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# Conjugated Macrocycles Related to the Porphyrins. 25.† Proton NMR Spectroscopic Evidence for a Preferred [18]Annulene Substructure in Carbaporphyrins from the Magnitude of Selected $^4J_{H,H}$ CH═C−CH$_3$ Coupling Constants

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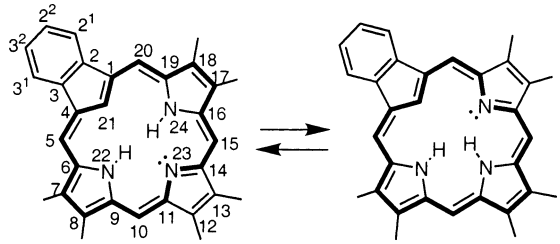
Two new benzocarbaporphyrins with four or five alkyl substituents have been synthesized by the "3 + 1" MacDonald methodology. At lower temperatures, the proton NMR spectrum of the asymmetrically substituted carbaporphyrin **8** gave two NH resonances, while carbaporphyrin **9**, which retains a plane of symmetry, gave only one resonance of this kind. As no additional peaks were seen for the remaining protons, these data strongly support the proposal that a single tautomer predominates in solution where the two NH protons flank the interior CH. Carbaporphyrin **8**, which has a CH═CMe unit on the pyrrolic ring opposite the indene moiety, gave a long-range coupling constant of $^4J_{Me,H}$ = 1.3−1.4 Hz. On the other hand, the CH═CMe units of **9**, which correspond to the pyrrole rings on each side of the carbocyclic moiety, gave $^4J_{Me,H}$ = 0.9−1.0 Hz. These values are in accord with those expected if the exterior carbon−carbon bonds of the pyrrole units next to the indene ring are part of a fully delocalized 18$\pi$ electron system, while the C═C bond of the remaining pyrrole ring retains substantial olefinic character.

## Introduction

Carbaporphyrins,[1] porphyrin analogues where one of the pyrrolic subunits has been replaced by a cyclopentadiene moiety, have emerged as an intriguing class of aromatic systems with unusual chemical and spectroscopic features.[2−6] Benzocarbaporphyrins **1** (Scheme 1),[2−4] the most easily synthesized members of this family, undergo regioselective oxidations with alcoholic ferric chloride solutions at the interior carbon atom to generate benzo[18]annulene ketals **2** in excellent yields,[5] while reactions with silver(I) acetate afford the corresponding silver(III) organometallic complexes **3** (Chart 1).[6] Together with the closely related azuliporphyrins,[4,7−10] carbaporphyrins are starting to rival the better studied N-confused porphyrins **4**[11] in terms of their unusual reactivity,[12] and their ability to form novel metal complexes.[6,10] Furthermore, carbaporphyrins provide a bridge between porphyrin and annulene chemistry,[1] and give insights into the aromatic characteristics of these macrocycles.[13]

**SCHEME 1**




A useful model for the aromaticity of porphyrins and related systems invokes the presence of an [18]annulene substructure within the macrocycle (**5**, shown in bold).[1,14−16]

† Part 24: Liu, D.; Lash, T. D. *Chem. Commun.* **2002**, 2426.

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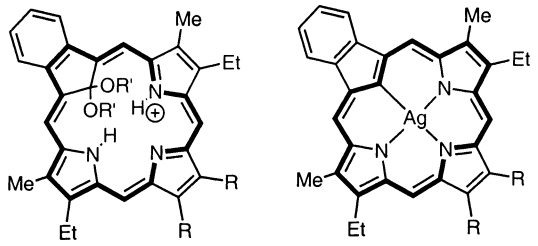
**CHART 1**



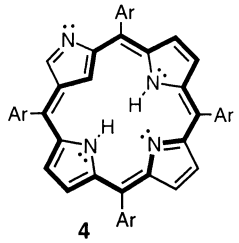
**2**

R = Et, Ph; R' = Me, Et, $^{i}$Pr, etc.



