cursor: 28% overall yield from commercially available 1.5hexadivne (3) and 40% from 2-methylcyclopent-2-enone (1). In addition, the reported scheme should allow for considerable variation of the structure of the final product. We have previously demonstrated the extensive electrophilic substitution chemistry of o-bis(trimethylsilyl)arenes<sup>2,11</sup> as well as the scope of the  $A \rightarrow B$  transformation (Scheme I). Easy access to a variety of steroids of the type 11 can thus be envisaged, in particular the unknown 7-azaestratriene derivatives, incorporating the tetrahydroisoquinoline moiety into the steroid nucleus, the unknown C norsteroids, and the synthetically useful 11-hydroxy<sup>12</sup> and A-ring aza analogues.<sup>13</sup>

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- iytical characteristics. ) **2**: colorless liquid; bp 48 °C (2.6 mm); *m/e* (rel intensity) 196 (M<sup>+</sup>, 22), 73 (Me<sub>3</sub>Si, 100); NMR (60 MHz) (CCl<sub>4</sub>) δ 0.22 (s, 9 H) 1.47 (br s, 3 H), 1.4–2.5 (m, 4H), 3.00 (m, 1 H), 4.93 (dd, *J* = 9, 2.5 Hz, 1 H), 5.00 (dd, *J* = 17.5, 2.5 Hz, 1 H), 5.70 (overlapping (5 lines) ddd, *J* = 17.5, 10, 9 Hz, 1 H). 5: colorless liquid; bp 92 °C (6 mm); *m/e* (rel intensity) 232 (M<sup>+</sup>, 0.3), 77 (100); NMR (60 MHz) (CCl<sub>4</sub>) δ 1.9–3.1 (m, 5 H), 2.33 (t, *J* = 2.5 Hz, 1 H), 3.28 (dt, *J* = 6, 1 Hz, 2 H); IR (neat)  $\nu_{C=CH}$  3310, 2145 cm<sup>-1</sup>. 6: colorless oil; *m/e* (rel intensity) 228 (M<sup>+</sup>, 0.2), 124 (100); NMR (60 MHz) (CCl<sub>4</sub>) δ 0.85, 1.03 (2s, 3 H), 1.2–2.8 (m, 14 H), 5.13 (dd, *J* = 16, 2.5 Hz, 1 H), 5.14 (dd, *J* = 10, 2.5 Hz, 1 H), 5.00 (m, 1 H); IR (neat)  $\nu_{C=CH}$  1740 cm<sup>-1</sup>. 7: colorless crystals; mp 155–157 °C; *m/e* (rel intensity) 309 (M<sup>+</sup>, 25), 383 (44), 73 (100); NMR (60 MHz) (CCl<sub>4</sub>)  $\delta$  0.37 (s, 18 H), 0.93 (s, 3 H), 1.0–3.0 (m, 15 H), 7.27 (br s, 1 H), 7.52 (br s, 1 H); IR (neat)  $\nu_{C=CH}$ (6)
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## strati-Bisporphyrins. A Novel Cyclophane System

## Sir:

The primary electron donor in bacterial photosynthesis is a dimer of bacteriochlorophyll molecules. The evidence for this assertion comes from ESR and ENDOR measurements on the cation resulting from the initial photoact.<sup>1</sup> Similar electron delocalization is known to occur in the radical-ion species of cyclophanes, triptycenes, and other intimate ring systems.<sup>2</sup> This delocalization is strongly dependent on the geometry of these multiring compounds. Linear and loosely stacked dimers of porphyrins have been synthesized,<sup>3,4</sup> but the ring-ring interactions appear to be minimal. In the cases of chlorophyll dimers held together by hydrogen-bonding nucleophiles and urea-linked binary prophyrins, substantial spectral alterations have been observed.<sup>5,6</sup> To evaluate the influence of distance and orientation parameters on the electron-transfer phenomena, we have begun the synthesis of well-defined dimeric systems in which transannular interactions can be observed. Recently, we reported the first member of a new class of macrocyclic cyclophanes, tetra-meso-[p,p'-(2-phenoxyethoxycar-bonylphenyl)]-strati-bisporphyrin, III.<sup>7,8</sup> Now we present theproof of structure and some interesting spectral properties of this compound.

strati-Bisporphyrin III was synthesized by application of the tetraaldehyde modification<sup>9</sup> of the Adler-Longo porphyrin condensation procedure.<sup>10</sup> A suitable porphyrin tetraaldehyde, II, was derived from a porphyrin tetrahydroxide, I, by acylation with *p*-chlorocarbonylbenzaldehyde (Figure 1).

