If *N*-(2-ammonioethyl)carbamate solutions are stored in open containers or purged with nitrogen, the pH rises. This implies that in aqueous solutions without added acid or base the equilibria (eq 1 and 2) are established. On the

$$H_3^+NCH_2CH_2NHCOO^- \rightleftharpoons CO_2 + H_2NCH_2CH_2NH_2 \quad (1)$$

$$H_2NCH_2CH_2NH_2 + H^+ \rightleftharpoons H_3^+NCH_2CH_2NH_2 \quad (2)$$

basis of the pK values,[7] we may estimate that in the pH range 8–9, at least 90% of the ethylenediamine is protonated. Under these conditions, there is little tendency for the formation of dicarbamate. If the pH is raised sufficiently, however, the zwitterion is deprotonated

$$H_3^+NCH_2CH_2NHCOO^- + OH^- \rightarrow H_2NCH_2CH_2NHCOO^- + H_2O$$

and the reaction to form dicarbamate can occur.

Experimental Section

N-(2-Ammonioethyl)carbamate was prepared by passing CO_2 into a solution of ethylenediamine (Eastman) in anhydrous methanol cooled in an ice bath. The resulting precipitate was filtered and dried in vacuum. Elemental analysis was satisfactory; the X-ray diffraction pattern was that of the orthorhombic polymorph. Dipotassium ethylenedicarbamate was prepared as described by Frank;[5] elemental analysis was satisfactory.

NMR spectra were obtained on either a Varian XL-200 or XL-300 spectrometer, operating at 50.3 or 75.4 MHz, respectively, for ^{13}C. All spectra were measured on samples containing 1.04 g (10 mmol) of the carbamate dissolved in 1.1 mL of 40% KOD in D_2O (Merck) plus 2.8 mL of D_2O (or $D_2O + H_2O$), with 0.1 mL of dioxane added as internal standard. Gated decoupled excitation with 10-s pulse delay, together with the addition of 0.1 M disodium (diethylenetriaminepentaacetato)chromate(III) hexahydrate as a relaxation reagent,[8] was used in attempting to obtain quantitative spectra. While these measures sufficed for quantitation of spectra of reference compounds, base-line resolution was not achieved between the carbamate peaks, and their spectra were therefore only semiquantitative.

Aging experiments without added strong base were performed by dissolving the carbamate in 1.5 mL of aqueous solution in a small screw-cap vial, which was allowed to stand tightly capped at room temperature for the desired period. The contents of the vial were then transferred to an NMR tube containing the rest of the ingredients noted above, and which had been pre-cooled in an ice–salt bath at −20 °C.

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Registry No. 1, 109-58-0; 2, 82357-56-0; ethylenediamine, 107-15-3.

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A Novel Synthesis of Triple-Deckered Triporphyrin

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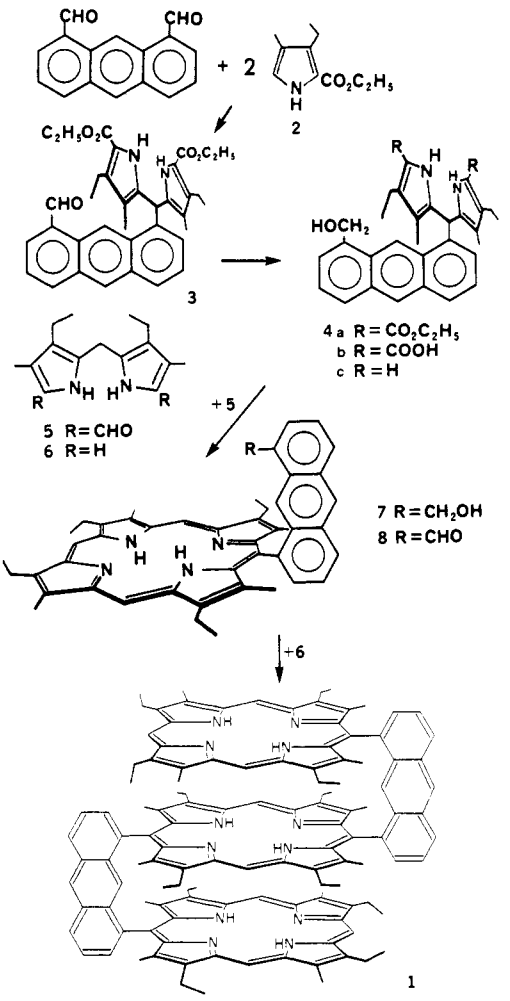
The structure of the primary electron-donor–acceptor complex in reaction centers as well as the molecular events involved in the electron-transport processes remain to be the central questions in photosynthesis. Many attempts have been made to model the light-driven charge separation step using porphyrin and chlorophyll molecules with varying degrees of success.[1-3] A critical element which often is difficult to control in synthetic models is the geometry and distance that separates the donor and acceptor. Furthermore, there has been substantial evidence indicating that the primary donor in the bacterial (also green plant) reaction center may involve dimeric porphyrinoid pigments.[1] Therefore an accurate model system perhaps should contain at least three components, e.g., a chlorophyll dimer in association with a Mg-free pheophytin. Boxer and Buck have indeed linked a difunctionalized chlorophyll to a chlorophyll and a pheophytin via ester groups.[4] Such a linear arrangement was unavoidably too flexible to allow the singly linked trimer to assume any well-defined geometry. Wasielewski et al.[5] more recently synthesized a stacked porphyrin trimer using doubly linked coproporphyrin I and diametrically substituted porphyrin dialcohol. However, because of the C_{2h} symmetry of the porphyrin monomers, the resultant trimer was a mixture of three diasteromers. In order to avoid the shortcomings