**3**

R = Et, Ph



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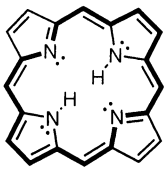

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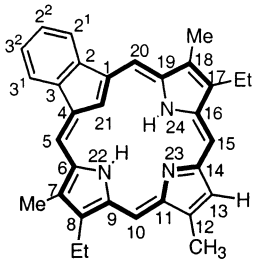
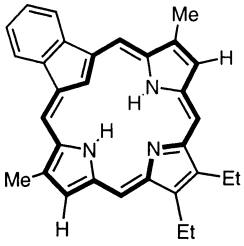


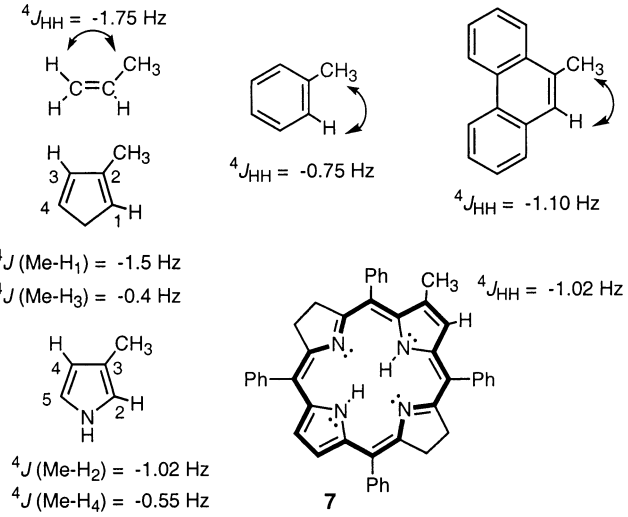
**8**



**9**

This description allows the porphyrins to be considered to be the bridged [18]annulenes of Nature.[1,14,15] Although the identification of comparable substructures in porphyrin isomers and expanded porphyrins has been of great value in predicting the properties of these molecules,[17,18] alternative hypotheses for the aromatic character of porphyrinoid systems have been proposed.[16,19] Nonetheless, there is strong evidence that the two exterior C=C bonds of the pyrrolene rings have greater double bond character based upon X-ray crystallography,[20] chemical reactivity,[21] and spectroscopic studies.[22]

**CHART 2. Selected $^{4}J_{H,H}$ Coupling Constants**




**7**

In principle, benzocarbaporphyrins could exist in two tautomeric forms, **1a** and **1b** (Scheme 1), although theoretical studies suggest that **1a** should be favored over **1b** by approximately 6 kcal·mol$^{-1}$.[23,24] This has been confirmed in the solid state for a 12,13-diphenyl-substituted carbaporphyrin by a single-crystal X-ray diffraction study.[3] Variable-temperature NMR studies also indicate that only tautomer **1a**, which has a plane of symmetry, is present at significant concentrations in solution, although the available data would also be consistent with a mixture of **1a** and **1b** if they rapidly interconvert at −50 °C.[3,4] If the [18]annulene substructure model provides a good description for the aromatic character of carbaporphyrins, the 12,13 carbon−carbon bond should possess significantly more double bond character than the 7,8 or 17,18 carbon−carbon bond. The bond lengths from the X-ray study do not provide an unambiguous answer to this question of bond order, and an alternative spectroscopic technique is required to assess this important feature.

Allylic or $^{4}J$ coupling of a −CH=C(CH$_3$)− fragment within a molecular structure has been shown to be an effective probe for bond order.[25] For alkenes, allylic coupling is commonly on the order of −2 Hz and for this reason commonly resolves in routine proton NMR spectra. However, this type of coupling is rarely observed for aromatic compounds. For instance, $^{4}J_{Me,H}$ cisoid coupling for propene is reported to be −1.75 Hz, while the analogous coupling between the methyl substituent and the 1-H of 2-methyl-1,3-cyclopentadiene is −1.5 Hz (Chart 2).[25] However, the equivalent $^{4}J_{Me,H}$ coupling for toluene is only −0.75 Hz, well below the usual resolution for most NMR spectrometers.[25] The 9,10-bond of phenanthrene provides a classical case where the bond charac-

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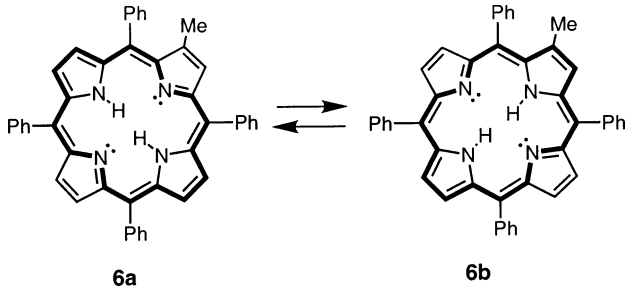
**SCHEME 2**



