Experimental Section

General. FTIR spectra for solids were obtained by diffuse reflectance. IR data are reported in cm^{-1}. Analyses by GC/MS (EI and CI-H_2 modes) employed a HP-1 (0.2-mm-i.d. × 12.5-m and 0.33-μm film, β = 150) capillary column while HPLC/PB/MS used a 5-μm C18 column with MeOH/H_2O solvents. Routine NMR spectra, ^1H (80 MHz) and ^{13}C (20 MHz), were run in $CDCl_3$ vs TMS. Other NMR data are specifically noted. Suitable data and spectra were obtained to match the literature data for all known compounds. When spectral data for known compounds was not available in the literature, it was included herein. Preparative plate chromatography was done on 20- × 20-cm silica gel 60 (PLK-F254) plates. Melting points were taken in capillary tubes and are reported uncorrected. Representative procedures are included.

Chalcone (10) and 2-Aminocrotononitrile (11) (Chatterjea's Reaction).[13] NaOEt/EtOH was generated by adding Na chips (1.0 g, 43.5 mmol) to 25 mL of absolute EtOH under N_2. After cooling 11 (3.28 g, ~85%, ~43.5 mmol) was added. After a short time, 10 (4.16 g, 20.0 mmol) was added, and the mixture was refluxed for 2 h. The reaction mixture was allowed to cool and recrystallize at rt for several days before being poured into 5% aqueous HCl and extracted with CH_2Cl_2. The solvent was dryed with anhyd Na_2SO_4 and evaporated in vacuo. The residual oil was recrystallized from hexane/acetone to give 0.92 g (16.9%) of 3-cyano-2-methyl-4,6-diphenyl-1,4,5,6-tetrahydropyridine (13): mp 201–206 °C [lit.[13] mp 207–208 °C (incorrectly reported as the dihydro compound)]; IR 3292 (NH), 2185 (C≡N); MS 274 (M^+, 100), 273 (26), 197 (24), 169 (28), 104 (42).

The mother liquid was evaporated and the residue recrystallized from EtOH to give in two crops 1.675 g (31.1%) of 3-cyano-2-methyl-4,6-diphenylpyridine (14): mp 117.5–118 °C (lit.[29] mp 121.5–122.5 °C).

General Procedure Using Base. 9 (1.08 g, 10.0 mmol) was dissolved in 25 mL of EtOH containing NaOEt (14 mmol). 10 (1.04 g, 5.0 mmol) was added, and the mixture was boiled under N_2 for 44 h. The EtOH was removed. The residue was partioned between CH_2Cl_2 and water. *NOTE: The water layer was treated with bleach before disposal to convert any free cyanide to harmless cyanate ion.* The CH_2Cl_2 was then treated with 3 M HCl [**HOOD**!] with efficient mixing for 30 min. Finally, the CH_2Cl_2 layer was extracted with 5% NaOH solution (to remove cyano ketone), washed with water, dried, and filtered through a short pad of silica gel. The column was sequentially rinsed with 50 mL each of $CHCl_3$ and EtOAc. Evaporation of the solvents gave 1.23 g of crude mixture. Analysis by GC/MS showed this to contain 786 mg (2.91 mmol, 58.3%) of 2,4-diphenyl-6,7-dihydro-5*H*-1-pyrindine (18). Recrystallization from cyclohexane/EtOAc gave material with mp 141–3 °C. Sublimation gave pure 18: mp 147–8 °C (lit.[20,22] mp 144–146 °C); MS 271 (M^+, 76), 270 (100), 215 (5), 165 (8); ^1H NMR (300 MHz) δ 2.20 (m, 2 H), 3.10 (t, 2 H, J = 7.28), 3.20 (t, 2 H, J = 7.63), 7.35–7.60 (m, 9 H), 8.01–8.05 (m, 2 H); ^{13}C NMR (75.7 MHz), δ 23.52, 30.62, 34.79, 118.06, 126.98, 128.15, 128.22, 128.42, 128.60, 128.63, 133.05, 139.06, 139.98, 145.88, 156.50, 166.67. Neutralization of the 3 M HCl and extractive workup gave only 59 mg of crude products, containing only a trace (0.6%) of 18. A similar reaction used a 1:1 ratio of 9 to 10. It was boiled overnite and allowed to stand for several days before workup. A 71% yield of 18 was obtained.

General Procedure Using Acid. 9 (1.08 g, 10.0 mmol) and 10 (1.04 g, 5.0 mmol) were added to NH_4OAc (1.16 g, 15 mmol) in 15 mL of HOAc and boiled under N_2 for 17 h. The HOAc was evaporated. The residue was partitioned between water [NOTE: see above caution] and CH_2Cl_2. The CH_2Cl_2 layer was treated with 3 M HCl [**HOOD**] for 30 min before being extracted with 5% NaOH solution. The organic layer was dried with $CaCl_2$ and evaporated to give 1.34 g of product. GC/MS analysis (external standard) indicated that 89% of this was 18, which calculates to an 88% yield of the desired product.

2-Aminocyclopentanecarbonitrile (9):[18] ^1H NMR δ 1.86–1.98 (m, 2 H), 2.40–2.49 (m, 2 H), 2.5–2.6 (m, 2 H), 4.57 (s, 2 H); ^{13}C NMR δ 21.90, 31.15, 34.18, 74.17, 119.0, 162.44.