Tetra-meso-[p-(2-hydroxyethoxy)phenyl] porphyrin, I, was made by the reaction of pyrrole with p-2-hydroxyethoxybenzaldehyde<sup>11</sup> in refluxing acidified xylene (8 mM in trifluoroacetic acid).<sup>12</sup> The xylene precipitate was recrystallized from dimethylformamide yielding 14% I: mp >330 °C;  $\nu_{max}$  (KBr) 1240, 1605 cm<sup>-1</sup>;  $\lambda_{max}$  (pyridine) 426 nm ( $\epsilon$  471 000, 14-nm half-width), 521 (16 500), 558 (13 000), 595 (5090), 653 (7500).<sup>13</sup> Anal. Calcd for C<sub>52</sub>H<sub>46</sub>N<sub>4</sub>O<sub>8</sub> (mol wt 854.9): C, 73.05; H, 5.42; N, 6.55; Found: C, 72.80; H, 5.36; N, 6.54. I was reacted with the thionyl chloride generated acid chloride of p-carboxybenzaldehyde in methylene chloride-pyridinediisopropylethylamine (DIEA) (50:25:2). At completion, the solution was neutralized with aqueous base and the products were extracted into chloroform, concentrated, and precipitated with methanol. The precipitate was chromatographed with chloroform on deactivated alumina<sup>14</sup> and the first band was collected. Crystallization from CHCl3-MeOH resulted in 40% yield of tetraaldehyde II: mp 225-228 °C; v<sub>max</sub> (KBr) 1240, 1275, 1605, 1705, 1725 cm<sup>-1</sup>;  $\lambda_{max}$  (pyridine) 425 nm ( $\epsilon$ 464 000, 14-nm half-width), 519 (17 400), 556 (12 700), 593 (5330), 651 (7170);<sup>13</sup> FT NMR (220 MHz, 1 mM in  $CDCl_3$ )<sup>15</sup>  $\delta$  NH at -2.77 (2 H, s), CH<sub>2</sub>O at 4.61 (8 H, t, J = 4 Hz),  $CO_2CH_2$  at 4.89 (8 H, t, J = 4 Hz),  $C_6H_4O$  at 7.31 (8 H, d, J = 8 Hz), 8.12 (8 H, d, J = 8 Hz), C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub> at 7.99 (8 H, d, J = 8 Hz), 8.32 (8 H, d, J = 8 Hz),  $\beta$ -pyrrole H at 8.83 (8 H, s), CHO at 10.11 ppm (4 H, s). Anal. Calcd for C<sub>84</sub>H<sub>62</sub>N<sub>4</sub>O<sub>16</sub> (mol wt 1383.4): C, 72.93; H, 4.52; N, 4.05. Found: C, 71.72; H, 4.36; N, 4.05.16a

strati-Bisporphyrin III was made by the addition of II and pyrrole (4 equiv) to refluxing propionic acid-ethylbenzene (1:1) (0.4 mM in II). After 1.5 h, the solvent was removed by evaporation and the pyridine-soluble products were collected and fractionated on a Bio-Beads S-X1 exclusion gel.<sup>17</sup> After a long, diminishing band of polymeric porphyrins (R 0.5-1.0), III eluted as a narrow, isolated purple band (R 0.45) followed by a faint yellow band of pyrrole by-products.<sup>18</sup> This elution pattern is consistent with III being a compact, stacked dimer. On this same column the more extended and solvated porphyrins I and II migrated with Rs of 0.61 and 0.67, respectively, while unsubstituted tetraphenylporphyrin eluted at R



Tetra-meso-[p,p'-(2-phenoxyethoxy carbonyl phenyl)] strati-bis porphyrin



Figure 1. Synthetic scheme showing most probably  $H_4$ -dimer tautomer of III ( $C_{100}H_{68}N_8O_{12}$ , mol wt 1573.6) and proof of structure by acid hydrolysis.