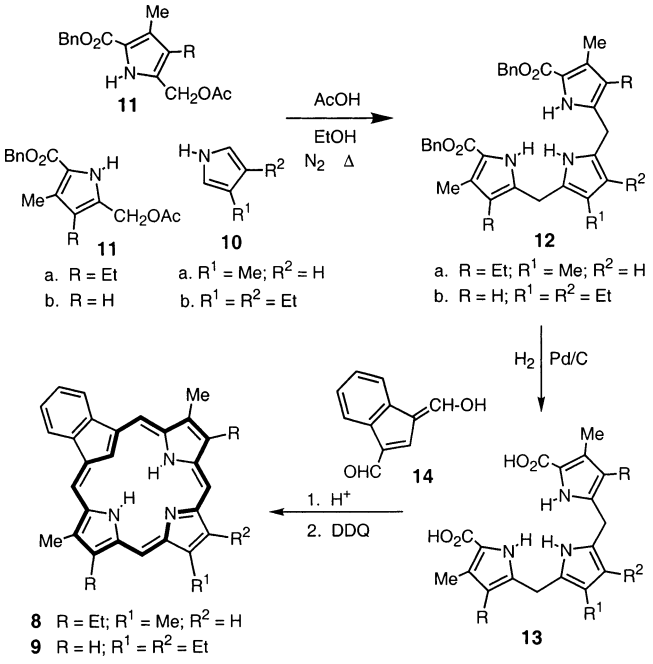
**6a** **6b**

teristics lie midway between benzene and an alkene-type double bond, and therefore, it is noteworthy that the $^4J_{Me,H}$ coupling for 9-methylphenanthrene has been reported to be −1.10 Hz.[25] 3-Methylpyrrole provides another good case for comparison, showing $^4J_{Me,H}$ coupling from the 2-H to the methyl of −1.02 Hz, but the 4-H gives a much lower coupling value due to the reduced bond order between C3 and C4 (Chart 2).[25] Although $^4J_{Me,H}$ coupling constants can be used as an effective measure of bond order, numerous factors need to be taken into account including ring size and bond angles. Hence, the data must be contrasted with the results for model compounds. In an early study of this type for tetrapyrrolic porphyrins, the CH═C−$CH_3$ $^4J_{Me,H}$ coupling for deuterioporphyrin III was shown to be 1.2 Hz.[22] This value is intermediary between the expected values for localized double bonds and a fully delocalized aromatic system.[22] A problem that arises in interpreting these data is that two tautomeric forms are present that rapidly interconvert on the NMR time scale.[26] To overcome this problem, Crossley et al. carried out variable-temperature NMR studies on a series of 2-methyl-5,10,15,20-tetraphenylporphyrins **6a,b** (Scheme 2).[27] These studies gave values of ca. $^4J_{Me,H}$ = 1.5 Hz for the tautomer **6a** with the methyl on the "isolated" double bond and ca. $^4J_{Me,H}$ = 1.0 Hz for **6b** where the methyl is attached to the fully delocalized system. The 2-methyltetraphenylbacteriochlorin **7** (Chart 2) also provided a useful model for the delocalized unit, showing a value of $^4J_{Me,H}$ = 1.02 Hz.[27] Taking all of these studies into account, we targeted the synthesis of carbaporphyrins **8** and **9** (Chart 1) to assess the bond order characteristics and preferred $\pi$-delocalization pathway for this system. If the favored delocalization pathway is the one shown in bold, **8** would give a value for $^4J_{Me,H}$ of ca. 1.5 Hz, while **9** should produce a smaller value of ca. 1.0 Hz.

## Results and Discussion

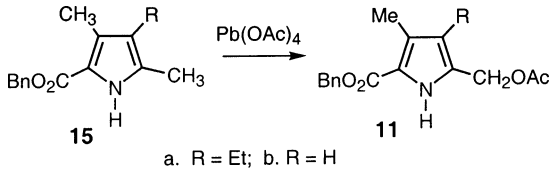
The synthesis of the required carbaporphyrins was carried out by the "3 + 1" version of the MacDonald condensation.[2,3,7,13,28,29] The route to the 13-unsubstituted benzocarbaporphyrin **8** was particularly efficient (Scheme 3). Condensation of 3-methylpyrrole (**10a**) with 2 equiv of acetoxymethylpyrrole **11a** in refluxing acetic acid−ethanol afforded the required tripyrrole **12a** in 68% yield. The benzyl ester protective groups were cleaved by hydrogenolysis over 10% palladium−charcoal to give the corresponding dicarboxylic acid **13a** in virtually quantitative yields. This was treated with TFA under nitrogen, diluted with dichloromethane, and condensed with 1,3-diformylindene (**14**) for 2 h. The solution was neutralized by the dropwise addition of triethylamine and oxidized with DDQ. Following extraction, chromatography on grade 3 alumina and recrystallization from chloroform−methanol, carbaporphyrin **8** was isolated in 50% yield.