2-Amino-2-[(2-cyano-1-penten-1-yl)amino]cyclopentanecarbonitrile (19):[17] IR 3397 and 3344 (NH_2), 3142 (NH), 2256 and 2182 (C≡N); MS 216 (M^+, 0.15), 176 (42), 162 (13), 149 (100), 109 (9), 54 (9); ^1H NMR δ 1.6–3.1 (m, 12 H), 4.0–5.5 (3 broad signals, 4 H).

(*E*)-3-Amino-2-methyl-2-pentenonitrile (20):[21] IR 3362 and 3239 (NH_2), 2181 (C≡N); MS 110 (M^+, 100), 109 (87), 95 (9), 82 (38), 69 (28), 56 (76).

2-Ethyl-3-methyl-4,6-diphenylpyridine (21):[22] bp 155 °C (0.1 Torr); MS 273 (M^+, 31), 272 (100), 257 (6), 244 (4).

4-Amino-1,2,5,6-tetrahydro-1-methylnicotinonitrile (22):[23] IR 3400 and 3169 (NH_2), 2176 (C≡N); MS 137 (M^+, 33), 136 (100), 119 (14), 95 (14), 94 (15).

6-Methyl-2,4-diphenyl-5,6,7,8-tetrahydro-1,6-naphthyridine (23): mp 141–6 °C; IR 776 and 698 (Ar); MS 300 (M^+, 52), 299 (100), 285 (12), 256 (6), 215 (7), 154 (11); ^1H NMR (300 MHz) δ 2.379 (s, 3 H), 2.807 (t, 2 H), 3.223 (t, 2 H), 3.47 (s, 2 H), 7.2–7.5 (m, 9 H), 7.96–7.99 (m, 2 H); ^{13}C NMR (75.47 MHz) δ 32.96, 45.95, 52.91, 55.87, 118.92, 125.83, 126.75, 127.93, 128.19, 128.34, 128.49, 138.56, 148.41, 154.64, 154.97; MS (high-resolution) calcd for $C_{21}H_{20}N_2$ 300.16265, found 300.16193.

(*E*)-3-Phenyl-1-(2-pyridyl)prop-2-en-1-one (24):[24] IR 1698 and 1670 (C=O); MS 209 (M^+, 73), 181 (19), 180 (100), 131 (27), 103 (45), 102 (33), 77 (19).

4-Phenyl-2-(2-pyridyl)-6,7-dihydro-5*H*-1-pyrindine (25): mp 133–135 °C; IR 775 and 700 (Ar); MS 272 (M^+, 67), 271 (100), 193 (4), 165 (4), 135 (5), 78 (8), 51 (7). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.71; H, 6.00; N, 10.30.

(*E*)-2-Benzylidenecyclohexanone (26):[25] IR 1680(C=O); MS 186 (M^+, 61), 185 (100), 129 (43), 115 (48), 102 (12).

9-Phenyl-1,2,3,4,5,6,7,8-octahydroacridine (28):[26] MS 263 (M^+, 100), 262 (96), 234 (16), 165 (11), 109 (10).

(*E*,*E*)-2,6-Dibenzylidenecyclohexanone (29):[27] IR 1662 (C=O); MS 274 (M^+, 76), 273 (100), 217 (14), 129 (10), 128 (14), 115 (36), 91 (12), 77 (11); ^1H NMR δ 1.74 (m, 2 H), 2.88 (m, 4 H), 7.27–7.47 (m, 10 H), 7.79 (m, 2 H).

1-Benzylidine-9-phenyl-1,2,3,4,5,6,7,8-octahydroacridine (30): mp 167–169 °C; IR 754 and 694 (Ar); MS 351 (M^+, 57), 350 (100), 322 (13), 274 (10), 91 (9). Anal. Calcd for $C_{28}H_{25}N$: C, 88.85; H, 7.17; N, 3.98. Found: C, 88.48; H, 7.11; N, 3.96.

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Synthesis of a 1,2-Phenylene-Bridged Triporphyrin

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Since the first report of a covalently-linked cofacial triporphyrin,[1] several cofacial triporphyrins[2] have appeared

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0022-3263/92/1957-7355$03.00/0

Table I. Physical Properties of 1, 2, and 3

porphyrin	absorption[a] λ_{max} (nm) Soret	Q bands	fluorescence[a] λ_{max} (nm)	ϕ_{rel}[b] (%)	$E(S_1)$[c] (cm^{-1})	$E_{1/2}$[d] (V)	^{1}H-NMR data ($CDCl_3$, ppm) meso-H	NH
1-H_2	407	505, 537 576, 629	631, 698	100	15900	0.33, 0.55	10.22	−2.42
2-H_4	382	512, 531 593, 640	674, 725	21	15200	0.15,[e] 0.31[e] 0.49,[e] 0.65[e]	8.39	−5.77, −6.31
3-H_6	373	523, 563 597, 652	693	9	14900	−0.08,[e] 0.34[e] 0.56,[e] 0.67,[e] 0.89[e]	7.59 6.54	−5.74, −7.05 −8.32
1-Zn	415	506, 545 578	584, 638	100	17200	0.13, 0.33	10.18	
2-Zn_2	402	500, 547 568, 593, 616	646	13	15900	−0.02, 0.18 0.38, 0.50	8.33	
3-Zn_3	396	563, 591 607, 652	671	12	15100	*f*	7.40[g] 6.80[g]	