0.44. Yields of III up to 6% in propionic acid and to 8% in propionic acid-ethylbenzene have been obtained.<sup>16b</sup>

Classical proof of structure III was obtained by identification of the products of acid hydrolysis.<sup>19,20</sup> Hydrolysis of III resulted in two distinct porphyrins, I and the de novo tetra*meso-[p-carboxyphenyl]*porphyrin, IV, in a molar ratio of 1.05  $\pm$  0.09. IV was unique to the dimer and was not obtained from any of the other fractions. Hydrolysates of the polymeric porphyrin fractions or II yielded the tetrahydroxide I as the sole porphyrin product. The equimolar presence of IV with I in the hydrolysis of III can be attributed only to the successful self-condensation of II with pyrrole to form a strati-bis structure.



Figure 2. Absorption spectra of III ( $1.0 \mu M$ ,  $25.0 \mu M$ ), T(p-OCH<sub>3</sub>)PP<sup>†</sup> (<sup>†</sup>, contains trace of chlorin<sup>13</sup>) ( $1.6 \mu M$ ,  $40.8 \mu M$ ), and T(p-CO<sub>2</sub>CH<sub>3</sub>)PP ( $1.7 \mu M$ ,  $42.2 \mu M$ ) in CH<sub>2</sub>Cl<sub>2</sub> and DIEA (0.1% v/v) and the uncorrected emission spectra of equally absorbant solutions at 420 nm of III and T(p-OCH<sub>3</sub>)PP:T(p-CO<sub>2</sub>CH<sub>3</sub>)PP (1:1) excited at 420 nm. III was homogeneous by excitation-emission spectral analysis.

The IR spectrum of III was similar to that of II except for the loss of the 1705-cm<sup>-1</sup> formyl carbonyl stretching frequency. The NMR spectrum was marred by extraneous peaks between 0.5 and 1.5 ppm due to impurities as well as by line broadening. Despite these imperfections, the NMR of III supported the proposed structure because (a) all resonances in the region above 2 ppm were assignable and suitably proportioned, (b) the  $A_2B_2$  degeneracies of the phenoxy and the benzoyl ring protons were broken into AA'BB' quadruplets due to distinguishable interior and exterior facing protons, and (c) the alkyl protons appeared as a nondegenerate AA'BB' multiplet due to restricted rotation about the O-C-C-O bonds.<sup>21</sup>

Both the absorption and the emission of III showed evidence of interaction between the component porphyrins:  $\lambda_{max}$  (pyridine) 426 nm (\$\epsilon 559 000, 18-nm half-width), 523 (19 600), 562 (sh), 584 (18 000), 677 (8650)<sup>20</sup> (Figure 2). The Soret band was significantly broadened (40% increased half-width) but was unmoved, while the visible absorptions were both broadened and red shifted ( $500 \text{ cm}^{-1}$  for the red-most band). The fluorescence intensity also was red shifted (660-cm<sup>-1</sup> peak shift) and broadened, but its quantum yield was relatively the same as those of its monomeric components.<sup>22</sup> The zinc chelate  $(\lambda_{max} (CH_2Cl_2) 422 \text{ nm} (\epsilon 750 000, 19-nm half-width), 562$ (30 900), 606 (18 500))<sup>20</sup> (Figure 3) showed an unmoved but broadened Soret (60% increased half-width) and fully shifted visible bands. Its emission was greatly broadened and quenched by 50%.<sup>23</sup> Both III and its zinc chelate showed unusual low energy absorption shoulders to the red of the Soret rather than the usual high energy shoulders seen in monomeric porphyrins. The absorption properties of III were independent of concentration from 0.1  $\mu$ M to 40.0  $\mu$ M in CH<sub>2</sub>Cl<sub>2</sub> and DIEA (0.1% v/v).