**SCHEME 3**



**8** R = Et; $R^1$ = Me; $R^2$ = H
**9** R = H; $R^1$ = $R^2$ = Et

**SCHEME 4**



a. R = Et; b. R = H

For **15a** AcOH, room temp., 3 h, ca. 80%
For **15b** $CHCl_3$, reflux, 5 h, 31%

The synthesis of benzocarbaporphyrin **9** proved to be much more difficult to accomplish. The key monopyrrolic precursor for this synthesis was acetoxymethylpyrrole **11b**. In the previous synthesis, acetoxymethylpyrrole **11a** was prepared in excellent yield by reacting the 5-methylpyrrole-2-carboxylate **15a** with lead tetraacetate in acetic acid (Scheme 4).[30,31] The chemistry occurs via a well-established regioselective oxidation at the α-alkyl substituent.[31] Although this chemistry is moderately general, the presence of an electron-withdrawing ester substituent on the pyrrole ring is necessary to give clean

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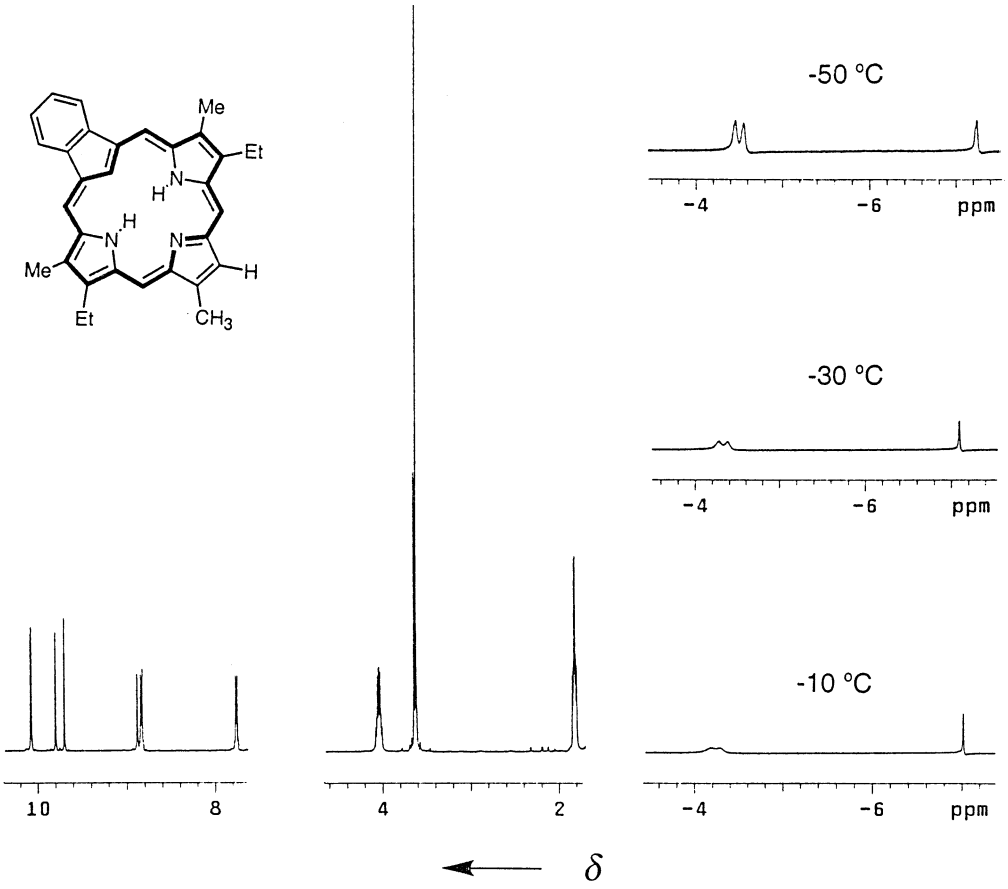


**FIGURE 1.** Proton NMR (400 MHz) spectrum of benzocarbaporphyrin **8** in deuteriochloroform at −10 °C. Inset: upfield region at −30 and −50 °C, showing further resolution of the NH resonances.

oxidation products.[32] Additionally, the nature of the alkyl substituents can also influence the outcome of this reaction.[33] The absence of a substituent at the 4-position is particularly problematic as this leads to low yields and complex mixtures of products.[33] Under the usual conditions, using acetic acid as a solvent at room temperature, very poor results are obtained for the reaction of **15b** with lead tetraacetate (Scheme 4). However, this chemistry has been shown to be somewhat solvent selective,[32−36] and reasonable yields of **11b** could be obtained by carrying out the reaction in refluxing chloroform for 5 h.[33] Following chromatography and recrystallization from ether−hexanes, **11b** was isolated in 31% yield.