[a] In THF. [b] Relative fluorescence intensity to the corresponding monomer. [c] Energy of the lowest singlet excited state. [d] One-electron oxidation potentials (vs ferrocene/ferrocenium) measured by cyclic voltammetry at a Pt electrode in CH_2Cl_2 containing 0.1 M n-Bu_4NClO_4 at 20 °C. [e] Peak potentials. [f] Not measured. [g] In $CDCl_3$–pyridine-d_5 (1:1).

in the literature as an extension of cofacial diporphyrin systems. These cofacial oligoporphyrins have attracted considerable interest not only in the area of intramolecular energy and/or electron-transfer reactions,[3] but also in the area of catalysis of electrochemical reduction of oxygen to water by a four-electron mechanism.[4,5]

We have recently reported the synthesis, properties, and molecular structure of a 1,2-phenylene-bridged diporphyrin **2**, and clarified its strong intramolecular porphyrin-porphyrin interactions.[6,7] As an extension of this approach, the synthesis of a 1,2-phenylene-bridged triporphyrin 3-H_6 is described here.

First, we attempted Chang's strategy[2a] which had been employed in the synthesis of an anthracene-pillared triporphyrin, i.e., the homocondensation of a formyl-substituted porphyrin with equimolar amounts of an α,α'-free dipyrrolylmethane under our improved conditions.[2e] Thus, 5-(2-formylphenyl)-15-tolyloctaalkylporphyrin (**4**)[6] and bis(3-ethyl-4-methylpyrrol-2-yl)methane (**5**)[8] were condensed in the presence of 2 equiv of trichloroacetic acid in CH_3CN, and the resulting reaction mixture was oxidized with *p*-chloranil. However, only a complicated mixture was formed in low yield. Although mass analysis of this mixture revealed the formation of the desired triporphyrin, its yield was too low to allow its further characterization.

In the second attempt, we examined a stepwise reaction sequence summarized in Scheme I. Cross-condensation of the formyl-substituted porphyrin **4** and monoprotected phthalaldehyde **6** and **5** in the presence of 3.6 equiv of trichloroacetic acid in CH_3CN followed by oxidation with *p*-chloranil gave stereoselectively a formyl-substituted diporphyrin **7**. The compound **6** was used in 7-fold excess toward **4**, and the diporphyrin **7** was obtained in 46% yield based on the amount of **4** used. In principle, another atropisomer could result from this reaction, but the ^{1}H-NMR spectrum shows that the obtained diporphyrin is composed of only one atropisomer. Probably, the steric bulk of the 5,5-dimethyl-1,3-dioxacyclohex-2-yl substituent does not allow the formation of the other, endo isomer.

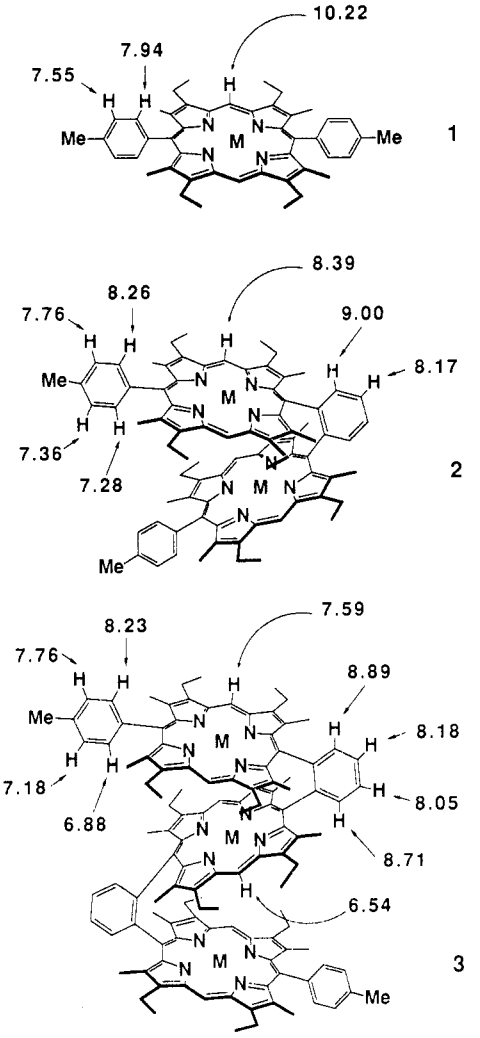

Figure 1. Structures of porphyrin models **1**, **2**, and **3**. Selected chemical shifts of the corresponding free bases are indicated. Chemical shifts of the pyrrole nitrogen protons are listed in Table I.

Subsequent hydrolysis of the acetal group in **7** under acidic conditions yielded the formyl-substituted diporphyrin **8** without atropisomerization. Then, the diporphyrin **8** was condensed with tolualdehyde (9-fold excess toward **8**) and **5** with the aid of trichloroacetic acid catalysis. The subsequent oxidation with *p*-chloranil and separation by silica