Scheme I



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of the earlier models and to improve the efficiency of synthesis, we explored other molecular designs which do not depend on a multistep, linear-sequence strategy.

We have recently reported the utilization of an anthracene molecule as a rigid spacer arm to fix two porphyrins in a well-defined cofacial configuration.[6] This system can be extended for the preparation of triple-layered triporphyrins. As shown in synthetic Scheme I, the key intermediate, (formylanthryl)dipyrrylmethane **3** was obtained in 73% yield by reacting 2 equiv of pyrrole **2** and 1,8-anthracenedicarboxaldehyde. The aldehyde group in **3** had to be converted into a nonreactive form before the dipyrrylmethane could be manipulated further. Thus **3** was reduced to alcohol **4a**, which after saponification and decarboxylation, was cyclized into meso-substituted porphyrin **7** by using a modified MacDonald procedure,[7] with an overall yield around 40%. The aldehyde functional group was then restored by oxidation. The aldehyde–porphyrin **8**, behaving analogously to a substituted benzaldehyde, was allowed to react with equimolar amounts of α,α'-free dipyrrylmethane **6** under mild acid catalysis to yield the triporphyrin **1**. This approach has been used for preparing 5,15-diphenylporphyrins.[8] In principle, atropisomers can result from this reaction, but in the present case, because of the steric bulk, the alternative cis arrangement of the two anthryl groups about the center porphyrin was not possible. Although the conversion yield from **8** to **1** was not high, the unreacted aldehyde **8** could be recovered for recycling.

The NMR spectrum of **1** is shown in Figure 1, along with its immediate precursor **8**. Perhaps the most conspicuous sign of **1** is its three sets of methyl groups standing out as three sharp singlet peaks in the spectrum, two being shifted upfield due to the diamagnetic ring current of anthracene. As well, the sharp signals of meso protons, the expected pattern of the anthryl protons, and the overall cleanliness of the spectrum easily rule out any other possible structures. The cofacial configuration of the porphyrin rings is evidenced by an upfield NMR shift of the pyrrole nitrogen protons and the appearance of a blue shift of the Soret peak in the visible spectrum; both have been documented in previous cofacial diporphyrins.[9,10] The triporphyrin undergoes metalations in a unique manner. In general, metal insertions to the two outer rings occur faster than those to the inner one and the reverse demetalation reactions proceed similarly. Since the TLC R_f value of **1** in different metalation levels vary greatly, separation of patially metalated complexes is possible by chromatography. Identification of complexes can then be accomplished by spectroscopic means. For example, the bis(copper) complex Cu–2H–Cu exhibits an ordinary square-planar Cu(II) EPR spectrum similar to most monomeric Cu porphyrins[11] but a tris(copper) complex has a broad, featureless single envelope in its EPR spectrum. The study of mixed Mg–free base trimer in their photochemically initiated electron-transfer reactions should prove to be very interesting.

Experimental Section

NMR spectra ($CDCl_3$, Me_4Si internal standard) were obtained with a Bruker WM-250 instrument. Mass spectra (direct insertion probe, 70 eV, 200–300 °C) were measured with a Finnigan 4021 GC–MS spectrometer. Elementary analyses were performed by MicAnal. Visible absorption spectra (in CH_2Cl_2) were measure with a Cary 219 spectrophotometer.

