in the cyclization of **3a**. The starting material (1.19 g, 95%) was recovered unchanged.

Acknowledgment. This research was supported in part by the U.S. Army Research Office through Grant DAAG29-77G-0170.

Synthesis of Porphinedipropionic Acid and Dealkylated Protoporphyrin Analogues

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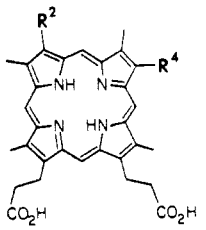
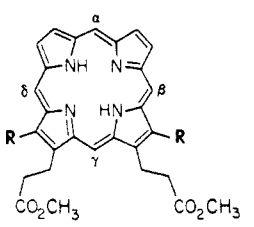
Received June 19, 1981

Hemoproteins, composed of an iron porphyrin active site and the apoprotein, exhibit an amazingly broad spectrum of functions including oxygen transport, electron transport, hydrogen peroxide decomposition, and oxidation of organic substrates. The variation in heme function among hemoproteins depends upon specific interactions between the heme prosthetic group and the apoprotein. An obvious method of probing the heme–protein relationship is to investigate structural modifications in the heme group and to relate these to alterations in the functional properties of hemoproteins reconstituted with these hemes.[2] The heme derivatives studied in previous reconstitution experiments invariably involved those hemes derived directly from protoporphyrin IX (1) with modification of the substituents at position 2 and 4 of the porphyrin ring, i.e., deutero, meso, diacetyl, and formyl derivatives.[3,4] However, the electronic effect and the steric effect of the side chains in such compounds have been altered simultaneously, and this blending of the two effects has made the interpretation of the results very ambiguous. For differentiation of these two effects, more synthetic hemes are required. We have previously prepared a hexamethyl porphyrin **2** and reconstituted the heme into hemoglobin[5] as well as peroxidase.[6] We now report the synthesis of two demethylated analogues **3** and **4**. Hemes of such porphyrins deprived of side chains should have greater freedom inside the protein pocket and therefore would exhibit properties approaching those of an unstrained system.



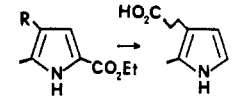
1) $R^2 = R^4$ = vinyl
2) $R^2 = R^4$ = Me



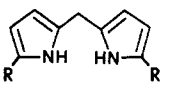
3) R = H
4) R = Me

Porphyrin Synthesis via the *a,c*-Biladiene Routes

The most convenient synthesis for porphyrin **3** is probably the *a,c*-biladiene route, using copper(II) salts for ring closure.[7,8] The required pyrrolepropionic acid **8** was synthesized from pyrrole **5**[9] via the acrylic ester **7**.[10] Condensation of (5,5′-diformyl-2,2′-dipyrryl)methane (**10**), prepared as previously described,[11] and 2 mol of the decarboxylated **9** in 40% HBr in acetic acid afforded a 75% yield of the *a,c*-biladiene dihydrobromide **12**. This tetrapyrrole was cyclized, using copper acetate in pyridine, to give the copper porphyrin, which was demetalated in sulfuric acid and esterified with methanol to give porphyrin **3**. The yield was very low (<2% from **12**) and the main product was an insoluble black powder. Since variations of the cyclization conditions failed to improve the yield, it was decided to try this method on different tetrapyrroles.

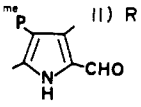


5) R = H
6) R = CHO
7) R = CH=CH$_2$CO$_2$Et
8) R = CH$_2$CH$_2$CO$_2$Et

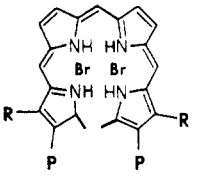


9)

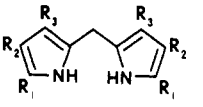
10) R = CHO
11) R = H



14)