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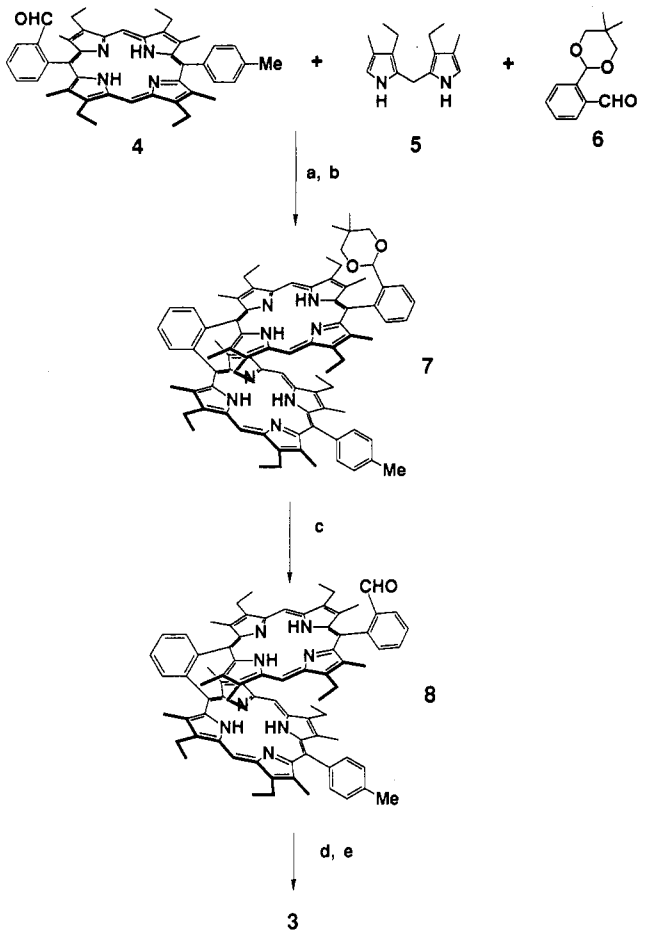
Scheme I. Synthetic Scheme to 3-H_6[a]



[a] (a) CCl_3CO_2H, CH_3CN, room temperature, 18 h; (b) *p*-chloranil, THF, room temperature, overnight; (c) CF_3CO_2H, 10% H_2SO_4, CH_2Cl_2, reflux, 4 h; (d) CCl_3CO_2H, CH_3CN, room temperature, 22 h; (e) *p*-chloranil, THF, room temperature, overnight.

gel flash column chromatography gave the triporphyrin 3-H_6 in 40% yield, based on the amount of 8 used. In this reaction, we could not detect the pentameric porphyrin which might be formed from self-condensation of 8.

The ^{1}H-NMR spectrum of 3-H_6 indicates its "Z"-shape structure, giving two sets of data for different porphyrins in a ratio of 2:1. One is for the outer two porphyrins, and the other is for the inner porphyrin. Chemical shifts of the selected protons are indicated in Figure 1. Typically, the meso protons appear at 10.22 ppm in 1-H_2, 8.39 ppm for 2-H_4, and 7.59 and 6.54 ppm for the outer and inner porphyrins in 3-H_6, respectively. The pyrrole nitrogen protons appear at −2.42 ppm for 1-H_2, −5.77 and −6.31 ppm for 2-H_4, −5.74 and −7.04 ppm for the outer porphyrin, and −8.32 ppm for the inner porphyrin in 3-H_6 (Table I), respectively. These observations are in line with a "Z"-shape structure of 3, in that the inner porphyrin experiences a much stronger ring-current shielding effect due to the presence of a doubly stacked porphyrin.

The triporphyrin 3-H_6 undergoes metalation in a unique manner. The triporphyrin 3-H_6 gave quantitatively a bis-zinc complex of the triporphyrin 3-H_2Zn_2 after refluxing with $Zn(OAc)_2$ in CH_2Cl_2 or $CHCl_3$ for 4 h. The metalation sites of 3-H_2Zn_2 still remain to be fully determined but are most probably assigned to the outer porphyrins, since serious steric hindrance may be expected for metalation at the inner porphyrin. Complete zinc insertion was only achieved by refluxing with $Zn(OAc)_2$ in $CHCl_3$ containing a small quantity of triethylamine or in pyridine for 2 h.

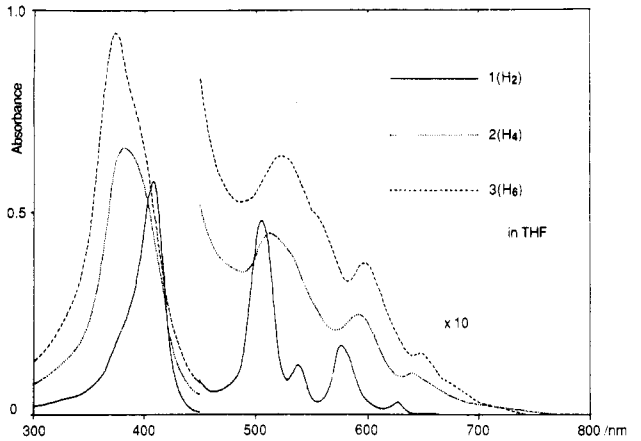


Figure 2. Absorption spectra of 1-H_2, 2-H_4, and 3-H_6 in THF. Concentrations are 2.4×10^{-6} M.

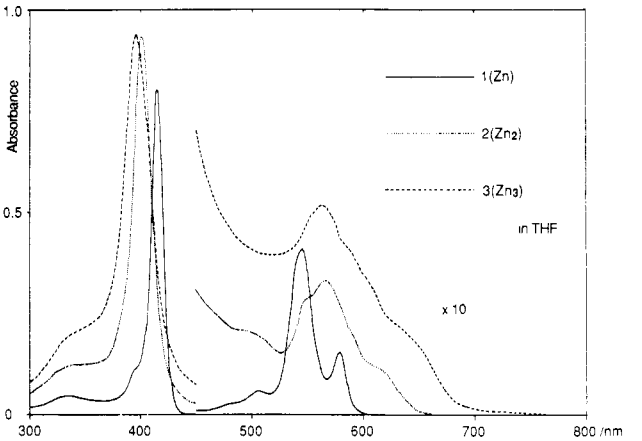


Figure 3. Absorption spectra of 1-Zn, 2-Zn_2, and 3-Zn_3 in THF. Concentrations are 1.6×10^{-6} M.