Similar spectral broadening and red shifting of visible bands have been seen upon porphyrin aggregation<sup>24</sup> and complexing with heterocycles.<sup>25</sup> A purely excitonic interaction would have shifted the Soret to the blue and would have affected the visible bands less.<sup>26,27</sup> We believe that the spectra of III and the zinc chelate can best be explained as due to weak incipient charge-transfer interactions.<sup>25</sup> The electron-withdrawing substituents on IV and the electron-donating substituents on I as components of III may enhance this effect.

In summary, we report a synthetic method for the preparation of well-defined, stacked porphyrins and the spectral characteristics of the first such *strati*-bisporphyrin. We an-



Figure 3. Absorption spectra of  $1.2-\mu M$  and  $30.0-\mu M$  solutions of the zinc metalloporphyrins in CH<sub>2</sub>Cl<sub>2</sub> with the baseline offset from zero for clarity. Uncorrected emission spectra of equally absorbant solutions at 420 nm were excited at this wavelength. Homogeneity was verified by excitation-emission spectral analysis.

ticipate that the method will be general and that the correlation of structures with properties will significantly aid the interpretation of in vivo and in vitro porphyrin systems such as the photosynthetic chlorophyll dimers. The effects of systematic changes in ring separation, orientation, donor-acceptor substituents, metal and mixed-metal chelates, and intercalates can now be examined.

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- (16) (a) Low carbon analyses (here 1.2%) occur in large aromatic heterocycles such as big tetraarylporphyrins despite long burning (5'), high temperatures (975 °C), and added catalyst ( $V_2O_5$ ). (b) Yields were determined spectroscopically after hydrolysis (19,20).
- (17) This 1% cross-linked polystyrene support in pyridine was chosen to minimize adsorption of aromatic elutants. Standardization of the system with

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- (20) Extinction coefficients for III and its zinc chelate were deduced from quantitative analysis of hydrolysis products I and IV based on their known es. This procedure was verified by hydrolysis of I, II, T(p-CO2CH3)PP, and  $T(p-CO_2CH_2CH_2OC_6H_5)PP$ . (21) The least strained CPK structures of III require interdigitation of the phenyl
- rings. This gives a slight twist to the molecule and results in a limited otation-barrier chirality.
- Of the several possible H4-dimer tautomers, III (Figure 1) with diagonally (22)staggered inner hydrogens would be most probable. This would lead to minimal interaction of the orthogonal local dipoles.
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# **Detection and Characterization of the** Long-Postulated Fe-OO-Fe Intermediate in the Autoxidation of Ferrous Porphyrins

#### Sir:

Dioxygen bridged diiron complexes have been frequently proposed as important, although unstable, intermediates in the autoxidation of ferrous complexes.<sup>1-3</sup> Such bridged species have also been proposed to represent the oxygenated state of the respiratory pigment, hemerythryn.<sup>4</sup> In the development of strategies for the synthesis of low molecular weight models of myoglobins and hemoglobins, steric protection of the iron site has been deemed useful to prevent autoxidation via an Fe-OO-Fe intermediate.<sup>5-8</sup> Nevertheless, and in contrast to the situation with other metals, notably cobalt,<sup>9,10</sup> no Fe-OO-Fe complex has been unambiguously identified and none of its structural and electronic properties or chemical reactivity characterized. Only a few reports of  $O_2$  uptake with a Fe: $O_2$ ratio of 2:1 have appeared which are suggestive of a Fe-OO-Fe species.<sup>11,12</sup> The proposed form for this bridged species has been variously described as Fe<sup>II</sup>-O<sub>2</sub>-Fe<sup>II</sup> (dioxygen bridge<sup>2,11</sup>) or Fe<sup>111</sup>-OO-Fe<sup>111</sup> (peroxo bridge<sup>2</sup>), while others have anticipated rapid cleavage to two Fe-O monomers.<sup>5</sup> We report here on the <sup>1</sup>H NMR characterization of such a Fe-OO-Fe complex and show that the linkage involves the peroxo bridge.

As an initial step in elucidating the general mechanism of oxidation of ferrous porphyrins, we have investigated the reaction between unligated meso-tetra-(m-tolylporphyrin)iron(II), designated PFe, and molecular oxygen in dry toluene- $d_8$ . The final product is the expected  $\mu$ -oxo dimer, PFeOFeP, and the proposed steps thought to account for the net reaction can be written