be smaller than that of $LiAl(OR_C)_4$ and $LiAl(OR_T)_4$.

The steric strain factor, $\Delta\sigma$, is a measure of the difference of steric strain between the approaching hydride and the ketone[4] at the transition states having a steric environment resembling the starting ketone. The fact that both $\Delta\sigma$ and $\Delta\sigma'$ are equal implies that it is the singular hydride alone, not $LiAlH_4$ or $LiAlH(OCH_3)_3$ as a whole, that is responsible for the difference in the steric strain between the ketone and the reducing agent.

In conclusion, the hydride reduction with lithium trimethoxyaluminohydride is characterized by its reduced contribution from the product stability difference to the final stereoselectivity. Whether the stereoselectivity increases or decreases when LAH is substituted by LTMAH is decided by the signs of $1.4\Delta G°H$ and $\Delta(\Delta G^{\ddagger})_{Me}$ and their relative magnitudes. The empirical equation $\Delta(\Delta G^{\ddagger})_{H'} = \Delta(\Delta G^{\ddagger})_{Me} + 0.4\Delta G°_{H}$ appears to provide a satisfactory explanation for all the available data bath qualitatively and quantitatively.

Experimental Section

Chemicals. Lithium aluminum hydride (LAH), used to prepare lithium trimethoxyaluminohydride (LTMAH), was purchased from Merck & Co. Inc. Tetrahydrofuran (THF) and methanol were the products of Alps Chemical Co. (Taipei, Taiwan). The THF solution of LTMAH (1.2 M) was prepared according to a literature method[6] by adding 3 mol of metanol to 1 mol of LAH in THF. All of the ketones used in this study have been characterized and reported in the literature. 2,2-Dimethyl-4-*tert*-butylcyclohexanone was purified by gas chromatography and gave a satisfactory ^1H NMR spectrum. 2,4,4-Trimethylcyclopentanone was purchased from Chemical Sample Co.

LTMAH Reduction. The method used by Brown and Deck was followed in this study. Typically, 2,4,4-trimethylcyclopentanone (1.2 M in THF) was placed in a round-bottomed flask and thermosatted to 0 °C by an ice–water mixture. An equal molar solution of LTMAH in THF was added dropwise into the ketone solution while the reaction mixture was magnetically stirred. After 3 h of reaction the products were hydrolyzed, decanted, and dried; the products were analyzed by GLPC[4] for distribution (76.5% trans alcohol) and characterized by ^1H NMR.[7]

Acknowledgment. Financial support from the National Science Council to allow preparation of 2,2-dimethyl-4-*tert*-butylcyclohexanone is acknowledged. I also express sincere gratitude to Miss Y. C. Kong for her help with the GLPC analysis.

Registry No. 1, 98-53-3; 2, 583-60-8; 3, 873-94-9; 4, 35413-38-8; 5, 1120-72-5; 6, 4694-12-6; 7, 497-38-1; 8, 10218-04-9; 9, 76-22-2; lithium trimethoxyaluminohydride, 12076-93-6; lithium aluminum hydride, 16853-85-3.

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Anthracene Pillared Cofacial Diporphyrin

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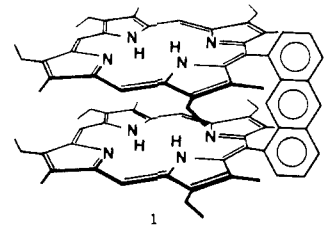
Porphyrin dimers whose macrocyclic rings are covalently linked in a cofacial configuration have recently received considerable attention.[1,2] They have been successfully applied to model photosynthetic reaction centers[3,4] as well as to effect electrocatalytic reduction of dioxygen on graphite electrode.[5,6] Our previous examples of diporphyrin were prepared by coupling monomeric porphyrin diacids and diamines under high dilution condition. While this method remains popular,[7] our continued interest in these compounds has resulted in the synthesis of a new type of cofacial diporphyrin. As shown by the example, 1,8-anthryldiporphyrin 1, the two porphyrin rings are anchored



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to a single rigid spacer; there are no amide linkages and the cofacial configuration is enforced by steric confines. It is anticipated that the stability and conformation of the new system would complement those of the existing amide type and thus may impart interesting new properties to the metallo complexes derived therefrom. We report here a rational synthesis of monoarylporphyrins in general and the anthryldiporphyrin in particular, via a dipyrrylmethane–dipyrrylmethene condensation.