The absorption and fluorescence spectra of these porphyrins are shown in Figures 2–4. The absorption and fluorescence properties of 3-H_6 and 3-Zn_3 are summarized in Table I, together with the data for the monomers 1, 1-Zn, diporphyrins 2, and 2-Zn_2 for comparison. The Soret bands of 3-H_6 and 3-Zn_3 are blue-shifted, compared to those observed for 1 or 2. The visible bands are exceedingly broadened and red-shifted. The fluorescence bands are also red-shifted in the order of 1 > 2 > 3, and the relative fluorescence quantum yield decreases in the same order. On the basis of the absorption and fluorescence spectra, the energy level of the lowest singlet excited states of 3-H_6 and 3-Zn_3 were estimated to be lower than that of the corresponding monomer by 1000 and 2100 cm^{-1}, respectively. Cyclic voltammetry of 3-H_6 in CH_2Cl_2 showed a complicated irreversible oxidation curve. The values of the one-electron oxidation peak potentials are listed in Table I. These data indicate that the triporphyrin 3-H_6 undergoes one-electron oxidation even more easily than diporphyrin 2. Unfortunately, the electrochemical properties of the zinc complex 3-Zn_3 could not be measured due to its quite limited solubility in most of organic solvents, but on the basis of the result of the free-base triporphyrin 3-H_6, it may be reasonable to assume lower oxidation potentials for 3-Zn_3 than 2-Zn_2. Now we are preparing different metal complexes of 2-H_4 and 3-H_6 such as copper(II) or iron(III) to study the interactions of the metal complexes in close proximity.

Incorporation of this triporphyrin unit into a more elaborate photosynthetic model is also under way and will be reported elsewhere.

Experimental Section

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Oxidation potentials were measured by cyclic voltammetry at a Pt electrode in CH_2Cl_2 containing 0.1 M n-Bu_4NClO_4 as supporting electrolyte on a PAR Model-174 polarographic analyzer. UV–visible spectra were recorded on Shimadzu and UV-3000 spectrometers. Steady-state fluorescence spectra were recorded by using a Shimadzu RF-502A spectrofluorimeter. ^{1}H-NMR spectra were recorded on a JEOL GX-400 spectrometer, and the isotope peaks in deuterated solvents were used as internal standards. Chemical shifts are reported in the δ scale (ppm) relative to tetramethylsilane. Mass spectra were recorded on JEOL DX-300 and HX-110 spectrometers. Mass spectra of porphyrins were measured by the FAB method; the matrix was $CHCl_3$/m-nitrobenzyl alcohol unless otherwise stated. Infrared spectra were taken on a Horiba FT-300 spectrometer. Preparative separations were usually performed by flash column chromatography on silica gel (Merck, Kieselgel 60H, Art. 7736).

For synthetic use, all reagents and solvents of the commercial reagent grade were used without further purification except where noted. THF was stored over potassium hydroxide and was passed through an alumina short column before use. Dry CH_3CN was obtained by reflux and distillation from P_2O_5 and anhydrous K_2CO_3 and stored over molecular sieves under nitrogen.

2-(5,5-Dimethyl-1,3-dioxacyclohex-2-yl)benzaldehyde (6). 2-Formylbenzoic acid (55.3 g, 0.37 mol), iodomethane (98 g, 0.69 mol), and K_2CO_3 (28 g, 0.20 mol) were heated in 200 mL of DMF. After refluxing for 1 h, the reaction mixture was poured into 300 mL of water and then extracted with CH_2Cl_2. The organic layer was washed successively with water, aqueous HCl, aqueous $NaHCO_3$, and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a colorless oil, which slowly crystallized to give methyl 2-formylbenzoate (60.5 g, 100%), mp 75 °C: ^{1}H NMR 3.98 (s, 3 H, CO_2Me), 7.66 (m, 1 H, Ar), 7.94 (m, 1 H, Ar), 7.97 (m, 2 H, Ar), and 10.62 (s, 1 H, CHO).

Methyl 2-formylbenzoate (60.5 g, 0.37 mol), 2,2-dimethyl-1,3-propanediol (42 g, 0.4 mol), and p-toluenesulfonic acid monohydrate (2 g) were dissolved in 150 mL of benzene, and the mixture was heated for 3 h under reflux using a Dean–Stark apparatus, to remove water from the reaction mixture. The reaction mixture was cooled, poured into aqueous $NaHCO_3$, and extracted with benzene. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The product was distilled in vacuo (0.2 mmHg, 135 °C) to give a colorless oil, which slowly solidified to yield methyl 2-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)benzoate (85.6 g, 0.34 mol, 93%), mp 50 °C: IR (KBr) 2950, 1728, 1724, 1295, 1130, 1106, and 752 cm^{-1}; ^{1}H NMR 0.80 (s, 3 H), 1.29 (s, 3 H), 3.71 and 3.76 (AB q, 4 H), 3.90 (s, 3 H, CO_2Me), 6.17 (s, 1 H), 7.39 (t, 1 H, Ar), 7.55 (t, 1 H, Ar), 7.84 (d, 1 H, Ar), and 7.89 (d, 1 H, Ar).

