6.06; N, 10.52. Found: C, 45.08; H, 6.05; N, 10.43.

Registry No. **3**, 102420-40-6; **3** (alcohol), 102420-37-1; **4**, 102491-83-8; **4** (acetate), 102420-43-9; **6a**, 689-89-4; GABA-T, 9037-67-6; **7**, 102420-31-5; **8**, 102420-34-8; **9**, 102420-33-7; **9** (alcohol), 102420-35-9; **10**, 102420-36-0; **11a**, 102420-38-2; **11a** (aldehyde), 102420-39-3; **12a**, 82006-54-0; **12b**, 102420-41-7; **13**, 102420-42-8; **14**, 102420-44-0; **6b**, 102420-32-6; $NCCOCCl_3$, 545-06-2.

A Convenient Synthesis of a "Gable"-Type Porphyrin

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A dimeric porphyrin with a "gable" orientation, 1,3-bis[5-(10,15,20-triphenylporphinyl)]benzene, has recently been prepared by Tabushi and co-workers.[1] Metal complexes of this gable porphyrin were demonstrated to bind various ligands in a cooperative fashion.[1,2] The gable porphyrin thus serves as an interesting example of an *artificial allosteric system*.[3,4] Moreover, the orientation of the two porphyrin rings in the gable dimer resembles that found in cytochrome c_3[5] and in the cytochrome associated with the active site of a structurally characterized photosynthetic bacterium.[6] Gable-type porphyrins may thus emerge as interesting models in electron and energy transfer studies.

Unfortunately, the synthesis reported for Tabushi's gable porphyrin is long and tedious: It involves six chemical steps, including two Rothemund condensations, and requires multiple chromatographic separations. It proceeds in an overall yield of ca. 1% from *m*-xylene.[1] We wish to report that gable-type dimeric porphyrins may be conveniently prepared from dipyrromethane intermediates by the MacDonald–Chang porphyrin synthesis.[7-10] We describe here the synthesis of a new gable-type dimeric porphyrin **1**. It is obtained in four steps from isophthalaldehyde in ca. 8% overall yield.[11]

The synthesis of **1** is outlined in Scheme I, part A. Condensation of ethyl 3-ethyl-4-methylpyrrole-2-carboxylate (**2**)[12] with isophthalaldehyde (**3**) in EtOH–HCl gave the bis(dipyrrylmethane) **4** in nearly quantitative yield. Saponification and decarboxylation by the procedure of Chang[8-10] gave the α-unsubstituted bis(dipyrrylmethane) **6**. The synthesis of the 5,5′-diformyldipyrrylmethane **11** is shown in part B of Scheme I. Ethyl 3,5-dimethyl-4-propylpyrrole-2-carboxylate (**7**), prepared by the method of Johnson,[13,14] was oxidized to the acetoxymethyl derivative **8** by using lead tetraacetate[14] and converted to the dipyrrylmethane **9** under acidic conditions.[15] Saponification and decarboxylation (to **10**) followed by Vilsmeier formylation, using the procedure of Clezy,[16] gave **11** in good yield. Various acidic catalysts and reaction conditions were employed in an effort to optimize the MacDonald[7] condensation between **6** and **11** (Scheme I, part C). These have included the use of MeOH, THF, HOAc, or mixtures thereof as solvents and HI, *p*-TsOH, or $HClO_4$ as acids. In general, our yields have been in the range of 10% (following oxidation and workup) and have proved to be rather insensitive to the reaction conditions. In fact, in our hands, the recently introduced Chang modification (0.4% $HClO_4$ in MeOH)[8-10] appears to be only slightly better than the original MacDonald procedure (HI in HOAc).[7] When the latter method is employed, it is possible to use the tetraacid **5** directly in the porphyrin synthesis; it is presumably decarboxylated to give **6** in situ.