12) R = H
13) R = Me



15) R_1 = H R_2 = Me R_3 = Me
16) R_1 = CHO R_2 = Me R_3 = CH$_2$CH$_2$CO$_2$Me
17) R_1 = H R_2 = Me R_3 = CH$_2$CH$_2$CO$_2$H
18) R_1 = CO$_2$Et R_2 = H R_3 = CH$_2$CH$_2$CO$_2$Et
19) R_1 = CO$_2$Et R_2 = H R_3 = Me

Condensation of **11** and 2 mol of **14** in HBr–HOAc afforded 82% of the biladiene **13** dimethyl ester, which was then treated with copper(II) chloride in hot DMF. After demetalation and esterification, porphyrin **4** was obtained again in less than 2% yield. Previously this copper cyclization method has been shown to give satisfactory yields (>20%) of porphyrins from fully substituted tetrapyrroles.[7,8] Indeed, when (3,3′,4,4′-tetramethyl-2,2′-dipyrryl)methane (**15**)[12] was condensed with **14**, subsequent ring closure under identical conditions provided 22% of the hexamethyl porphyrin **2**. It appears, therefore, that the cause of the poor yield is associated with the unsubstituted *a,c*-biladienes.

Porphyrin Synthesis by the MacDonald Procedure

Porphyrins like **3** and **4**, having a C_{2v} symmetry, can be prepared by condensation of two symmetric dipyrrylmethanes (north–south direction) via formyl groups.[13] Thus the condensation of (5,5′-dipyrryl)methane **16**[11] and

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the unsubstituted 2,2′-dipyrrylmethane (11) in acetic acid with hydriodic acid gave porphyrin 4 in 10% yield. A recent report[14] of the condensation of 10 and 17 followed by esterification provided the same porphyrin in about 12% yield. Again, these yields were somewhat lower than usually encountered with this method.[15]

For the synthesis of porphyrin 3, the required 4,4′-unsubstituted dipyrrylmethane 18 is an unknown compound. Normally unsubstituted dipyrrylmethanes are obtained by protection and deprotection via bromo derivatives.[16] However, Clezy[17] has observed that a similar dipyrrylmethane 19 can be obtained by direct self-condensation of 2-acetoxy-3-methyl-5-(ethoxycarbonyl)pyrrole. Therefore, pyrrole 8 was oxidized with lead tetraacetate to give quantitatively the 2-acetoxypyrrole, which was then heated in 70% aqueous acetic acid to afford 18. After hydrolysis and decarboxylation in trifluoroacetic acid, 18 was condensed with 10 in the usual manner to yield the porphyrin.

Porphyrins 3 and 4 have solubilities in organic solvents comparable to that of deuteroporphyrin IX dimethyl ester. Their structures were unambiguously characterized by, among other analyses, NMR spectra; the unique AX pattern of the β protons and the splittings of the meso protons can be clearly discerned in the aromatic region. Both porphyrins exhibit a visible spectrum of the phyllo type (IV > II > III > I). In comparison with hexamethyl porphyrin 2, deuteroporphyrin, and porphine, it seems clear that successive removal of the methyl substituents shifts the strength of the Q(0,0) bands (I,III) to the B(0,0) band (Soret), while the overtone Q(0,1) bands (II,IV) are unaffected. The pK_3 value of 2 and 3 is about 5.4, identical with that of deuteroporphyrin,[18] making them ideal systems for studying steric effects in reconstituted hemoproteins. Ligand-binding studies of myoglobin reconstituted with these hemes will be reported elsewhere.[19]

Experimental Section

Electronic absorption spectra (in methylene chloride) were measured with a Cary 219 spectrophotometer. NMR spectra (in $CDCl_3$, Me_4Si internal standard) were obtained with a Varian T-60 or a Bruker WM-250 instrument. Mass spectra (direct insertion probe, 70 eV, 200–300 °C) were measured with a Finnigan 4021 GC–MS. Elemental analyses were performed by Spang; C, H, N analyses were within ±0.4%.