Two equivalents of pyrrole **11b** was reacted with 3,4-diethylpyrrole in refluxing acetic acid−ethanol, and the resulting tripyrrole **12b** was isolated in 40% yield (Scheme 3). Following cleavage of the ester protective groups (quantitative), the dicarboxylic acid **13b** was condensed with **14** in the presence of TFA in dichloromethane, and subsequent oxidation with DDQ gave the required tetrasubstituted benzocarbaporphyrin **9** in 12% yield. The lower yields obtained in this case may in part reflect the absence of two electron-donating alkyl substituents which will decrease the reactivity of the tripyrrole terminal pyrrole units. Alternatively, competitive electrophilic substitution may be occurring at the open $\beta$-positions, in which case macrocyclic products are unlikely to be generated.

Carbaporphyrins **8** and **9** gave UV−vis spectra that showed strong absorptions at 424 nm. The NMR spectra in $CDCl_3$ also showed powerful diamagnetic ring currents as expected for aromatic structures of this type, with the internal CH protons resonating upfield near −7 ppm while the external *meso*-protons appeared downfield at ca. 10 ppm (Figure 1). The $\beta$-proton for carbaporphyrin **8** was observed at 8.85 ppm, while the two equivalent pyrrole protons in **9** showed up at 8.83 ppm. On the basis of the chemical shifts, no conclusion could be drawn on the preferred pathway for $\pi$-delocalization. In routine proton NMR spectra, the $^4J_{Me,H}$ coupling could not be observed. However, the required information could be obtained by carefully shimming the instrument and recording the spectra at lower temperatures.

The NH protons for **8** gave a broad peak near −4 ppm at 20 °C, but when the temperature was lowered to −10

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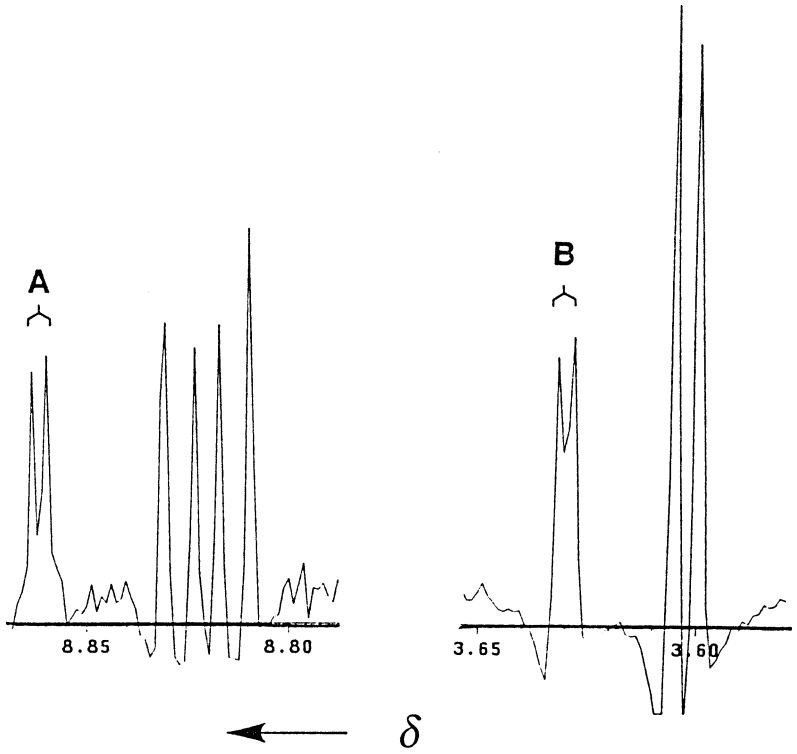


**FIGURE 2.** Partial 400 MHz proton NMR spectrum of benzocarbaporphyrin **8** in $CDCl_3$ at −10 °C showing the $^4J_{Me,H}$ coupling for the CH═C—Me unit. The sb parameter (sine-bell function) was set to a value of 0.50 to enhance resolution. Peak A corresponds to the partially resolved quartet for the pyrrolic H, while peak B shows the doublet for the 12-methyl group. The two singlets at 3.60 ppm correspond to the remaining 7,18-methyl substituents, while the multiplet centered on 8.82 ppm is due to the benzo protons closest to the porphyrinoid ring.