The dimeric gable-type porphyrin **1** was characterized by ^1H NMR, ^{13}C NMR, electronic spectroscopy, mass spectrometry, and elemental analysis. The ^1H NMR spectrum of **1** was notable for two sharp low-field singlets (in 2:1 ratio) ascribable to the meso protons. This and the clean nature of the alkyl peaks suggest that the porphyrin condensation conditions do not cause scrambling of the substituents. Evidence for the gable orientation was obtained from electronic spectroscopy. As was observed in the case of the Zn_2·gable porphyrin of Tabushi,[1] the biszinc complex Zn_2·**1** shows a split Soret band. In contrast to the Tabushi system,[1] however, the free base **1** does not show such splitting. It presents instead a broad Soret band centered at 410 nm, which is considerably red shifted compared to etioporphyrin II (2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin) (λ_{max} 397 nm)[17] or the monophenyloctaalkylporphyrin, 5-phenyl-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphine, recently prepared by Chang (λ_{max} 402 nm).[18]

Experimental Section

NMR spectra were obtained in $CDCl_3$ with Me_4Si as an internal standard and recorded on either a Varian EM-390 or Nicolet FT-360 spectrometer. Routine mass spectra were measured with either a Finnigan MAT 4023 or a Bell and Howell 21-110B instrument. The mass spectrum of **1** was recorded by using fast atom bombardment on a Kratos MS-50 instrument at the University of Texas Health Science Center, Houston. Electronic spectra were measured in CH_2Cl_2 on a Beckman Instruments DU-7. Elementary analyses were performed by Galbraith Laboratories. Isophthalaldehyde was obtained from Aldrich Chemical

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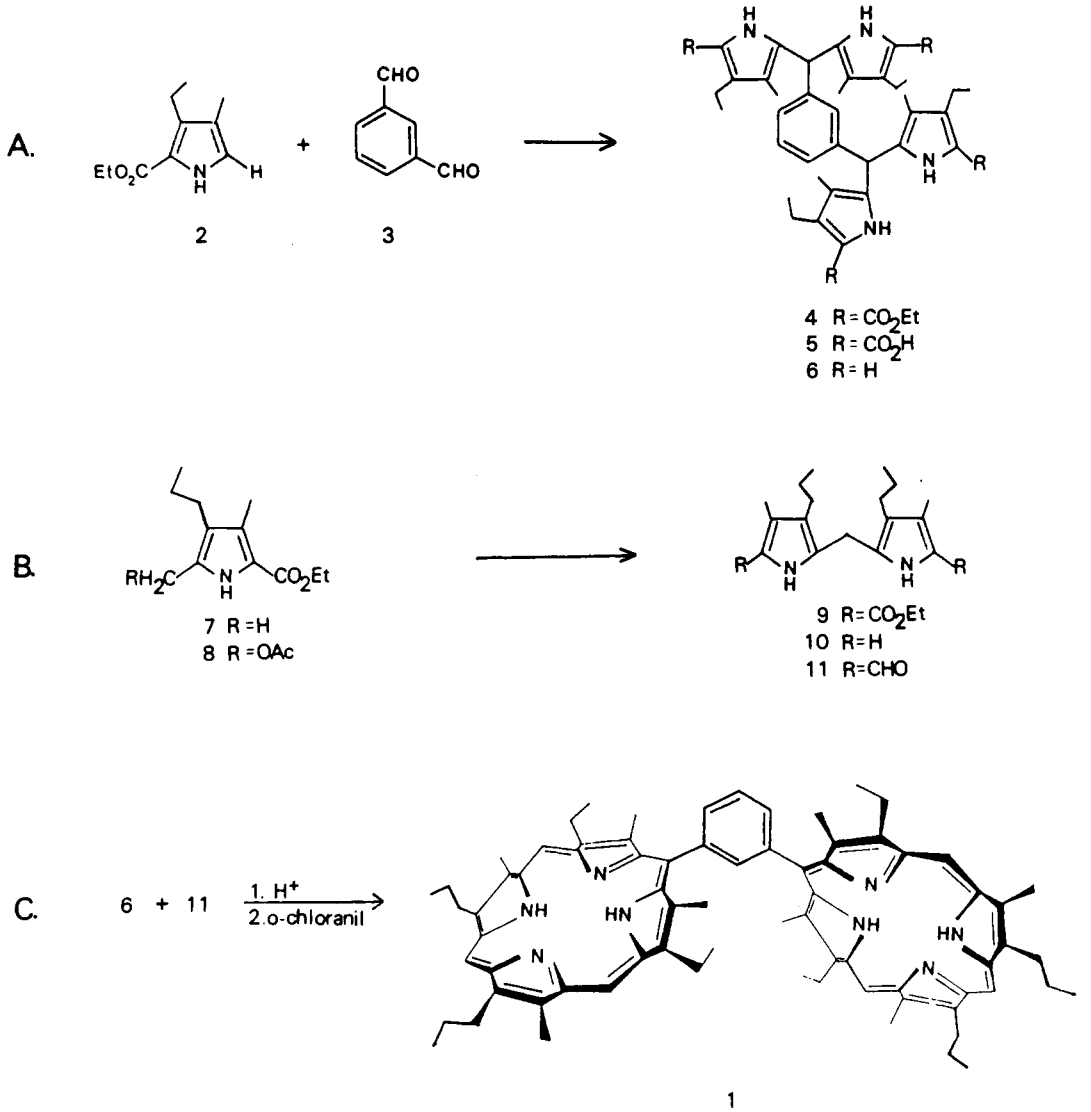
Scheme I