5-(Ethoxycarbonyl)-3-formyl-2-methylpyrrole (6). This pyrrole has been prepared from 5-(ethoxycarbonyl)-2-methylpyrrole by the Gatterman method using hydrogen cyanide.[20] In the present study, the pyrrole was formylated via the Vilsmeier–Haack procedure. (The modified procedure of Clezy using benzoyl chloride/DMF[11] failed to give satisfactory results.)

5-(Ethoxycarbonyl)-2-methylpyrrole (15.3 g, 0.1 mol) obtained according to a more modern synthesis[9] was dissolved in dimethylformamide (100 mL) and treated at 0 °C with phosphorus oxychloride (4.5 mL) and the mixture was heated on a steam bath for 20 min. The mixture was cooled and poured into water (200 mL), ammonium hydroxide (50 mL) was added, and the mixture was immediately filtered to remove dark-colored precipitates. The solids were thoroughly washed with water, and the combined aqueous portion was extracted with ether (2 × 200 mL). Evaporation of the ether solution yielded the crude aldehyde, which was recrystallized from ethanol–water to give 6 (16.5 g, 91%) as pale-yellow needles: mp 118–119 °C (lit.[20] mp 119 °C); NMR δ 1.35 (3 H, t, OEt), 2.60 (3 H, s, 2-Me), 4.26 (2 H, q, OEt), 7.11 (1 H, s, pyrrole H), 9.77 (1 H, s, CHO), 10.5 (1 H, br s, NH); mass spectrum, *m/e* (%) 181 (100), 134 (87).

3-[2-(Ethoxycarbonyl)ethyl]-5-(ethoxycarbonyl)-2-methylpyrrole (8). A solution of the formylpyrrole 6 (8.9 g) in pyridine (50 mL) and toluene (50 mL) was heated to reflux in a flask equipped with a Dean–Stark trap. A mixture of malonic acid monoethyl ester (7.5 g), toluene (10 mL), glacial acetic acid (3 Ml), and piperidine (1.2 mL) was added; water evolution became noticeable immediately. The reaction was completed within 30 min and 1.1 mL of water was collected in the trap. The mixture was evaporated to almost dryness on a rotorvap and water (300 mL) added with gentle swirling. The crystals formed were filtered to give 12 g (96.5%) of essentially pure acrylic ester 7, mp 152 °C. The vinyl hydrogens were seen in the NMR spectrum at δ 5.86, 6.12, 7.33, 7.60 (2 H); other signals were two triplets at 1.30, 1.34 and two quartets at 4.14, 4.26 (OEt), 2.37 (3 H, s, 2-Me), 6.91 (1 H, d, pyrrole H), 9.83 (1 H, br s, NH). This acrylic pyrrole (11.2 g) and 10% palladium on charcoal (1 g) were stirred under hydrogen in tetrahydrofuran (80 mL) and methanol (40 mL) at 1 atm and room temperature until hydrogen uptake ceased (1.1 L). The catalyst was removed by filtration, and the solvent was evaporated to give an oil, which crystallized on standing: 11.4 g, mp 74–75 °C; NMR δ 1.26 (3 H, t), 1.30 (3 H, t), 4.05 (2 H, q), 4.20 (2 H, q), 2.11 (3 H, s, 2-Me), 2.57 (4 H, A_2B_2,CH_2CH_2), 6.56 (1 H, d, pyrrole H), 9.23 (1 H, br s, NH); mass spectrum, *m/e* (%) 253 (49), 166 (100), 120 (55). Anal. $C_{13}H_{19}O_4N$.