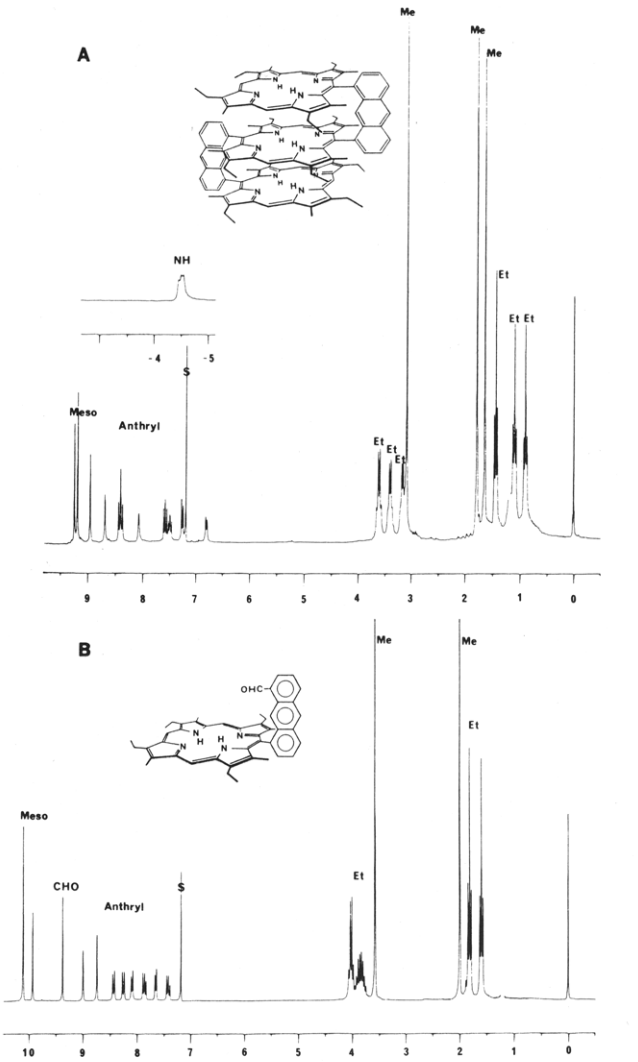

Figure 1. ^1H NMR spectrum (250 MHz) of **1** (A) and **8** (B) in $CDCl_3$.

8-Formyl-1-[[5,5′-bis(ethoxycarbonyl)-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrryl]methyl]anthracene (3). To 1,8-anthracenedicarboxaldehyde[12] (500 mg, 2.1 mmol) suspended in dry ethanol (30 mL) was added concentrated HCl (0.5 mL). The mixture was stirred at room temperature until all dialdehyde dissolved. To this solution was added ethyl 3-ethyl-4-methyl-2-pyrrolecarboxylate[13] (774 mg, 4.27 mmol) in ethanol (10 mL) in three portions over a period of 15 min. After the additions, the solution was allowed to reflux for 30 min under N_2. The dark solution was then cooled in an ice bath and the yellow crystalline solid was collected by filtration (750 mg). The filtrate was concentrated to one-half of the volume and cooled to give a second batch (250 mg) of the dipyrrylmethane. The solids were combined and recrystallized from benzene to give yellow crystals (900 mg, 73%): mp 217–218 °C; MS, m/e 578 (M^+); NMR δ 1.1 (6 H, t, Et), 1.3 (6 H, t, OEt), 2.0 (6 H, s, Me), 2.8 (4 H, q, Et), 4.1 (4 H, q, OEt), 6.5 (1 H, s, methane CH), 7–7.7 (7 H, m, anthryl), 8.2 (1 H, s, 9H-an), 8.4 (2 H, br, NH), 10.1 (1 H, s, CHO). Anal. Calcd for $C_{36}H_{38}N_2O_5$: C, 74.71; H, 6.62; N, 4.84. Found: C, 74.58; H, 6.75; N, 4.46.

8-(Hydroxymethyl)-1-[[5,5′-bis(ethoxycarbonyl)-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrryl]methyl]anthracene (4a). To

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the aldehyde **3** (578 mg, 1.0 mmol) in ethanol (20 mL) was added sodium borohydride (30 mg in 0.1 mL of H_2O), and the mixture was stirred at room temperature for 15 min. A solution of NaOH (6 N, 0.4 mL) was added, and the mixture was heated on a steam bath for 5 min and then poured onto ice. The product was extracted with CH_2Cl_2 (3 × 20 mL) to give a white solid (550 mg): mp 128–130 °C; MS, *m/e* 580 (M^+); NMR δ 1.1 (6 H, t, Et), 1.3 (6 H, t, OEt), 2.0 (6 H, s, Me), 2.8 (4 H, q, Et), 4.1 (4 H, q, OEt), 5.0 (2 H, s, CH_2O), 5.3 (1 H, s, OH), 6.5 (1 H, s, methane CH), 7–7.77 (7 H, m, anthryl), 8.2 (1 H, s, 9H-an), 8.4 (2 H, br, NH). This solid was used in the next step without further purification.