In spite of the vast amount of literature on porphyrins, reliable syntheses of meso-substituted monoarylporphyrins hardly exist. Ogoshi et al.[8] reported 5-aryl-2,3,7,8,12,13,17,18-octaethylporphyrins as side products in the condensation of α,α'-unsubstituted dipyrrylmethane and benzaldehydes. Others[9,10] have used mixed benzaldehydes to react with pyrrole to obtain mixtures of *meso*-tetraphenylporphyrins from which the desired compound bearing a dissimilar aryl group may be isolated through chromatography. Both of these approaches, in our hands, failed to meet the demand of 1,8-anthracenedicarboxaldehyde and yielded no diporphyrin.[11] We are therefore forced to adopt a stepwise approach.

1,8-Anthracenedicarboxaldehyde (**2**)[12] reacted with 4 equiv of ethyl 3-ethyl-4-methyl-2-pyrrolecarboxylate (**3**)[13]

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(11) In the former case, when the dialdehyde **2** and 4 equiv of (3,4,3',4'-tetraethyl-2,2'-dipyrryl)methane (ref 8) were heated in propionic acid, with or without zinc acetate, only small amounts of OEP were yielded. In the latter approach using mixtures of various ratios of **2**, benzaldehyde, and (3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrryl)methane, only etioporphyrin II, phenyl etioporphyrin **8**, and 5,15-diphenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine were isolated.

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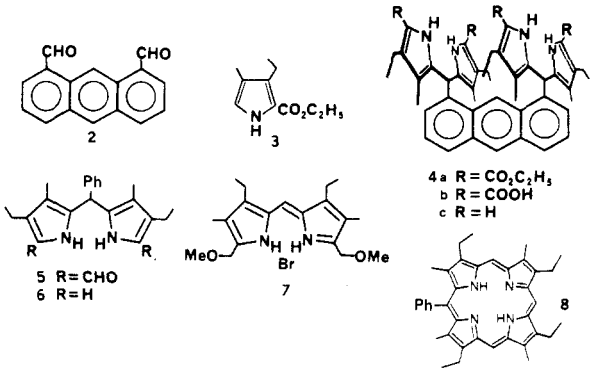
to yield almost quantitatively the bis(dipyrrylmethane) **4a**.



After hydrolysis, the carboxyl groups were cleaved smoothly in boiling ethanolamine. Cyclization of the bis(dipyrrylmethane) **4c** and dipyrrylmethane-5,5′-dialdehydes such as (5,5′-diformyl-4,4′-dimethyl-3,3′-diethyl-2,2′-dipyrryl)methane or the phenyl-substituted **5**, using the standard MacDonald procedure[14] (HI–HOAc at room temperature), produced no evidence at all of the desired diporphyrin. We suspected that this failure may be caused by an unfavorable orientation of the pyrroles in the bridge-substituted dipyrrylmethane and that more vigorous conditions may be needed to bring about the cyclization. After some trials, the dimethoxymethyldipyrrylmethene **7** was found to react with **4c** in boiling benzene and subsequent oxidation produced the anthryldiporphyrin in 8–10% yield. Dimethoxymethyl dipyrrylmethanes have been employed to construct *b*-bilenes[15] previously, but the condensation with dipyrrylmethane in such a direct manner to form porphyrin, to our knowledge, has not been reported. This route may well be a useful alternative for general 2 + 2 porphyrin cyclizations. The reaction was carried out in the absence of excess protons; there should be little danger of scrambling of substituents. Indeed, the two sharp singlet NMR peaks of the meso protons as well as of the methyl groups in **1** clearly ruled out any other substitution patterns. We have applied this reaction successfully to prepare monophenylporphyrin **8** from **6** and **7**, and as well, octaethylporphyrin from appropriate precursors.