[5,5′-Bis(ethoxycarbonyl)-3,3′-bis[2-(ethoxycarbonyl)-ethyl]-2,2′-dipyrryl]methane (18). Pyrrolepropionic ester 8 (4.5 g) was dissolved in glacial acetic acid (60 mL) and acetic anhydride (5 mL), and treated all at once with lead tetraacetate (9.2 g, Aldrich, slightly wet). The mixture was stirred magnetically and gradually warmed to 70 °C; all lead tetraacetate dissolved at this point. The solution was kept at this temperature for 10 min, cooled, and diluted with water (100 mL). After 1 h, the crystalline 2-acetoxypyrrole formed was filtered, washed with water, and sucked dry. The acetoxypyrrole was redissolved in 75% aqueous acetic acid (50 mL) and the mixture heated on a steam bath for 20 min. The cooled solution was diluted with water (100 mL) and extracted twice with methylene chloride (100 + 50 mL). The organic phases were combined and evaporated, and the pale-yellow oil was redissolved in ethanol (20 mL) and water (10 mL) and allowed to stand in a refrigerator for 2 h. The crystals were collected by filtration to give 3 g of 18 (69%): mp 111–113 °C; NMR δ 1.23 (12 H, 2 t), 4.14 (8 H, 2 q, OEt), 2.63 (8 H, A_2B_2, CH_2CH_2), 3.90 (2 H, s, CH_2), 6.57 (2 H, d, pyrrole H), 9.06 (2 H, br s, NH); mass spectrum, *m/e* (%) 490 (63), 444 (82), 417 (77), 252 (100), 224 (40.5), 132 (49). Anal. $C_{25}H_{34}O_8N_2$.

5,8-Dimethyl-6,7-bis[2-(methoxycarbonyl)ethyl]porphine (4). Method 1. [5,5′-Diformyl-4,4′-dimethyl-3,3′-bis[2-(methoxycarbonyl)ethyl]-2,2′-dipyrryl]methane (16,[11,21] 402 mg) and 2,2′-dipyrrylmethane (11,[11,22] 150 mg) were dissolved separately in glacial acetic acid (150 mL each). The two solutions were joined and diluted with glacial acetic acid (200 mL) containing 56% hydriodic acid (3.5 mL). The reaction was allowed to proceed in the dark for 1 h. Anhydrous sodium acetate (10 g) was then added, and the mixture was aerated in the dark for 30 h; the solvent was evaporated by the end of aeration. The residue was refluxed briefly with methanol (300 mL) containing trimethylorthoformate (20 mL, optional) and concentrated sulfuric acid (3 mL) and then set aside for 2 days. The mixture was evaporated and methylene chloride (200 mL) added; this was washed with water (2 × 100 mL) and then evaporated. The product was purified by chromatography on silica gel (1 × 3 in. column), using CH_2Cl_2 as eluant. The red fraction was collected and the porphyrin 4 was recrystallized from CH_2Cl–MeOH (55 mg, 10.8%): mp 205 °C (lit.[14] mp 214–215 °C); NMR δ 3.23 (4 H, t, CH_2CO), 3.54 (6 H, s, ring Me), 3.63 (6 H, s, OMe), 4.31 (4 H, t, CH_2), 9.36 (4 H, q, AX pattern, J = 4.4 Hz, ring H), 10.04 (1 H, s, methine γ), 10.14 (2 H, s, methine β, δ), 10.26 (1 H, s, methine α), −4.15

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(2 H, br s, NH); mass spectrum, m/e (%) 510 (100), 437 (38), 255 (6); UV-vis λ_{max} (ϵ_M) 616 nm (2200), 563 (5500), 524 (5400), 492 (13600), 395 (184000). Anal. $C_{30}H_{30}N_4O_4$.