°C, two separate resonances were evident. These resolved and sharpened as the temperature was further lowered to −50 °C. Porphyrinoid **8** is the first example of a benzocarbaporphyrin that lacks a plane of symmetry, and for that reason the two NH protons can lie in two slightly different chemical environments for the expected tautomer. The data demonstrate that the exchange rate for these protons is slow, at least at −10 °C or below, and given the absence of any additional peaks, the data are only consistent with a single tautomer of type **1a** being present at significant concentrations in solution. Having established this preference, the $^4J_{Me,H}$ coupling constant for **8** was examined. Careful measurements were made at −10, −30, and −50 °C, although some loss of resolution was observed at lower temperatures due to increases in solvent viscosity.[27] The coupling constant for the CH═C—Me unit was consistently found to be 1.3−1.4 Hz (Figure 2).[37] Similar measurements were made for carbaporphyrin **9**. As expected, at lower temperatures the NH resonance for **9** sharpened but remained a single peak due to the symmetrical substitution in this macrocycle. The $^4J_{Me,H}$ coupling constant for the CH═C—Me units was found to be 0.9−1.0 Hz in this case,[37] and again this result was reproducible at different temperatures.

The results for the $^4J_{Me,H}$ coupling constants are in good agreement with those expected for a porphyrin-like system that favors the 18-$\pi$-electron delocalization pathway proposed for the major tautomer **1a**. These data suggest that the 12,13 carbon−carbon bond should have significant olefinic character, and this property may well produce regioselective chemistry at this site on the macrocycle.

(37) The $^4J_{Me,H}$ coupling constants are known to have negative values.[25] However, our measurements only give the magnitude for the coupling and not its sign.

## Conclusions

The application of long-range coupling constants in proton NMR spectroscopic analyses provides strong evidence for enhanced olefinic character for the C12−C13 bond over the C7−C8 and C17−C18 bonds in benzocarbaporphyrins. Furthermore, the resolution of two separate NH resonances in the low-temperature proton NMR spectra of an asymmetrically substituted carbaporphyrin, **8**, indicates that only one tautomer is present in solution at significant concentrations. The insights from this study should be of great value in investigating the chemistry of this important porphyrin analogue system.

## Experimental Section

Chromatography was performed using grade 3 neutral alumina or 70−230 mesh silica gel. EI and FAB mass spectral determinations were made at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029). Elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

**3-Methylpyrrole (10a).** Ethyl 3-methylpyrrole-2-carboxylate[38] (20.01 g) and sodium hydroxide (7.85 g) were stirred under nitrogen with ethylene glycol (80 mL) and heated under reflux for 2 h. The solution was cooled to room temperature, diluted with dichloromethane (100 mL), washed with water (200 mL), and back-extracted with dichloromethane. Following evaporation of the solvent under reduced pressure, the residue was steam distilled. The resulting distillate was extracted with dichloromethane (3 × 50 mL), and the organic phases were combined, dried over magnesium sulfate, and evaporated on a rotary evaporator to give 3-methylpyrrole (4.67 g, 44%) as a colorless oil. $^1$H NMR ($CDCl_3$): $\delta$ 2.02 (3H, s), 6.14 (1H, br m), 6.61 (1H, br m), 6.75 (1H, br m), 7.97 (1H, br s). $^{13}$C NMR ($CDCl_3$): $\delta$ 12.0, 109.9, 115.8, 118.0, 119.0.

**Benzyl 5-Acetoxymethyl-3-methylpyrrole-2-carboxylate (11b).** Benzyl 3,5-dimethylpyrrole-2-carboxylate[39] (**15b**; 2.29 g) was dissolved in chloroform (100 mL), lead tetraacetate (95%; 4.63 g) was added immediately, and the mixture was stirred vigorously under reflux for 5 h. The mixture was cooled, filtered through Celite, and evaporated under reduced pressure. The residue was chromatographed on grade 3 alumina eluting with dichloromethane. Recrystallization from ether/hexanes gave the acetoxymethylpyrrole (0.892 g, 31%) as white crystals. Mp: 119−120 °C. $^1$H NMR ($CDCl_3$): $\delta$ 2.07 (3H, s), 2.33 (3H, s), 4.99 (2H, s), 5.31 (2H, s), 6.08 (1H, d, $J$ = 2.8 Hz), 7.38 (5H, m), 9.09 (1H, br s). $^{13}$C NMR ($CDCl_3$): $\delta$ 13.0, 21.1, 58.8, 66.0, 113.9, 120.0, 128.3, 128.4, 128.7, 128.8, 130.4, 136.5, 161.4, 171.8. Anal. Calcd for $C_{16}H_{17}NO_4 \cdot {}^1/_4H_2O$: C, 65.85; H, 6.04; N, 4.80. Found: C, 65.88; H, 5.79; N, 4.88.

