

STERICALLY CROWDED PORPHYRINS: MESO-TETRAPHENYL-OCTAETHYLPORPHYRIN

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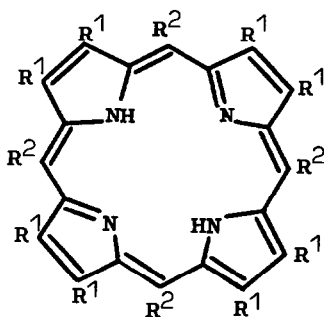
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Early¹ and more recent^{2,3} publications have discussed the effects of steric constraints upon the chemical properties of porphyrins, chlorins, phlorins, and porphyrinogens. In particular, porphyrinogens formally derived from sterically crowded porphyrins have been shown³ to be exceptionally stable towards dehydrogenation. Both octaethylporphyrin (1) and meso-tetraphenylporphyrin (2) have been widely used⁴ as models in the porphyrin series; in this Letter we describe the synthesis and some anomalous properties of the hybrid, meso-tetraphenyl-octaethylporphyrin (3).⁵



(1) $R^1 = Et$; $R^2 = H$

(2) $R^1 = H$; $R^2 = Ph$

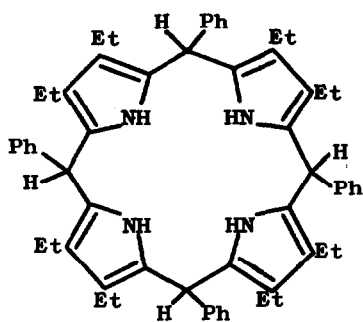
(3) $R^1 = Et$; $R^2 = Ph$

Treatment of 3,4-diethylpyrrole with benzaldehyde in refluxing propionic acid during 30 min gave a low yield (approx. 10%) of the porphyrin

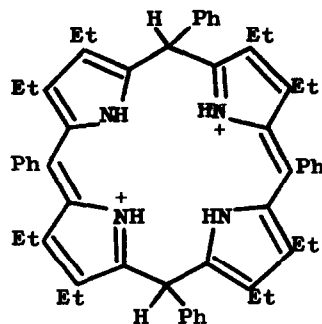
(3). Considerable steric crowding in (3) was indicated by the NMR spectrum (which showed large upfield shifts of the resonances from the ethyl side-chains owing to the enforced proximity of these substituents to the shielding effect of the phenyl rings), and by the enhanced basicity of the porphyrin, which can be transformed into the dication merely by washing with water. It is known⁶ that the dication of meso-tetraphenylporphyrin (2) is extensively puckered, and in the more extreme case of porphyrin (3) this type of distortion would be expected to relieve steric crowding.

During the course of the propionic acid reaction a white solid crystallised from solution and this was shown to be the porphyrinogen (4) (cf. Ref. 5). A higher yield of (4) was obtained by condensation of 3,4-diethylpyrrole with benzaldehyde in benzene containing a catalytic quantity of trifluoroacetic acid. Oxidation of the porphyrinogen (4) with iodine gave initially the porphodimethene (5) (λ_{max} 520 nm) which was smoothly transformed into the chlorin (6) without intermediacy of the porphyrin (3). On the other hand, treatment of the porphyrinogen (4) with 2,3-dichloro-5,6-dicyanobenzoquinone gave a high yield of the chlorin (6) at such a rate that even intermediacy of the porphodimethene (5) could not be observed. Thus, these oxidising agents do not have a sufficiently high potential to accomplish dehydrogenation of these highly crowded intermediates (5) and (6) to give porphyrin (3). Similar rearrangements of metal complexes of porphodimethenes to give chlorins have been reported by other workers,⁷ and this is one possible source of the chlorin impurity obtained⁸ in the synthesis of meso-tetraphenylporphyrin (2) from pyrrole and benzaldehyde. In contrast, photo-oxidation of the porphodimethene (5) in acetic acid gave directly the porphyrin (3) without intermediacy of the chlorin, and this confirms the observations of Dolphin⁵ who has proposed that the chlorin by-product in (2) is derived by reduction of the porphyrin.