Co. and used without further purification.

1,3-Bis[bis(5-(ethoxycarbonyl)-4-ethyl-3-methyl-2-pyrryl)methyl]benzene (4). Isophthalaldehyde (3) (0.335 g, 2.5 mmol) and ethyl 3-ethyl-4-methylpyrrole-2-carboxylate[12] (2) (1.81 g, 10 mmol) were dissolved in 50 mL of absolute ethanol containing 1 mL of concentrated HCl and heated at reflux for 3 h under nitrogen. After the mixture was cooled overnight in the freezer, filtration and drying in vacuo gave 4 as a white powder (1.92 g, 93% yield): mp 178–180 °C; ^{1}H NMR δ 1.08 (12 H, t, CH_2CH_3), 1.31 (12 H, t, OCH_2CH_3), 1.74 (12 H, s, CH_3), 2.72 (8 H, q, CH_2CH_3), 4.25 (8 H, q, OCH_2CH_3), 5.86 (2 H, s, CH), 6.83 (1 H, s, Ar), 7.00 (2 H, d, Ar), 7.29 (1 H, t, Ar), 8.28 (4 H, s, NH); MS, *m/e* (relative intensity) 822 (72), 776 (100), 730 (66).

1,3-Bis[bis(4-ethyl-3-methyl-2-pyrryl)methyl]benzene (6). The tetraester 4 (1.75 g, 2.13 mmol) was dissolved in 50 mL of 95% ethanol, and a solution of 3 N NaOH (30 mL) was added. After the mixture was heated at reflux for 8 h under nitrogen, the bulk of the solvent was removed on the rotorary evaporator and the residue acidified with acetic acid. The pink precipitate was filtered off and dried in vacuo to yield the tetraacid 5 (mp 140 °C dec). This crude product was decarboxylated directly without further purification by dissolving in ethanolamine (30 mL) and heating at reflux for 3 h under nitrogen. After cooling, the gold solution was poured onto crushed ice (400 mL). The yellow foam which separated off was collected by filtration and dried to yield 1.0 g of 6 (88% yield based on 4): mp 65 °C dec; ^{1}H NMR δ 1.10 (12 H, t, CH_2CH_3), 1.70 (12 H, s, CH_3), 2.37 (8 H, q, CH_2CH_3), 5.36 (2 H, s, CH), 6.29 (4 H, s, pyrrole H-5), 6.88 (2 H, br, Ar), 6.98 (1 H, br, Ar), 7.11 (1 H, br, Ar); MS, *m/e* (relative intensity) 534 (47), 425 (84), 316 (100); high resolution MS, M^+ 534.3713 (calcd for $C_{36}H_{46}N_4$ 534.3722).