8-(Hydroxymethyl)-1-[[4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrryl]methyl]anthracene (4c). The diester dipyrrylmethane **4a** (500 mg, 0.86 mmol) was saponified by refluxing for 8 h in ethanol (10 mL) containing NaOH (300 mg) and water (1 mL). After the hydrolysate was concentrated to remove ethanol, water (20 mL) was added, and the solution was extracted with CH_2Cl_2 (20 mL). The aqueous layer was kept in an ice bath and neutralized with glacial acetic acid; the precipitated white solid was extracted into ether (3 × 20 mL). The crude diacid, after removal of solvent, was mixed with ethanolamine (3 mL) and heated to a gentle reflux under nitrogen for 1 h. The dark solution was poured into ice water; the resultant light yellow solid was collected by filtration. This material was chromatographed on silica gel (CH_2Cl_2) to give pure α-free dipyrrylmethane **4c** (360 mg): mp 98–100 °C; MS, *m/e* 436 (M^+); NMR δ 1.1 (6 H, t, Et), 2.0 (6 H, s, Me), 2.3 (4 H, q, Et), 5.0 (2 H, s, CH_2O), 5.2 (1 H, s, OH), 6.2 (1 H, s, methane CH), 6.3 (2 H, s, 5,5′-pyrrole), 7–7.77 (7 H, m, anthryl), 8.2 (1 H, s, 9-an), 8.4 (2 H, br, NH).

5-[8-(Hydroxymethyl)-1-anthryl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphine (7). To a solution of the decarboxylated pyrrylmethane **4c** (530 mg, 1.2 mmol) and the (diformyldipyrryl)methane **5**[14] (347 mg, 1.2 mmol) in dry methanol (70 mL) was added 70% perchloric acid (0.5 mL). The dark red solution was stirred for 12 h at room temperature in the dark; after which a solution of NaOAc (0.5 g) in methanol (10 mL) was added, followed by another solution of *o*-chloroanil (200 mg) in methanol (10 mL). After 1 h, the mixture was evaporated; the residue was taken up in CH_2Cl_2 (20 mL) and a solution of zinc acetate (200 mg) in methanol (10 mL) was added. After being stirred for 1 h, the mixture was evaporated and the residue separated by chromatography (silica gel, CH_2Cl_2). The isolated Zn(II) porphyrn was demetalated by washing with 10% HCl in CH_2Cl_2: yield of **7**; 400 mg, 48%; NMR δ −3.0 (2 H, d, NH), 1.7 (6 H, t, Et), 1.9 (6 H, t, Et), 2.1 (6 H, s, Me), 3.7 (6 H, s, Me), 3.8 (2 H, s, CH_2O), 3.9 (4 H, q, Et), 4.1 (4 H, q, Et), 10.0 (1 H, s, meso), 10.3 (2 H, s, meso), anthryl: 7.1 (1 H, d), 7.4 (1 H, t), 7.8 (2 H, m), 8.0 (1 H, d), 8.1 (1 H, d), 8.4 (1 H, d), 8.7 (1 H, s); UV-vis λ_{max} (ϵ_M) 624 nm (2400), 569 (6000), 535 (6500), 502 (13000), 405 (129000). Anal. Calcd for $C_{47}H_{48}N_4O$: C, 82.42; H, 7.06; N, 8.18. Found: C, 82.33; H, 7.15; N, 8.09.

5-(8-Formyl-1-anthryl)-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphine (8). Oxidation of the anthracene alcohol was effected by addition of **7** (280 mg) in pyridine (30 mL) to a solution of CrO_3 (325 mg) in pyridine (20 mL). The mixture was stirred at room temperature for 4 h and then poured into water (100 mL). The product was extracted into CH_2Cl_2 (3 × 50 mL) and purified by chromatography (siica gel, CH_2Cl_2) to give **8** in quantitative yield: NMR δ −3.1 (2 H, d, NH), 1.67 (6 H, t, Et), 1.85 (6 H, t, Et), 2.03 (6 H, s, Me), 3.68 (6 H, s, Me), 3.85 (4 H, q, Et), 4.03 (4 H, q, Et), 9.38 (1 H, s, CHO), 9.91 (1 H, s, meso), 10.15 (1 H, s, meso), anthryl: 7.40 (1 H, t), 7.67 (1 H, d), 7.85 (1 H, t), 8.10 (1 H, d), 8.28 (1 H, d), 8.46 (1 H, d), 8.75 (1 H, s), 9.00 (1 H, s); UV-vis λ_{max} (ϵ_M) 624 nm (2400), 569 (6100), 535 (6600), 502 (13500), 404 (140000).