In comparison with the monophenylporphyrin **8**, the anthryl diporphyrin exhibits a visible absorption spectrum of the phyllo type with the Soret peak shifted to the blue due to exciton interactions.[1] That the clean, sharp NMR peaks for the meso and methyl protons of **1** appear at positions similar to those of **8** further suggests a nonslipped, stack-on-top conformation. Although the two macrocycles may not rock sideways due to combined steric restrictions of the rigid anthracene pillar and the flanking methyl groups, they appear to be able to bend back and forth along the ridge of anthracene. This can be demonstrated by the observation that 5,6,7,8-tetrahydroimidazo[1,5-*a*]pyridine, a bicyclic imidazole,[16] which requires at least 6-Å clearance to fit inside a gap, can in fact form the hexacoordinate hemochrome readily with the bis-Fe(II) complex. An X-ray crystal structure as well as ligand binding properties of such binuclear porphyrins will be described elsewhere.

Experimental Section

NMR spectra ($CDCl_3$, 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. The high-resolution mass spectrum of **1** was obtained from the Mass Spectrometry Center of University of British Columbia. Elementary analyses were performed by Spang. Visible absorption spectra (in dichloromethane) were measured with a Cary 219 spectrophotometer.

1,8-Bis{[5,5′-bis(ethoxycarbonyl)-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrryl]methyl}anthracene (4a). 1,8-Anthracenedicarboxaldehyde (**2**; 7 g, 0.03 mol)[12] and ethyl 3-ethyl-4-methyl-2-pyrrolecarboxylate (**3**; 21.7 g, 0.12 mol)[13] were heated in absolute ethanol (200 mL) containing 5 mL of concentrated HCl. The solution was refluxed for 1 h and allowed to cool in a refrigerator. The yellow crystals (25 g, 91% yield) were filtered and dried; mp 183–185 °C; NMR δ 1.10 (12 H, t, Et), 1.30 (12 H, t, OEt), 1.65 (12 H, s, Me), 2.75 (8 H, q, Et), 4.23 (8 H, q, OEt), 5.88 (2 H, s, CH), 6.96 (2 H, d, 2, 7H-anthracene), 7.40 (2 H, t, 3,6H-an), 8.0 (2 H, d, 4,5H-an), 8.38 (1 H, s, 10H-an), 8.5 (4 H, br, NH), 8.55 (1 H, s, 9H-an); MS, *m/e* 922 (39), 921 (39), 877 (74), 876 (42), 875 (100). Anal. Calcd for $C_{56}H_{66}N_4O_8$: C, 72.86; H, 7.21; N, 6.07. Found: C, 71.67; H, 7.24; N, 6.08.

1,8-Bis[4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrryl)methyl]anthracene (4c). The tetraester **4a** (21 g, 22.7 mmol) was dissolved in refluxing ethanol (95%, 250 mL) and hydrolyzed by addition of aqueous NaOH (5 g in 30 mL of H_2O). The mixture was kept refluxing for 10 h before the ethanol solution was removed as much as possible on a rotary evaporator. The residue was diluted with water (200 mL) and filtered. The filtrate was acidified by addition of HOAc; the precipitated tetraacid **4b** was filtered and dried: mp 170 °C dec; yield 19 g (93%). The tetraacid **4b** was then added to ethanolamine (200 mL) and the mixture refluxed under nitrogen for 1 h. The solution, while still hot, was poured into ice water. Gold crystals soon separated and were filtered and dried: mp 150 °C; yield 11.5 g (84%); NMR δ 1.15 (12 H, t, Et), 1.62 (12 H, s, Me), 2.43 (8 H, q, Et), 5.98 (2 H, s, CH), 6.38 (4 H, s, 5H-pyrrole), 7.05 (2 H, d, 2, 7H-an), 7.4 (6 H, br, 3,6H-an, NH), 7.9 (2 H, d, 4,5H-an), 8.45 (1 H, s, 9H-an), 8.70 (1 H, s, 10H-an); MS, *m/e* 635 (65), 634 (45), 525 (100).