Ethyl 3,5-dimethyl-4-propylpyrrole-2-carboxylate (7) was prepared in 48% yield from ethyl acetoacetate and 3-propyl-2,5-pentanedione by the general procedure of Johnson et al.:[13] mp 102–103.5 °C; ^{1}H NMR δ 0.90 (3 H, t, $CH_2CH_2CH_3$), 1.35 (3 H, t, OCH_2CH_3), 1.40 (2 H, m, $CH_2CH_2CH_3$), 2.20 (3 H, s, pyrrole 3-CH_3), 2.28 (3 H, s, pyrrole 5-CH_3), 2.35 (2 H, t, $CH_2CH_2CH_3$), 4.32 (2 H, q, OCH_2CH_3), 9.1 (1 H, br, NH); MS, *m/e* (relative intensity) 209 (53), 180 (88), 134 (100).

Ethyl 5-(Acetoxymethyl)-3-methyl-4-propylpyrrole-2-carboxylate (8). The dimethyl pyrrole 7 (40 g, 0.191 mol) was dissolved in glacial acetic acid (440 mL), and lead tetraacetate (90 g, 0.202 mol) was added all at once. The resulting mixture was stirred for 2 h, during which time it turned into a clear red solution. The solution was then poured into water (700 mL) with vigorous stirring. The precipitate was collected by filtration, washed with water, and air-dried. Recrystallization from hexane (1 L) gave 8 as fluffy white needles (33 g, 65%): mp 124 °C; ^{1}H NMR δ 0.80 (3 H, t, $CH_2CH_2CH_3$), 1.25 (3 H, t, OCH_2CH_3), 1.48 (2 H, m, $CH_2CH_2CH_3$), 1.95 (3 H, s, $CH_2O_2CCH_3$), 2.19 (3 H, s, CH_3), 2.33 (2 H, t, CH_2CH_2), 4.24 (2 H, q, CO_2CH_2), 4.95 (2 H, s, $CH_2O_2CCH_3$), 9.39 (1 H, br, NH); MS, *m/e* (relative intensity) 267 (58), 238 (63), 208 (50), 180 (23), 135 (100); high-resolution, MS, M^+ 267.14744 (calcd for $C_{14}H_{21}NO_4$ 267.14705).

Bis(5-(ethoxycarbonyl)-4-methyl-3-propyl-2-pyrryl)-methane (9). The (acetoxymethyl)pyrrole 8 (47.2 g, 0.177 mol) was added to a 1-L round-bottom flask. Absolute ethanol (380 mL) and concentrated hydrochloric acid (15 mL) were added, and the solution was heated at reflux for 3 h under nitrogen. The clear dark solution was then poured into a beaker and cooled in the

freezer for 3 h. The product was collected by filtration, washed with cold ethanol, and dried in vacuo to yield **9** (33 g, 93%): mp 144–145 °C; ^{1}H NMR δ 0.83 (6 H, t, $CH_2CH_2CH_3$), 1.19 (6 H, t, $CO_2CH_2CH_3$), 1.35 (4 H, m, $CH_2CH_2CH_3$), 2.20 (6 H, s, CH_3), 2.29 (4 H, t, $CH_2CH_2CH_3$), 3.82 (2 H, s, pyrrole$_2$-CH_2), 4.18 (4 H, q, $CO_2CH_2CH_3$), 9.32 (2 H, br, NH); high-resolution MS, M^+ 402.25245 (calcd for $C_{23}H_{34}N_2O_4$ 402.25184).