**2,5-Bis(5-benzyloxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)-3-methylpyrrole (12a).** 3-Methylpyrrole (0.36 g) and benzyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate[40] (**11a**; 2.79 g) were dissolved in ethanol (30 mL) and acetic acid (2 mL), and the was mixture stirred and heated under reflux under a nitrogen atmosphere for 16 h. The mixture was cooled in an ice bath and the resulting precipitate suction filtered, washed with cold ethanolc and dried in vacuo overnight to give the title tripyrrole (1.761 g, 68%) as a pale yellow powder. Mp: 198 °C. $^1$H NMR ($CDCl_3$): $\delta$ 0.94−0.99 (6H, 2 overlapping triplets), 2.07 (3H, s), 2.24 (6H, s), 2.32−2.36 (4H, 2 overlapping quartets), 3.51 (2H, s), 3.58 (2H, s), 4.41 (4H, br s), 5.75 (1H, s), 7.04 (4H, m), 7.25 (6H, m), 8.88 (1H, br s), 10.98 (2H, br s). $^{13}$C NMR ($CDCl_3$): $\delta$ 11.1, 11.2, 15.8, 15.9, 17.3, 17.4, 22.3, 24.5, 65.5, 107.1, 113.2, 117.3, 117.5, 123.5, 124.0, 126.9, 127.0, 127.5, 128.4, 132.8, 137.2, 162.8. EI MS: $m/z$ (rel intens) 591 (100, $M^+$), 483 (73). HRMS (EI): $m/z$ calcd for $C_{37}H_{41}N_3O_4$ 591.3097, found 591.3087. Anal. Calcd for $C_{37}H_{41}N_3O_4 \cdot {}^1/_4H_2O$: C, 74.53; H, 7.07; N, 7.05. Found: C, 74.47; H, 6.96; N, 7.08.

**2,5-Bis(5-benzyloxycarbonyl-4-methyl-2-pyrrolylmethyl)-3,4-diethylpyrrole (12b).** 3,4-Diethylpyrrole[41] (0.22 g) and benzyl 5-acetoxymethyl-3-methylpyrrole-2-carboxylate (1.00 g) were dissolved in ethanol (20 mL) and acetic acid (1 mL), and the mixture was refluxed under a nitrogen atmosphere for 16 h. The mixture was cooled in an ice bath and the resulting precipitate filtered, washed with cold ethanol, and dried under vacuum overnight. The tripyrrole diester (402 mg, 40%) was obtained as a light brown powder. Mp: 175−176 °C. $^1$H NMR ($CDCl_3$): $\delta$ 1.05 (6H, t, $J$ = 7.6 Hz), 2.21 (6H, s), 2.40 (4H, q, $J$ = 7.6 Hz), 3.74 (4H, s), 4.42 (4H, br s), 5.85 (2H, d, $J$ = 2 Hz), 7.14 (4H, m), 7.29 (6H, m), 8.91 (1H, br s), 11.11 (2H, br s). $^{13}$C NMR ($CDCl_3$): $\delta$ 13.7, 16.8, 17.8, 24.6, 66.0, 111.4, 118.5, 119.3, 122.6, 127.7, 128.3, 129.2, 136.0, 136.7, 163.0. EI MS: $m/z$ (rel intens) 577 (100, $M^+$), 469 (58). HRMS (EI): $m/z$ calcd for $C_{36}H_{39}N_3O_4$ 577.2940, found 577.2936. Anal. Calcd for $C_{36}H_{39}N_3O_4 \cdot {}^1/_4H_2O$: C, 74.27; H, 6.84; N, 7.22. Found: C, 74.29; H, 6.78; N, 7.24.

