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Condensation of Tetraaldehydes with Pyrrole. Direct Synthesis of "Capped" Porphyrins

Sir:

In order to develop simple methods for the synthesis of sterically hindered macrocycles, we have examined the direct condensation of suitable tetraaldehydes with pyrrole, as a route to "capped" porphyrins.[1] We report here the results of these experiments which lead to a method for the synthesis of sterically hindered porphyrins without the need for chromatographic separation of isomers.[2] The strategy behind our approach is exemplified in Figure 1; thus a suitable tetraaldehyde could condense with four molecules of pyrrole, **1**, to provide, in one step, only *one* possible stereoisomer of the tetrameso-substituted porphyrin **2**.

A suitable tetraaldehyde **3** was prepared by alkylation of salicylaldehyde with bromoethanol in aqueous alkali to yield (70%) hydroxyethyl ether **4**,[3] mp 37°, which on acylation with pyromellitoyl chloride in tetrahydrofuran–triethylamine gave the aldehyde **3**: mp 113–114° (30%), ν_{max} ($CHCl_3$) 1690, 1735 cm^{-1}; nmr ($CDCl_3$) δ 4.39 (8 H, m),

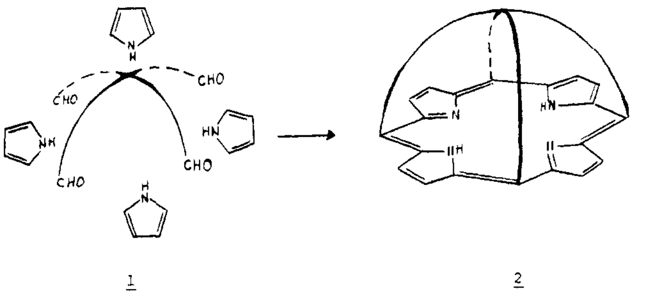
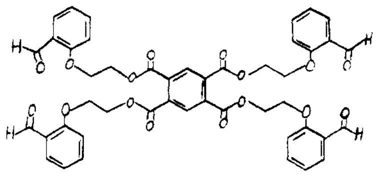


Figure 1.



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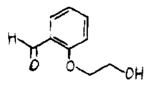

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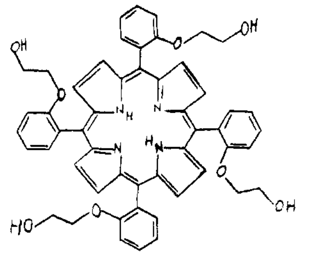

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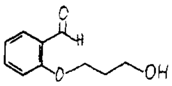

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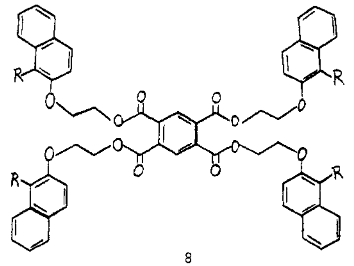

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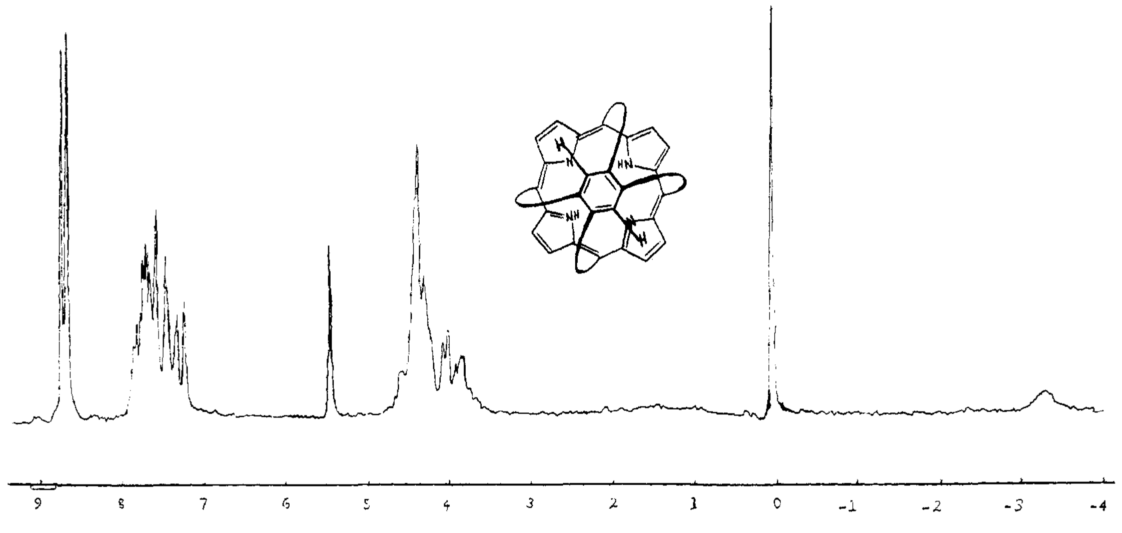
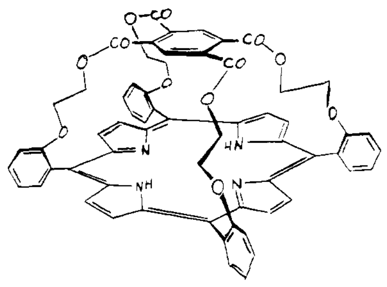


Figure 2.