Bis(4-ethyl-3-propyl-2-pyrryl)methane (10). The above bis(pyrryl)methane diester (40 g, 0.099 mol), 95% ethanol (140 mL), and 1 N aqueous sodium hydroxide (40 mL) were mixed in a 500-mL round-bottom flask and heated at reflux for 2 h. The condenser was then removed and the clear yellow solution concentrated to half its original volume by boiling. Water (100 mL) was added, and the solution was concentrated until its boiling point reached a minimum of 100 °C. The condenser was then replaced and heating continued for 12 h. The contents were then poured while hot into a 250-mL beaker and allowed to cool in the refrigerator. The oil-like product which solidified over the course of 2 days was collected, washed with water, and dried. This air- and light-sensitive compound was generally used without further purification. For analysis, samples were purified by chromatography on silica gel (dichloromethane eluent): ^{1}H NMR δ 0.95 (6 H, t, $CH_2CH_2CH_3$), 1.53 (4 H, m, $CH_2CH_2CH_3$), 2.05 (6 H, s, CH_3), 2.41 (4 H, t, $CH_2CH_2CH_3$), 3.79 (2 H, s, pyrrole$_2$-CH_2), 6.3 (2 H, s, pyrrole H-5); MS, *m/e* (relative intensity) 258 (52), 215 (21), 197 (17), 136 (100).

Bis(5-formyl-4-methyl-3-propyl-2-pyrryl)methane (11). The α-free bis(pyrryl)methane **10** (5 g, 0.0194 mol) was dissolved in freshly distilled DMF (25 mL) and cooled to 0 °C, and $POCl_3$ (6 mL, 0.066 mol) was added dropwise to the stirred solution. The temperature was maintained below 5 °C. After the addition was complete, the mixture was stirred for 2 h at room temperature. The gray precipitate was collected and washed with DMF. The solid was then dissolved in water (50 mL) and made basic with 7.5 N sodium hydroxide solution. An oil separated off, which gradually solidified. This brown solid was collected by filtration, washed with water, and dried in vacuo to yield 4.0 g (66%) of **11**. Further purification to yield a yellow powder was effected by multiple recrystallizations from chloroform–hexane: mp 195–196 °C; ^{1}H NMR δ 0.86 (6 H, t, $CH_2CH_2CH_3$), 1.39 (4 H, m, $CH_2CH_2CH_3$), 2.20 (6 H, s, CH_3), 2.35 (4 H, t, $CH_2CH_2CH_3$), 3.90 (2 H, s, pyrrole$_2$-CH_2), 9.48 (2 H, s, CHO), 11.00 (2 H, br, NH); MS, *m/e* 314 (43), 285 (36), 271 (10), 163 (100).

1,3-Bis[5-(2,8-diethyl-3,7,12,18-tetramethyl-13,17-dipropyl)porphyrinyl]benzene (1). This compound was prepared by several different procedures.

Procedure I. The bis[bis(pyrryl)methane] **6** (200 mg, 0.375 mmol) and the bis(formylpyrryl)methane **11** (235 mg, 0.75 mmol) were dissolved in 70 mL of MeOH or in 70 mL of MeOH/THF (1:1 v/v), and the reaction vessel was flushed with nitrogen. The acid catalyst, $HClO_4$ (0.5 mL) or *p*-toluenesulfonic acid (0.5 g), was then added and the reaction left to stir for 24 h in the dark. Sodium acetate (0.5 g) in MeOH was then added followed by a solution of *o*-chloranil in MeOH (0.55 g, 2.25 mmol). After being stirred in the dark for several hours, the reaction mixture was poured into water (300 mL) and extracted with 100-mL portions of chloroform until the extracts were pale in color. After the mixture was dried over $MgSO_4$ and filtered, a saturated solution of zinc acetate in MeOH (20 mL) was added to the organic layer and the whole heated at reflux for 20 min. After cooling, the solution was washed with water (3 × 100 mL) and dried over $MgSO_4$. After being taken to dryness on the rotorary evaporator, the biszinc complex of **1** was purified from undesired byproducts by filtration through a plug of silica gel (dichloromethane eluent). Demetalation was effected by stirring for 8 h in 7 mL of a mixture of trifluoroacetic acid, concentrated HCl, and water (2:2:1 by volume). After neutralization with an aqueous bicarbonate solution, the free base porphyrin was extracted into dichloromethane, dried over $MgSO_4$, and taken to dryness in vacuo to yield between 38 and 45 mg of **1** (9–11% yield). This product was one clean spot on TLC (silica gel/3% MeOH in chloroform). Material for analysis could, however, be obtained by chromatography on silica gel (1% MeOH in CH_2Cl_2 eluent) followed by recrystallization from dichloromethane–hexane.

