be omitted and that the reaction proceeded in good yield by refluxing **1** and tosylhydrazine (2 equiv.) in toluene. These data strongly suggest an alternative reaction pathway. The determining factor for the phlorin formation must be the steric crowding induced by the *N*-phenyl group as illustrated by X-ray structural data.[14–17] Addition of tosylhydrazine on a *meso* carbon may release these interactions, but also trigger an intramolecular elimination of sulfinate, a pyrrolic nitrogen atom acting as a base, followed by loss of molecular nitrogen. That the *N*-phenyl–porphyrin interaction is the determining factor was demonstrated by the fact that *N*-methylTPP was slowly reduced to the chlorin and not to the corresponding phlorin.

The zinc complex of *N*-phenylTPP also reacted in an unexpected manner with tosylhydrazine–K_2CO_3 in pyridine. Instead of a reduced product, ZnTPP was isolated in good yield (63%), although the phenyl substituent is considered to be by far the most difficult to cleave from the pyrrolic nitrogen, as compared to alkyl and benzyl groups.[15] Analysis of the reaction mixture by mass spectrometry and ^{1}H NMR allowed the detection of a mixture of phenylpyridines (2-Ph > 3-Ph and 4-Ph) suggesting the thermal homolysis of the *N*-phenyl bond, followed by trapping of the phenyl radical by pyridine.[19] The starting material was stable in boiling pyridine in the presence of K_2CO_3 and the homolysis only occurred upon addition of tosylhydrazine, indicating that a reduced product–possibly a phlorin–suffers the cleavage.

Phlorin **3** is not air sensitive. However, metallation with zinc (zinc acetate in $CHCl_3$–MeOH) did not produce the corresponding metal complex but dehydrogenation took place and the zinc complex of *N*-phenylTPP was isolated in almost quantitative yield. It is likely that the flattening of the phlorin induced by metal coordination favours the restoration of a fully conjugated porphyrin π system. Also acid treatment (aqueous HCl added to a solution of **3** in CH_2Cl_2) was accompanied by aromatisation to the protonated form of *N*-phenylTPP (80%).

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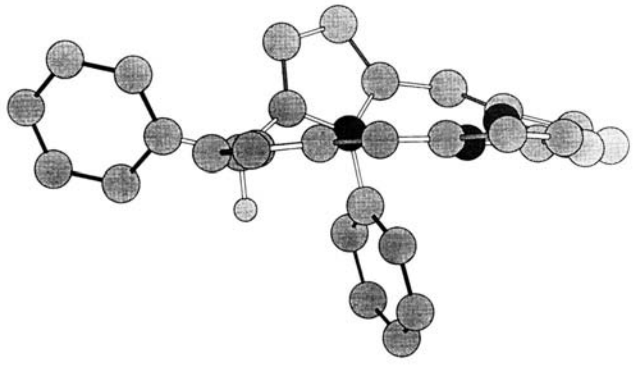

Fig. 2 Side-view of **3** [*meso* phenyl groups at C(5), C(10) and C(20) omitted]. Note hydrogen atom at C(5) and *N*-phenyl group in pseudo-axial and parallel orientation.

Footnote

† *Crystal data* for **3**: $C_{54}H_{36}N_4{\cdot}C_6H_5Cl$, $M = 853.5$, triclinic, space group $P\bar{1}$; $a = 10.977(3)$, $b = 14.688(4)$, $c = 14.866(4)$ Å, $\alpha = 66.02(2)$, $\beta = 80.39(2)$, $\gamma = 87.42(2)°$, $V = 2158.7$ Å^3, $Z = 2$, $D_c = 1.313$ g cm^{-3}. A total of 9240 $\pm h \pm k + l$ reflections was collected on a dark-green crystal of dimensions 0.35 × 0.30 × 0.25 mm^3, using a Nonius CAD4-F diffractometer, graphite monochromated Mo-Kα ($\lambda = 0.7107$ Å), $\mu = 1.320$ cm^{-1}, $2° < \theta < 26°$, room temperature. 3262 unique reflections having $I > 3\sigma(I)$ were used to determine (direct methods) and refine the structure (refinements against $|F|$). Hydrogen atoms were introduced as fixed contributors, C–H = 0.95 Å, B(H) = 1.3*Beqv(C) Å^2. 550 parameters. Final results: R(F) = 0.046, R_w(F) = 0.062, GOF = 1.197, maximum residual electronic density = 0.04 e Å^{-3}. For all computations the Enraf-Nonius MolEN (C.K. Fair in MolEN. 'An Interactive Intelligent System for Crystal Structure Analysis', Nonius, Delft, The Netherlands, 1990) package was used running on a DEC Alpha3600S computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/77.

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