Method 2. 2,2'-Dipyrrylmethane (**11**, 146 mg) and 2,4-dimethyl-3-[2-(methoxycarbonyl)ethyl]-5-formylpyrrole (**14**,[21] 418 mg) were dissolved in 20 mL of methanol. This mixture was treated immediately with 48% HBr (0.6 mL). After 10 min, the dark orange-red solution was diluted with ether (50 mL) and the biladiene salts began to deposit. More ether (50 mL) was added and the solid product collected by filtration to give the *a,c*-biladiene dihydrobromide **13** (380 mg, 55%): mp 300 °C; NMR δ 2.28 (6 H , s, 1',8'-Me), 2.72 (6 H, s, 2,7-Me), 2.5-2.8 (8 H, m, CH_2Cl_2), 3.60 (6 H, s, OMe), 4.81 (2 H, s, *b*-CH_2), 6.98 (4 H, q, 3,4,5,6-H), 7.05 (2 H, *a,c*-CH), 13.45 (4 H, br, NH^+); UV-vis λ_{max} (relative absorbance) 439 nm (1), 504 (2.53). The biladiene salts and copper (II) chloride (3 g) were stirred in 20 mL of DMF at 140 °C for 10 min. The solution was poured into ice water (200 mL), and the precipitates were collected by filtration. The black solid was dried and pulverized with 10 mL of concentrated sulfuric acid. After 30 min, the mixture was cautiously diluted with anhydrous methanol (100 mL) and set aside for 2 days. The mixture was filtered, the solid washed with CH_2Cl_2 (150 mL), and the solution washed twice with water. The organic layer was filtered through a 1-in. silica gel pad and the red solution, after concentration, chromatographed on a 20 × 20 cm preparative TLC plate (Analtech, silica gel, 1.5 mm thick), using CH_2Cl_2-2% methanol as solvent; 6 mg of porphyrin was obtained (1.2% yield). This compound was characterized by UV-vis, mass spectrum, NMR, and TLC to be identical with the porphyrin **4** obtained by method 1.

6,7-Bis[2-(methoxycarbonyl)ethyl]porphine or Dimethyl 1,2-Porphinedipropionate (3). Method 1. Dipyrrylmethane **18** (490 mg) was heated on a steam bath in a solution of 0.35 g of KOH in water (10 mL) and ethanol (10 mL) for 4 h. The solution was then evaporated to dryness in vacuo. The residue was treated with trifluoroacetic acid (10 mL) and left at room temperature for 1 h to effect decarboxylation. [5,5'-Diformyl-2,2'-dipyrryl]methane (**10**,[11] 202 mg) was dissolved in acetic acid (15 mL). The two solutions were joined and diluted immediately with glacial acetic acid (400 mL) containing 56% hydriodic acid (4 mL); acetic anhydride (10 mL) was added and the reaction mixture was set aside in the dark for 4 h. Anhydrous sodium acetate (10 g) was added and the mixture aerated overnight. Water (250 mL) and 50 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were added to the mixture, and aeration was continued for 30 h. The solvent was then removed under reduced pressure and the residue esterified and purified by chromatography in the same manner as described above. The porphyrin fraction after rechromatography on silica gel plates gave the title porphyrin (28 mg, 6%): mp 196 °C; NMR δ 3.45 (4 H, t, CH_2CO), 3.80 (6 H, s, OMe), 4.51 (4 H, t, CH_2), 9.14 (2 H, s, 5,6-H), 9.43 (4 H, q, AX pattern, J = 4.4 Hz, 1,2,3,4-H), 10.18 (3 H, s, β, γ, δ), 10.26 (1 H, s, α), -4.18 (2 H, br s, NH); mass spectrum, m/e (%) 482 (100), 309 (41), 241 (4); UV-vis λ_{max} (ϵ_M) 618 nm (1700), 563 (5400), 521 (4900), 491 (14100), 496 (218000). Anal. $C_{28}H_{26}O_4N_4$.