[5,5′-Bis(methoxymethyl)-4,4′-dimethyl-3,3′-diethyl-2,2′-dipyrryl]methene Hydrobromide (7). Ethyl 4,5-dimethyl-3-ethyl-2-pyrrolecarboxylate (**3**; 15 g, 0.066 mol)[17] suspended in formic acid (88%, 50 mL) was heated on a steam bath. HBr (48%, 20 mL) was added and the heating was continued for 8 h. The solution was allowed to stand at room temperature overnight and the orange (3,3′-diethyl-4,5,4′,5′-tetramethyl-2,2′-dipyrryl)methene hydrobromide precipitates were isolated by filtration, washed with HOAc (20 mL) and ether (50 mL), and dried: yield 13 g (59%).

To a stirred suspension of the above dipyrrylmethene in HOAc (120 mL) was added bromine (6 mL) and the mixture was kept at 80 °C for 30 min. The solution was allowed to cool, and the precipitates were filtered and washed with ether to yield [5,5′-bis(bromomethyl)-4,4′-dimethyl-3,3′-diethyl-2,2′-dipyrryl]methene hydrobromide (10 g, 53% yield). NMR showed the 5,5′-methylene protons at δ 4.95, in contrast to the unbrominated methyl signals at δ 2.67.

The [(bromomethyl)]dipyrrylmethene (5 g) was refluxed in dry methanol (50 mL) for 30 min. The solution was cooled to room temperature and diluted with ether (50 mL), and the precipitates were filtered to yield **7** (3.2 g, 81% yield): mp 285 °C dec; NMR δ 1.31 (6 H, t, Et), 2.22 (6 H, s, Me), 2.77 (4 H, q, Et), 3.55 (6 H, S, OMe), 5.13 (4 H, s, CH_2), 7.38 (1 H, s, methine); MS, *m/e* 316 (98, M^+ – HBr), 287 (80), 255 (76), 242 (100).

α,α-[5,5′-Diformyl-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrryl]toluene (5). Benzaldehyde (3.18 g, 0.03 mol) and pyrrole **3** (10.86 g, 0.06 mol) were heated in absolute ethanol (300 mL) containing concentrated HCl (5 mL). The solution was refluxed for 1 h and then allowed to stand in ice water for 2 h. The white

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crystalline material formed was collected by filtration; mp 150–152 °C; MS, *m/e* 450 (95), 270 (100).

The above diester was dissolved in hot ethanol (300 mL), to which NaOH solution (5 g in 20 mL) was added, and the mixture was refluxed continually for 8 h. The solvent was then evaporated, and the residue was redissolved in water (750 mL) and acidified with HOAc to give a white solid. The diacid, after collection by filtration and drying in vacuum, was decarboxylated in boiling ethanolamine (100 mL). The hot mixture was poured into ice water and extracted twice with dichloromethane (200 mL). Evaporation of the organic phase afforded the tarry dipyrrylmethane **6**, which was then formylated via the Vilsmeier reaction without purification. $POCl_3$ (3 mL) was added dropwise to a stirred, cold solution of **6** (5 g) in DMF (50 mL) at 0–5 °C. The mixture was allowed to stir at room temperature under nitrogen overnight. At the end of the period, water (200 mL) was added and the mixture extracted several times with CH_2Cl_2 until the organic layer was almost colorless. NaOH solution (10%) was added dropwise to the aqueous layer until complete precipitation was obtained. The light brown crystalline material was collected by filtration and recrystallized from 95% ethanol to give white needles (3.5 g, 60% yield): mp 210–212 °C; NMR δ 1.10 (6 H, t, Et), 1.75 (6 H, s, Me), 2.60 (4 H, q, Et), 5.45 (1 H, s, CH), 7.1 (5 H, m, Ph), 9.25 (2 H, s, CHO), 9.55 (2 H, br, NH); *m/e* 362 (100), 226 (50). Anal. Calcd for $C_{23}H_{26}N_2O_2$: C, 76.21; H, 7.23. Found: C, 75.95; H, 7.20.