Methyl 2-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)benzoate (33 g, 0.13 mol) was dissolved in THF, and this solution was cooled to 0 °C. Lithium aluminum hydride (LAH, 5 g, 0.13 mol) was added slowly to this solution. The mixture was stirred at 0 °C under nitrogen for 4 h. Ethyl acetate was carefully added to quench excess LAH. The reaction mixture was poured into 1 N aqueous HCl and extracted with CH_2Cl_2. The organic layer was washed successively with aqueous $NaHCO_3$, water, and brine and dried over anhydrous Na_2SO_4. Hexane was added to this solution, which was concentrated to give colorless needles of 2-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)benzyl alcohol (31.2 g, 100%), mp 71–73 °C: IR (KBr) 3470, 2964, 2952, 1471, 1218, 1114, 1054, and 767 cm^{-1}; ^{1}H NMR 0.83 (s, 3 H), 1.34 (s, 3 H), 3.08 (t, 1 H, OH), 3.71 (d, 2 H), 3.81 (d, 2 H), 4.75 (d, 2 H, benzyl), 5.57 (s, 1 H), 7.35 (m, 3 H, Ar), and 7.55 (dd, 1 H, Ar).

To a suspension of PCC (38 g, 0.18 mol) and anhydrous sodium acetate (10 g) in 100 mL of dry CH_2Cl_2 was added slowly a solution of 2-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)benzyl alcohol (31.2 g, 0.13 mol) in 150 mL of dry CH_2Cl_2, and the mixture was stirred for 3 h. Additional PCC (5 g) was added, and stirring was continued for 2 h. Then, 300 mL of ether was added to the reaction mixture, and the liquid phase was separated by decantation. The residual gummy solids were repeatedly washed with ether, and the combined liquid phase was passed through a short Florisil column, washed with water, dried, and evaporated. Colorless crystals of 6 (28.3 g, 0.13 mol, 98%) were obtained, mp 42 °C: IR (KBr) 2978, 2954, 1695, 1687, 1216, 1110, 1106, and 763 cm^{-1}; ^{1}H NMR 0.83 (s, 3 H), 1.31 (s, 3 H), 3.74 (d, 2 H), 3.81 (d, 2 H), 6.02 (s, 1 H), 7.51 (t, 1 H, Ar), 7.62 (t, 1 H, Ar), 7.80 (d, 1 H, Ar), 7.90 (d, 1 H, Ar), and 10.43 (s, 1 H, CHO). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.67; H, 7.31.

15-[2-(5,5-Dimethyl-1,3-dioxacyclohex-2-yl)phenyl]-15′-(4-methylphenyl)-5,5′-(1,2-phenylene)bis(2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine) (7). The formyl-substituted porphyrin 4 (202 mg, 0.3 mmol) and 2-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)benzaldehyde (6) (463 mg, 2.1 mmol) were dissolved in 12 mL of dry CH_3CN containing trichloroacetic acid (176 mg, 1.1 mmol). Then, the dipyrrolylmethane 5 (553 mg, 2.4 mmol) was added, and the mixture was stirred for 18 h in the dark under nitrogen. p-Chloranil (0.89 g, 3.6 mmol) was added, and the mixture was stirred overnight. The reaction mixture was poured into water and extracted several times with CH_2Cl_2. The combined organic layers were washed twice with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, treated with $Zn(OAc)_2$, and evaporated. Porphyrin products were separated by flash chromatography on a silica gel column with elution by CH_2Cl_2 and treated with aqueous HCl to give the corresponding free-base porphyrin mixture, consisting of monomeric porphyrins and 7, which were separated by silica gel flash column chromatography. The monomeric porphyrins were eluted with CH_2Cl_2, and 7 was eluted with CH_2Cl_2/MeOH (98/2). After evaporation of the solvent, the product was triturated with MeOH to give blue crystals of 7 (181 mg, 0.14 mmol, 46% based on the amount of 4 used), mp 295–297 °C: mass m/z 1312 (calcd for $C_{89}H_{98}N_8O_2$ 1311.8); IR (KBr) 2962, 2958, 2927, 1468, 1448, 1111, 1095, 1059, and 756 cm^{-1}; ^{1}H NMR −6.46 (br, 1 H, NH), −6.32 (br, 1 H, NH), −5.79 (br, 1 H, NH), −5.74 (br, 1 H, NH), −0.21 (s, 3 H, acetal), 1.01 (s, 3 H, acetal), 1.29 (t, 6 H, Et), 1.31 (t, 6 H, Et), 1.46 (t, 6 H, Et), 1.48 (t, 6 H, Et), 1.90 (d, 2 H, acetal), 2.25 (s, 6 H, Me), 2.31 (s, 6 H, Me), 2.77 (s, 3 H, tolyl-Me), 2.89 (s, 12 H, Me), 2.90 (d, 2 H, acetal), 3.35 (m, 4 H, Et), 3.50 (m, 8 H, Et), 3.55 (m, 4 H, Et), 3.99 (s, 1 H, acetal), 7.27 (d, 1 H, Ar), 7.33 (d, 1 H, Ar), 7.67 (d, 1 H, Ar), 7.88 (t, 1 H, 2-acetal phenyl), 7.93 (t, 1 H, 2-acetal phenyl), 8.01 (d, 1 H, 2-acetal phenyl), 8.14 (d, 1 H, Ar), 8.15 (m, 2 H, 1,2-phenylene-Ar), 8.22 (d, 1 H, 2-acetal phenyl), 8.35 (s, 2 H, meso-H), 8.37 (s, 2 H, meso-H), and 8.98 (m, 2 H, 1,2-phenylene-Ar).