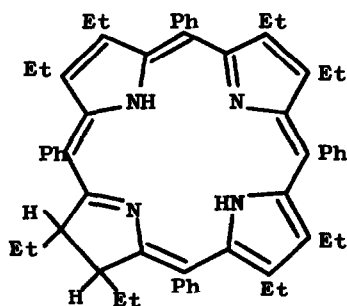
Treatment of 3,4-diethylpyrrole with benzaldehyde in refluxing propionic acid for extended time periods resulted in reduced yields of the porphyrin (3) with a concomitant increase in the yield of chlorin (6), presumably by reduction of the initially formed porphyrin.⁹ After a total reaction time of 4 hours only the chlorin was isolated.



(4)



(5)



(6)

Unlike meso-tetraphenylporphyrin (2), the sterically crowded porphyrin (3) did not rapidly form a zinc complex when treated in CH_2Cl_2 with zinc(II) acetate in methanol; heating was required before spectrophotometric evidence of complexation was apparent. As yet, attempts to prepare a stable zinc(II) complex of the chlorin (6) have been unsuccessful.

We anticipate that an X-ray investigation of the zinc(II) complex from compound (3), which is in hand, will provide more quantitative evidence of the steric crowding in the title compound.

(3) : M.p. 280-282°. (Found: C, 84.87, 84.87; H, 7.43, 7.44; N, 6.62, 6.92. $\text{C}_{60}\text{H}_{62}\text{N}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires: C, 84.96; H, 7.49; N, 6.61%). λ_{max} (CHCl_3 + 0.5% NEt_3) 452 (ϵ 173,800), 547 (12,200), 588 (7300), 625 (5000), and 693 nm (4100); in CHCl_3 + 0.5% TFA, 469 (ϵ 255,900), 630 (10,500), and

685 nm (29,500). NMR (CDCl_3) τ , 1.7-1.85 (8H,m), 2.38-2.5 (12H,m), 7.4-7.8 (8H,m), 7.9-8.35 (8H,m), 9.5-9.75 (t,br 24H). MS, 838 (100%).

(Zinc complex: Found: C, 79.00; H, 6.75; N, 6.20; Zn, 7.39. $\text{C}_{60}\text{H}_{60}\text{N}_4\text{Zn} \cdot \frac{1}{2}\text{H}_2\text{O}$ requires: C, 79.05; H, 6.75; N, 6.15; Zn, 7.17%).

(4) : M.p. Dec. \gg 250°. (Found: C, 85.72; H, 8.13; N, 6.66. $\text{C}_{60}\text{H}_{68}\text{N}_4$ requires: C, 85.55; H, 8.11; N, 6.63%). NMR (CDCl_3) τ , 2.8-3.2 (20H,m), 3.35 (1H,s), 3.53 (2H,s), 3.70 (1H,s), 4.61 (4H,s), 7.55 (4H,q), 7.75 (12H,m), 9.02 (6H,t), 9.12 (18H, t br). MS 844 (100%).

(6) : M.p. $>$ 300°. (Found: C, 76.51; H, 6.91; N, 6.11. $\text{C}_{60}\text{H}_{64}\text{N}_4 \cdot \text{CHCl}_3$ requires: C, 76.27; H, 6.82; N, 5.83%). λ_{max} (CHCl_3 + 0.5% NEt_3), 453 (ϵ 143,900), 618 (6000), and 677 nm (9900); in CHCl_3 + 0.5% TFA: 467 (ϵ 272,700), 622 (9000), and 674 nm (29,400). NMR (CDCl_3) τ , 1.5-1.65 (8H,m), 2.2-2.4 (12H,m), 7.5-8.4 (18H,m), 10.2-10.6 (24H,m). MS 840 (100%).

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- 9 Both the porphyrin (3) and chlorin (6) were stable under these conditions in pure refluxing propionic acid.