Procedure II. The precursors **6** (106 mg, 0.20 mmol) and **11** (125 mg, 0.40 mmol) were dissolved in HOAc (50 mL), and HI (3 mL) was added. After the flask was flushed with nitrogen, the reaction was allowed to stir for 24 h in the dark. The red slurry was poured into an excess of aqueous potassium carbonate. After reaction was extracted into dichloromethane, dried over $MgSO_4$, and taken to dryness, 50 mL of MeOH–THF (1:1 v/v) was added. The oxidation and purification steps were then effected as outlined above to yield 17 mg of **1** (8%).

Procedure III. This was carried out exactly as above only the tetraacid **5** (141 mg, 0.20 mmol) was used as a precursor instead of **6**. The yield of **1** was 14 mg (5%). **1**: ^{1}H NMR δ −3.0 (4 H, br, pyrrole NH), 1.22 (12 H, t, $CH_2CH_2CH_3$), 1.72 (12 H, t, CH_2CH_3), 2.25 (8 H, m, $CH_2CH_2CH_3$), 3.07 (12 H, s, CH_3), 3.55 (12 H, s, CH_3), 3.99 (16 H, m, porphyrin CH_2CH_2), 7.82 (1 H, s, phenyl H-2), 8.27 (1 H, t, phenyl H-5), 8.90 (2 H, d, phenyl H-4 and -6), 9.78 (2 H, s, meso H-15), 10.04 (4 H, s, meso H-10 and -20); ^{13}C NMR δ 11.8, 14.5, 17.2, 20.2, 26.1, 28.3, 34.1, 96.0, 96.4, 118.0, 125.6, 127.6, 133.8, 135.3, 136.2, 140.0, 141.0, 141.9, 143.7, 144.8, 145.2, 146.1; UV–vis λ_{max} 627, 576, 540, 507, 410 nm. Anal. Calcd for $C_{74}H_{86}N_8$: C, 81.68; H, 7.97; N, 10.30. Found: C, 81.68; H, 8.11; N, 10.08. Zn_2·**1**: UV–vis λ_{max} 574, 541, 421, 405 nm; FAB MS (glycerol–oxalic acid matrix) shows a cluster of peaks at 1087–1091 amu (calcd for $C_{74}H_{86}N_8$·H^+: 1087).

Note Added in Proof. In acting as a reviewer for this paper, Professor C. K. Chang indicated that an analogue of **1**, 1,3-bis-[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrinyl]benzene, has been independently prepared in his laboratory;[19] he requested that this be noted.

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Registry No. **1**, 102613-57-0; **1**·2Zn, 102538-52-3; **2**, 4949-58-0; **3**, 626-19-7; **4**, 102586-94-7; **5**, 102613-58-1; **6**, 102586-95-8; **7**, 4758-64-9; **8**, 102586-96-9; **9**, 102586-97-0; **10**, 102586-98-1; **11**, 102586-99-2.

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An Investigation of the O- and C-Alkylation of Coal

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Liotta and co-workers developed a method for the selective O-alkylation of bituminous coal under mild conditions.[1] This valuable procedure, which has been used for the synthesis of a variety of modified coals,[1,2] employs tetrabutylammonium hydroxide as the basic catalyst and methyl iodide or another alkyl halide as the alkylation agent (eq 1). In recent applications of the method, it

$$(1\text{-}C_4H_9)_4N^+,OH^- + \text{coal-OH} + RI \xrightarrow[THF-H_2O]{} (1\text{-}C_4H_9)_4N^+,I^- + \text{coal-OR} + H_2O \quad (1)$$

became apparent that trace amounts of tetrabutylammonium ions were tenaciously retained in the alkylated coals. The presence of this material complicates the interpretation of ^{1}H and ^{13}C NMR spectra of extracts and of the products obtained in conversion reactions. In ad-

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