Method 2. Pyrrolepropionic ester **8** (506 mg) was heated on a steam bath in a solution of 0.35 g of KOH in water (10 mL) and ethanol (10 mL) overnight. The solvent was then removed in vacuo. The residue was dissolved in trifluoroacetic acid (10 mL); after 10 min, the acid solution was pumped to dryness at room temperature. The residue, taken in 10 mL of glacial acetic acid, was added to a solution of (5,5'-difromyl-2,2'-dipyrryl)methane (**10**,[11] 202 mg) in glacial acetic acid (10 mL). This mixture was treated immediately with 1 mL of 40% HBr in acetic acid, and after 20 min, the biladiene was precipitated by addition of ether (100 mL). The *a,c*-biladiene salt **12** has visible absorption maxima at 504 and 440 nm. This salt was redissolved in pyridine (40 mL), copper acetate (3 g) was added, and the mixture was stirred at room temperature for 10 min and then heated to 70 °C for 1 h. Fifty milliliters of water was added, the mixture was filtered, and the black precipitates, after being filtered and dried, were redissolved in concentrated sulfuric acid (10 mL). Methanol (100 mL) was added and the solution was set aside for 1 week. Purification of the porphyrin dimethyl ester by chromatography on silica gel TLC plates using CH_2Cl_2-2% MeOH as solvent gave 7 mg (1.5%) of **3**, characterized by NMR, UV-vis, mass spectrum, and TLC to be identical with that obtained by method 1.

1,2,3,4,5,8-Hexamethyl-6,7-bis[2-(methoxycarbonyl)-ethyl]porphine (Dimethyl Ester of 2). Dipyrrylmethane **15** (204 mg) obtained by hydrogenolysis of [5,5'-bis[(benzyloxy)-carbonyl]-3,3',4,4'-tetramethyl-2,2'-dipyrryl]methane,[12] followed by decarboxylation in trifluoroacetic acid, was dissolved in glacial acetic acid (10 mL) and mixed with another solution of pyrrole aldehyde **14**[21] in glacial acetic acid (10 mL). This mixture was treated with 0.6 mL of 48% hydrobromic acid and after 10 min diluted with ether (50 mL) to complete the precipitation of the biladiene dihydrobromide. This salt was isolated by filtration and treated with copper(II) chloride in hot DMF as described above. Demetalation, methylation, and purification in the same manner gave 124 mg (22%) of **2** dimethyl ester: mp >300 °C; NMR δ 3.64 (3 H, s, OMe), 3.21 (4 H, t, CH_2CO), 4.30 (4 H, t, CH_2), 3.35, 3.38, 3.49 (6 H each, s, ring Me), 9.89 (1 H, s), 9.75 (2 H, s), 9.60 (1 H, s, meso protons), -4.0 (2 H, br s, NH); mass spectrum, *m/e* 566; UV-vis λ_{max} (ϵ_M) 620 nm (5200), 566 (6800), 531 (10100), 497 (14500), 497 (162000). The data are consist with literature reports of **2** prepared by other methods.[5,6,23,24]

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Perdeuteriotetramethyltetraselenafulvalene

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Received June 2, 1981

Spin density wave (SDW) depinning was the original interpretation of the resurrection of spins (observed by solid-state ESR) and the reinstatement of metallic conductivity at low temperature and low electric fields in the organic superconductor bis(tetramethyltetraselenafulvalenium) hexafluorophosphate[1] [$(TMTSF)_2PF_6$]. There have been attempts to corroborate this interpretation[2] and to find other elucidations for the above observations.[3] There is, however, only one *definitive* way to confirm the existence of SDW's, and that is by means of neutron-scattering experiments. Since the background due to incoherent neutron scattering is much larger for protons than for deuterons and since SDW's would be expected to be of weak intensity,[4] they would be more easily observed in $(TMTSF\text{-}d_{12})_2PF_6$. Therefore, it was necessary to prepare the fully deuterated analogue of TMTSF. Also, since the carbon-deuterium bond is slightly shorter than the carbon-hydrogen bond, TMTSF-d_{12} is expected to be slightly smaller than TMTSF. This difference in size might have an effect on both the metal-to-semiconductor transition temperature and the metal-to-superconductor transition temperature (under pressure).[5] For the above reasons we decided to prepare TMTSF-d_{12}, and here we report on its preparation and spectroscopic properties.

Results and Discussion

We did not expect to be able to exchange the protons in TMTSF; therefore, the most logical approach was to

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