1,8-Bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrinyl]anthracene (1). A solution of the 5,5′-unsubstituted **4c** (634 mg, 1 mmol) and the [bis(methoxymethyl)dipyrryl]methene **7** (794 mg, 2 mmol) in benzene (100 mL) was heated to reflux for 1 h. Tetrachloro-*o*-benzoquinone (1 g) was added and the solution was stirred at room temperature for $^1/_2$ h. TLC (silica gel/chloroform) revealed that two porphyrins were produced: the one migrated near the solvent front was etioporphyrin II and the other, which exhibited a very faint fluorescence, was the diporphyrin **1**. To facilitate separation of **1** from the remaining dark-colored waste, the mixture, after removal of the benzene solvent, was heated in dichloromethane with methanolic copper(II) acetate. The red copper porphyrins were isolated by chromatography on silica gel (CH_2Cl_2). Copper was then removed by shaking the eluent with 12 N sulfuric acid. After neutralization and back extraction the two demetalated porphyrins were separated by column chromatography (silica gel/CH_2Cl_2): yield, 80 mg of **1** and 150 mg of etioporphyrin II. NMR of **1**: δ 1.27 (12 H, t, Et), 1.66 (12 H, t, Et), 1.87 (12 H, s, Me), 3.17 (12 H, s, Me), 3.38 (8 H, q, Et), 3.9 (8 H, 2 q, Et), 7.58 (2 H, t, 2, 7H-an), 7.71 (2 H, t, 3,6H-an), 8.50 (2 H, d, 4,5H-an), 8.90 (1 H, s, 10H-an), 8.95 (4 H, s, meso-H), 9.00 (1 H, s, 9H-an), 9.34 (2 H, s, meso-H), −4.98 (4 H, br, NH); MS, *m/e* 1131 (89), 1130 (100), 565 (81); high-resolution MS, 1130.6670 ($C_{78}H_{82}N_8$); UV–vis λ_{max} (ϵ_{mM}) 625 nm (4.0), 572 (9.0), 537 (10), 503 (22), 394 (232). Anal. Calcd: C, 82.79; H, 7.30; N, 9.90. Found: C, 82.81; H, 7.41; N, 9.85.

5-Phenyl-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphine (8). Phenyldipyrrylmethane **6** (470 mg, 1.5 mmol) and dipyrrylmethene **7** (650 mg, 1.55 mmol) were dissolved and heated to reflux in benzene (80 mL) for 1 h. After cooling, tetrachloro-*o*-benzoquinone (200 mg) was added to complete oxidation. The products were chromatographed on a silica gel column with dichloromethane/hexane mixture as eluent to yield 160 mg (17.8%) of the desired monophenylporphyrin. A small amount (30 mg) of etioporphyrin II, which was eluted first, was also obtained. **8**: NMR δ 1.81 (6 H, t, Et), 1.90 (6 H, t, Et), 2.45 (6 H, s, Me), 3.69 (6 H, s, Me), 4.05 (8 H, 2 q, Et), 7.78 (3 H, m, 3,4,5H–Ph), 8.05 (2 H, d, 2, 6H-Ph), 9.96 (1 H, s, meso-H), 10.15 (2 H, s, meso-H), −3.3 (2 H, br, NH); MS *m/e* 554 (100), 277 (34); UV–vis λ_{max} (ϵ_{mM}) 626 nm (2.5), 559 (6.7), 534 (7.0), 501 (15.5), 402 (188). Anal. Calcd for $C_{38}H_{42}N_4$: C, 82.27; H, 7.63; N, 10.10. Found: C, 82.14; H, 7.71; N, 10.17.