15-(2-Formylphenyl)-15′-(4-methylphenyl)-5,5′-(1,2-phenylene)bis(2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine) (8). The porphyrin 7 (130 mg, 0.1 mmol), trifluoroacetic acid (4 mL), 10% H_2SO_4 (1 mL), and 20 mL of CH_2Cl_2 were mixed, and the resulting solution was refluxed for 4 h, cooled to room temperature, and poured into water. The organic layer was washed successively with water, aqueous $NaHCO_3$, and brine, dried over anhydrous Na_2SO_4, and evaporated. The residue was triturated with MeOH to give blue-violet crystals of 8 (118 mg, 0.1 mmol, 97%), mp >300 °C: mass m/z 1226 (calcd for $C_{84}H_{88}N_8O$ 1224.7); IR (KBr) 2962, 2927, 2870, 1695, 1597, 1448, and 754 cm^{-1}; ^{1}H NMR −6.35 (br, 1 H, NH), −6.34 (br, 1 H, NH), −5.74 (br, 1 H, NH), −5.69 (br, 1 H, NH), 1.30 (t, 6 H, Et), 1.31 (t, 6 H, Et), 1.50 (t, 6 H, Et), 1.52 (t, 6 H, Et), 2.21 (s, 6 H, Me), 2.33 (s, 6 H, Me), 2.78 (s, 3 H, tolyl-Me), 2.89 (s, 6 H, Me), 2.91 (s, 6 H, Me), 3.37 (m, 4 H, Et), 3.49 (m, 8 H, Et), 3.54 (m, 4 H, Et), 7.29 (d, 1 H, Ar), 7.36 (d, 1 H, Ar), 7.69 (d, 1 H, Ar), 8.00 (t, 1 H, 2-formylphenyl), 8.11 (t, 1 H, 2-formylphenyl), 8.13 (d, 1 H, Ar), 8.17 (m, 2 H, 1,2-phenylene), 8.23 (d, 1 H, Ar), 8.38 (s, 2 H, meso-H), 8.39 (s, 2 H, meso-H), 8.42 (d, 1 H, 2-formylphenyl), 8.63 (s, 1 H, CHO), and 8.99 (m, 2 H, 1,2-phenylene).

2,8,12,18-Tetraethyl-5,15-bis{2-[2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(4-methylphenyl)porphin-5-yl]-phenyl}-3,7,13,17-tetramethylporphine (3-H_6). The formyl-substituted dimeric porphyrin 8 (78 mg, 0.064 mmol) and p-tolualdehyde (69 mg, 0.57 mmol) were dissolved in 8 mL of dry CH_3CN containing trichloroacetic acid (94 mg, 0.57 mmol). Then the dipyrrolylmethane 5 (147 mg, 0.64 mmol) was added, and the mixture was stirred for 22 h in the dark under nitrogen. p-Chloranil (235 mg, 096 mmol) was added, and stirring was continued overnight. The reaction mixture was poured into water and extracted several times with CH_2Cl_2. The combined organic layers were washed twice with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and evaporated. The residual mixture consisted of monomeric porphyrin 1, diporphyrin 8, and the desired tri-

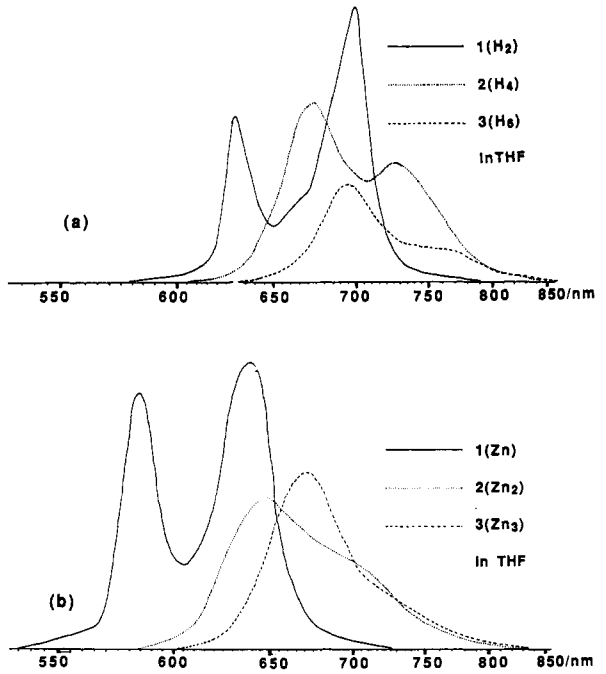


Figure 4. Fluorescence spectra of 1-H_2, 2-H_4, and 3-H_6 (the upper) and of 1-Zn, 2-Zn_2, and 3-Zn_3 (the lower) in THF excited at their respective Soret maxima. The fluorescence intensities of the monomers were one-fifth those of the dimers and trimers.