4.74 (8 H, m), 7.05 (8 H, m), 7.31-7.91 (8 H, m), 8.03 (2 H, s), 10.47 (4 H, s). Condensation of **3** with pyrrole (1 equiv) for 1.5 hr in propionic acid at reflux[4] gave a black mixture. After filtration from a black granular polymer the chloroform solubles were chromatographed on silica gel. The resultant crude porphyrin was treated with dichlorodicyanobenzoquinone in methylene chloride-benzene to oxidize traces of chlorin.[5] A single chromatography over silica gel gave pure porphyrin, **5**, as lustrous violet crystals, recrystallized from methylene chloride-methanol (2%, based on aldehyde **3**).

The structure assigned to **5** is based on its constitution (*Anal.* Calcd: C, 71.5; H, 4.47; N, 5.6; mol wt, 1036. Found: C, 71.8; H, 4.25; N, 5.4; mol wt (osmometric) 985, $C_{62}H_{44}N_4O_{12}$.) and spectral properties: ν_{max} ($CHCl_3$) 3450, 1740 cm^{-1}; λ_{max} ($CHCl_3$) 422 nm (305,000), 517 (15,800), 548 (4200), 591 (5000), 647 (2100); nmr ($CDCl_3$) (Fig. 2) NH, δ −3.32 (2 H), aliphatic 3.65-4.71 (16 H, m), aromatic 7.68-7.91 (16 H, m) and a sharp singlet at δ 5.41 (2 H) which we attributed to the two protons on the "capping" benzene ring, shifted upfield (relative to **3**) by the diamagnetic anisotropy of the suspended porphyrin. Furthermore the C_2 symmetry implicit in structure **5** was clearly indicated by the pyrrole resonances of **5** which appear as a sharp doublet centered at δ 8.70 (8 H). The same compound **5** could be obtained from the isomeric mixture of porphyrins **6**[6] by esterification with pyromellitoyl chloride in boiling phenol in 15% yield, based on **6**. However, the difficulty in obtaining **6** renders the first method the preferred one. Attempts to condense the homologous aldehyde, derived from the ether **7**, with pyrrole in propionic acid were unsuccessful.



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Even more hindered porphyrins are available by the tetraaldehyde approach. Thus when tetraether **8** (R = H)[7] was formylated by the Vilsmeier procedure, aldehyde **8** (R = CHO) was produced in 70% yield. Condensation with pyrrole in propionic acid over 10 hr, followed by the above work-up, gave the naphthalene analog of **5** (0.4%, based on **8** (R = CHO)), the lower yield reflecting the increased hindrance in the precursor.

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References and Notes

(1) A multistep synthesis of a cyclophane porphyrin has been described in a preliminary communication; *cf.* H. Diekmann, C. K. Chang, and T. G. Traylor, *J. Amer. Chem. Soc.*, **93**, 4068 (1971).
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(7) This compound was readily obtained (73%) by condensation of β-naphthol with ethylene oxide.

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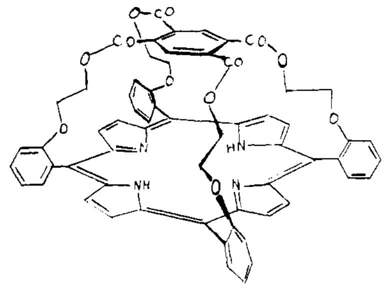
Reversible Oxygenation and Autoxidation of a "Capped" Porphyrin Iron(II) Complex

Sir:

Recently we reported that steric inhibition of an irreversible bimolecular process between an iron(II) dioxygen complex and an iron(II) species, eq 1, enabled observation of reversible oxygen binding in a solution of a ferrous octaazamacrocycle at low temperatures.[1] Similar low temperature behavior was observed for unhindered iron(II) porphyrins,[2,3] whereas a sterically hindered, so-called "picket fence" porphyrin bound oxygen reversibly at room temperature and gave a crystalline complex.[4] In an accompanying report[5] we describe a method for the direct formation of "capped" porphyrins and here we describe its conversion to an iron(II) complex and its reaction with oxygen.

$$\mathrm{Fe^{II}(O_2) + Fe(II) \longrightarrow Fe(III)} \qquad (1)$$

Reaction of porphyrin **1**[5] with anhydrous ferrous chloride in tetrahydrofuran under nitrogen provided a good yield (95%) of crystalline ferric porphine chloride, λ_{max} ($CHCl_3$) 513 nm,[6] μ 5.98 *M*.[7] Following the procedure of Collman[8] this iron(III) complex was reduced with chromous bis(acetylacetonate) in benzene to the crystalline ferrous porphine, represented schematically as **2:** λ_{max} (benzene) 420, 447, 537 nm; (pyridine) 535, 565 nm; μ 4.10 BM. Exposure of a pyridine solution of **2** to oxygen at 25° was accompanied by an immediate change in the spectrum, to λ_{max} 434, 545, and 580 nm.[10] Deaeration by freeze-thawing restored the spectrum of the ferrous complex, Figure 1. Hardly any deterioration of the complex was observed, even after several such cycles; the lifetime of the dioxygen adduct **4** in pyridine being *ca.* 20 hr. After this time only the spectrum of an iron(III) species can be observed. Similarly, benzene solutions of **2,** containing 5% 1-methylimidazole showed identical reversible spectral behavior at 25°, but the lifetime of the dioxygen adduct decreased to 5 hr. The crystalline product of autoxidation in both solvents was the μ-oxo dimer **5:** λ_{max} (pyridine) 424, 575; (benzene) 424, 580 nm.[11] At



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