Octaethylporphyrin from the [(Methoxymethyl)dipyrryl]methene Condensation. [5,5′-Bis(bromomethyl)-3,4,3′,4′-tetraethyl-2,2′-dipyrryl]methene hydrobromide[18] (12 g) in methanol (200 mL) was heated under reflux for 30 min. The mixture was evaported to dryness and the residue triturated with ether/methanol (5:1). The resultant [(methoxymethyl)dipyrryl]methene (7.5 g) was used without further purification to condense with (3,4,3′,4′-tetraethyl-2,2′-dipyrryl)methane[8] in hot benzene. After oxidation by *o*-chloroanil, octaethylporphyrin was isolated in 28% yield: NMR δ 1.09 (24 H, t, Et), 2.40 (16 H, q, Et), 10.1 (4 H, s, meso-H), −3.88 (2 H, br, NH); mp 324 °C (lit.[19] mp 324–325 °C). This porphyrin was identical in every respect with an authentical sample of OEP.

Acknowledgment. This work was supported by NSF. C.K.C. is an Alfred P. Sloan Fellow, 1980–1984, and a recipient of Camille and Henry Dreyfus Teacher–Scholar Grant, 1981–1985. We thank Professor Dolphin for the access to the UBC Mass Spectrometry Facilities.

Registry No. 1, 87597-38-4; 2, 34824-75-4; 3, 4949-58-0; **4a**, 87597-39-5; **4b**, 87597-40-8; **4c**, 87597-41-9; 5, 87597-42-0; 6, 87597-43-1; 7, 87597-44-2; 8, 87597-45-3; (3,3′-diethyl-4,5,4′,5′-tetramethyl-2,2′-dipyrryl)methene hydrobromide, 66145-65-1; [5,5′-bis(bromomethyl)4,4′-dimethyl-3,3′-diethyl-2,2′-dipyrryl]-methene hydrobromide, 87597-46-4; benzaldehyde, 100-52-7; α,α-[5,5′-bis(ethoxycarbonyl)-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrryl]toluene, 87597-47-5; α,α-[5,5′-dicarboxy-4,4′-diethyl-3,3′-dimethyl-2,2′-dipyrryl]toluene, 87597-48-6; [5,5′-bis(bromomethyl)-3,4,3′,4′-tetraethyl-2,2′-dipyrryl]methene hydrobromide, 87597-49-7; [5,5′-(methoxymethyl)-3,4,3′,4′-tetraethyl-2,2′-dipyrryl]methene hydrobromide, 87597-50-0; (3,4,3′,4′-tetraethyl-2,2′-dipyrryl)methane, 65858-34-6; octaethylporphyrin, 2683-82-1.

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Poly(ethylene glycol) Ethers as Recoverable Phase-Transfer Agents in Permanganate Oxidations

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There has been much recent interest in poly(ethylene glycols) (PEG'S) as inexpensive, nontoxic, thermally stable phase-transfer agents (PTA's).[1-3] In our work we have demonstrated the added feature of recovery of the PEG by precipitation.[1] One problem with PEG's as PTA's is the difficulty in controlling PEG partitioning between aqueous and organic phases. In general, PEG partitions almost totally in favor of water relative to the organic layer (e.g., 99.9% PEG in water vs. benzene); an exception is methylene chloride, where the partitioning shifts dramatically in the other direction (75–99% PEG in methylene chloride vs. water, depending on concentration).[1] This difficulty can be avoided by conducting reactions without an aqueous phase (solid–liquid phase transfer) or by preparing derivatized PEG's, providing control of partitioning between aqueous and organic layers; here we describe an approach to the latter solution using PEG alkyl ethers.

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