***trans*-5,15-Bis[8-[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]-1-anthryl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine (1).** To the porphyrin–aldehyde **8** (50 mg, 0.073 mmol) suspended in methanol (10 mL) was added first the α-free dipyrrylmethane **6**[8b] (17.3 mg, 0.073 mmol) and then toluenesulfonic acid (3.4 mg, 0.018 mmol).[8a] The mixture was stirred at room temperature for 10 h before the solvent was pumped dry. The residue was dissolved in THF (10 mL), treated with a solution of *o*-chloranil (10 mg) in THF (5 mL), and stirred for 1 h, and the solvent was removed again by evaporation. This mixture contained a large amount of unreacted **8** which can be recovered during the isolation of trimer **1**. The chromatography was carried out with a silica gel column, using pure CH_2Cl_2 to elute **8** and 5% MeOH–CH_2Cl_2 for **1**. The trimer thus obtained was purified further by converting into and chromatography of the Zn complex, which moves much faster than the free base, to remove impurities of low R_f values. Pure triporphyrin **1** was then derived by demetalation of the zinc complex using 10% HCl: yield, 7 mg; NMR δ −4.5 (6 H, three singlets clustered together, NH, see Figure 1), 0.95 (12 H, t, Et), 1.10 (12 H, t, Et), 1.45 (12 H, t), 1.60 (12 H, s, Me), 1.80 (12 H, s, Me), 3.02 (12 H, s, Me), 3.20 (8 H, q, Et), 3.41 (8 H, q, Et), 3.55 (8 H, q, Et), anthryl: 6.81 (2 H, d), 7.35 (2 H, d), 7.50 (2 H, t), 7.59 (2 H, d), 7.60 (2 H, s), 8.05 (2 H, s), 8.45 (2 H, t), 8.72 (2 H, s), meso: 8.95 (2 H, s), 9.25 (4 H, s), 9.30 (2 H, s); UV-vis λ_{max} (ϵ_M) 625 (3900), 573 (9300), 538 (9300), 506 (18000), 395 (169000). Anal. Calcd for $C_{124}H_{126}N_{12}$: C, 83.46; H, 7.12; N, 9.42. Found: C, 83.75; H, 7.30; N, 9.32. High-resolution positive ion mass spectra of **1** have been obtained on a Kratos MS-50RF equipped with Ionteck FAB gun, operated at 8 kV. The sample was prepared in 1-thioglycerol matrix containing trifluoroacetic acid.[15] Calcd for monoprotonated **1**: 1784.0306. Found: 1784.0140.

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Registry No. **1**, 94347-88-3; **2**, 4949-58-0; **3**, 94324-82-0; **4a**, 94324-83-1; **4b**, 94324-84-2; **4c**, 94324-85-3; **5**, 967-68-0; **6**, 92415-30-0; **7**, 94347-89-4; **7** Zn(II) complex, 94324-87-5; **8**, 94324-86-4; 1,8-anthracenedicarboxaldehyde, 34824-75-4.

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A Spontaneous Sulfoxide Dehydration

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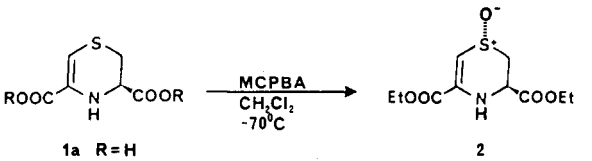
In the course of studies on 3,4-dihydro-2*H*-1,4-thiazine-3,5-dicarboxylic acid (**1a**), diester **1b** was oxidized with 1 equiv of *m*-chloroperbenzoic acid. A proton NMR spectrum of the product before chromatography suggested that predominantly one compound had formed which, when compared with spectra obtained by Kitchin and Stoodley[1] on 3,4-dihydro-1-oxo-2*H*-1,4-thiazine-3,6-dicarboxylates, appeared to be the trans sulfoxide **2**. This stereochemical assignment was supported by an aromatic solvent-induced shift study (see Table I). It has been



1a R=H
1b R=Et

2

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