porphyrin 3-H_6 and was separated by flash chromatography on a silica gel column. The monomeric porphyrin 1 was eluted with CH_2Cl_2, and the diporphyrin 8 was eluted with CH_2Cl_2/THF (97/3 to 90/10). The triporphyrin 3-H_6 was eluted with CH_2Cl_2/THF (90/10 to 50/50), which was crystallized from CH_2Cl_2/MeOH to give blue crystals (45 mg, 0.026 mmol, 40% based on the amount of 8 used). Upon refluxing with $Zn(OAc)_2$ in CH_2Cl_2 or $CHCl_3$ solution for 4 h, 3-H_6 provided the bis-zinc complex of the triporphyrin 3-H_2Zn_2 (m/z 1892; calcd for $C_{122}H_{126}N_{12}Zn_2$ 1890.9) quantitatively. Complete zinc insertion in the porphyrin was achieved by refluxing for 2 h with $Zn(OAc)_2$ in either $CHCl_3$ containing a small quantity of triethylamine or in pyridine. 3-H_6: mp >300 °C; mass m/z 883 and 1765 (calcd for $C_{122}H_{130}N_{12}$ 1764.1); IR (KBr) 2962, 2927, 2870, 1460, 1448, and 752 cm^{-1}; ^1H NMR −8.32 (br, 2 H, NH), −7.05 (br, 2 H, NH), −5.74 (br, 2 H, NH), 0.88 (t, 12 H, Et), 1.10 (t, 12 H, Et), 1.21 (t, 12 H, Et), 2.16 (s, 12 H, Me), 2.54 (s, 12 H, Me), 2.62 (m, 4 H, Et), 2.73 (s, 6 H, tolyl-Me), 2.74 (s, 12 H, Me), 2.80 (m, 12 H, Et), 2.95 (m, 4 H, Et), 3.24 (m, 4 H, Et), 6.54 (s, 2 H, meso-H), 6.88 (d, 2 H, Ar), 7.18 (d, 2 H, Ar), 7.59 (s, 4 H, meso-H), 7.76 (d, 2 H, Ar), 8.05 (t, 2 H, Ar), 8.18 (t, 2 H, Ar), 8.23 (d, 2 H, Ar), 8.71 (d, 2 H, Ar), 8.89 (d, 2 H, Ar). 3-Zn_3: mp >300 °C; mass m/z 977, 1953 (calcd for $C_{122}H_{124}N_{12}Zn_3$ 1954.8); ^1H NMR (pyridine-d_6–$CDCl_3$ (1:1)) 1.12 (t, 12 H, Et), 1.44 (t, 24 H, Et), 2.43 (s, 12 H, Me), 2.77 (s, 6 H, tolyl-Me), 2.79 (s, 12 H, Me), 3.05 (s, 12 H, Me), 3.0–3.6 (m, 24 H, Et), 6.80 (s, 2 H, meso-H), 6.88 (br, 2 H, Ar), 6.95 (d, 2 H, Ar), 7.40 (s, 4 H, meso-H), 7.89 (broad, 2 H, Ar), 7.93 (d, 2 H, Ar), 8.08 (t, 2 H, Ar), 8.25 (t, 2 H, Ar), 8.80 (d, 2 H, Ar), and 9.14 (d, 2 H, Ar). The ^1H-NMR spectrum of 3-H_2Zn_2 could not be measured due to its limited solubility in most organic solvents.

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Supplementary Material Available: ^1H NMR spectra of 2, 3, 4, 6, 7, and 8 (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Ring Enlargement of Diaziridinone: Reactions with Bifunctionalized Carbanions Leading to Functionalized Pyrazolines or Novel Spiroheterocycles

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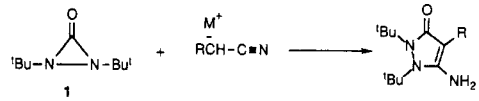
Much attention has been focused on the development of new synthetic reagents or new routes to functionalized heterocycles since the functional groups will allow novel uses of heterocycles. Ring enlargement reactions of small-ring heterocyclic compounds promoted by the release of large ring strain have provided versatile methods for the synthesis of medium-sized heterocycles.[1] Among these small rings, a diaziridinone[2] is expected to show high ring-opening reactivity because of its highly strained three-membered structure containing an sp^2 carbon and polar bonds.[1-3] In fact, cycloaddition and addition–cyclization reactions of diaziridinones leading to nitrogen-containing heterocycles have been reported by our group[4] and by Greene and co-workers.[5] In a previous paper,[4a] we reported that the ring enlargement reactions of *N,N'*-di-*tert*-butyldiaziridinone (1) with α-metalated nitriles led to aminopyrazolines via ring opening and recyclization.



(1)

The reactions of 1 with bifunctionalized carbanions derived from activated methylene compounds such as malononitrile and malonates instead of the above-mentioned monofunctionalized carbanions should give rise not only to multifunctionalized pyrazolines but also to novel spiroheterocyclic compounds. To test this hypothesis, we studied the ring enlargement reactions of diaziridinone 1 with some α-metalated malonic acid derivatives.

Treatment of *N,N'*-di-*tert*-butyldiaziridinone (1) with an equimolar amount of dicyano carbanion **3a**, generated from malononitrile (**2a**) and sodium hydride, in refluxing THF for 24 h afforded functionalized pyrazoline 3-amino-4-cyano-1,2-di-*tert*-butyl-3-pyrazolin-5-one (**4a**) in 31% yield. When 2 equiv of diaziridinone 1 was employed and the reaction was continued for 36 h, the isolated yield of pyrazolinone **4a** was improved to 92%. The structure of **4a** was determined from spectral data and elemental analysis. The amino group was detected by IR and ^1H NMR, and the existence of the cyano group was clearly supported by IR (2230 cm^{-1}) and ^{13}C NMR (δ 114.0). The

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