**8,17-Diethyl-7,12,18-trimethyl-21-carbabenzo[*b*]porphyrin (8).** Triethylamine (10 drops) was added to a solution of tripyrrole dibenzyl ester **12a** (1.00 g) in THF (150 mL) and methanol (50 mL). The air was displaced with nitrogen, 10% Pd/C (200 mg) was added, and the resulting mixture was shaken under a hydrogen atmosphere at room temperature and 40 psi for 16 h. The catalyst was removed by suction filtration, the solvent evaporated under reduced pressure, and the residue taken up in 3% aqueous ammonia. The solution was neutralized with acetic acid, the temperature being maintained between 0 and 5 °C throughout. After 1 h, the resulting precipitate was suction filtered, washed well with water, and dried under vacuum overnight to give the tripyrroledicarboxylic acid **13a** (702 mg, 94%) as a pink powder that was used without further purification. Tripyrrole **13a** (100 mg) was stirred with TFA (1 mL) under nitrogen for 10 min. The solution was diluted with dichloromethane (19 mL) and 1,3-diformylindene[42] (42 mg) added immediately. The resulting mixture was stirred under nitrogen for 2 h. The solution was neutralized with triethylamine, DDQ (56 mg) was added, and the resulting mixture was stirred at room temperature for 1 h. The solution was diluted with chloroform, washed with water, and evaporated to dryness on a rotary evaporator. The residue was chromatographed on grade 3 alumina eluting with dichloromethane. The product fraction was evaporated and the residue recrystallized from chloroform−methanol to give the benzocarbaporphyrin (55 mg, 50%) as brown crystals. Mp: >300 °C. UV−vis ($CHCl_3$): $\lambda_{max}$ (log $\epsilon$) 381 (4.56), 424 (5.08), 512 (4.21), 545 (4.15), 601 (3.83), 661 (3.50). UV−vis (0.01% TFA−$CHCl_3$, monocation): $\lambda_{max}$ (log $\epsilon$) 392 (sh, 4.67), 436 (4.87), 475 (4.39), 548 (4.07), 587 (3.92), 610 (3.87), 669 (3.40). UV−vis (50% TFA−$CHCl_3$, dication): $\lambda_{max}$ (log $\epsilon$) 346 (4.55), 424 (5.00), 607 (3.88), 660 (4.21). $^1$H NMR ($CDCl_3$): $\delta$ −7.04 (1H, s), −4.24 (2H, br s), 1.81−1.85 (6H, 2 overlapping triplets), 3.60 (6H, s), 3.62 (3H, s), 3.99−4.06 (4H, 2 overlapping quartets), 7.73−7.75 (2H, m), 8.80−8.82 (2H, m), 8.85 (1H, s), 9.65 (1H, s), 9.77 (1H, s), 10.04 (2H, s). $^1$H NMR (1 drop TFA−$CDCl_3$): $\delta$ −6.90 (1H, s), −4.60 (1H, br s), −3.32 (1H, s), −3.25 (1H, s), 1.69−1.74 (6H, 2 overlapping triplets), 3.57 (3H, s), 3.58 (3H, s), 3.74 (3H, s), 4.02−4.09 (4H, 2 overlapping quartets), 7.71−7.72 (2H, m), 8.67−8.69 (2H, m), 9.18 (1H, s), 10.04 (1H, s), 10.08 (1H, s), 10.31 (1H, s), 10.34 (1H, s). $^1$H NMR (50% TFA−$CDCl_3$): $\delta$ −5.02 (2H, s), −1.43 (2H, br s), 1.75−1.79 (6H, 2 overlapping triplets), 3.57 (3H, s), 3.58 (3H, s), 3.59 (3H, s), 3.99−4.04 (4H, 2 overlapping quartets), 8.93−8.95 (2H, m), 9.16 (1H, s), 10.12−10.14 (2H, m), 10.43 (1H, s), 10.46 (1H, s), 11.02 (1H, s), 11.03 (1H, s). $^{13}$C NMR (TFA−$CDCl_3$): $\delta$ 11.7, 13.9, 16.7, 16.8, 19.9, 20.0, 94.8, 96.5, 104.2, 104.5, 118.4, 121.7, 127.7, 128.4, 135.4, 135.7, 137.1, 137.7, 138.1, 139.6, 141.6. EI MS: $m/z$ (rel intens) 457 (100, $M^+$), 442 (18), 427 (3), 229 (20, $M^{2+}$). HRMS (EI): $m/z$ calcd for $C_{32}H_{31}N_3$ 457.2518, found 457.2522.

**12,13-Diethyl-7,18-dimethyl-21-carbabenzo[*b*]porphyrin (9).** Tripyrrole dibenzyl ester **12b** (400 mg) was placed in a hydrogenation vessel and dissolved in THF (67 mL) and methanol (27 mL). Triethylamine (10 drops) was added, the air flushed out with nitrogen, and 10% Pd/C added (67 mg). The resulting mixture was shaken under an atmosphere of hydrogen at room temperature and 40 psi for 16 h. The catalyst was removed by suction filtration and the solvent evaporated under reduced pressure. The residue was taken up in 3% aqueous ammonia and then neutralized with glacial acetic acid, the temperature being maintained between 0 and 5 °C throughout. The mixture was allowed to stand at 0 °C for 1 h and the precipitate filtered and washed well with water to remove all traces of acetic acid. After being dried overnight in vacuo, the tripyrroledicarboxylic acid **13b** (270 mg; 98%) was obtained as a light purple powder that was used without

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further purification. Tripyrrole **13b** (100 mg) was stirred with TFA under nitrogen for 10 min. The solution was diluted with dichloromethane (19 mL), and 1,3-diformylindene[42] (43 mg) was added immediately. The resulting mixture was stirred under nitrogen for 2 h. The solution was neutralized with triethylamine, DDQ (58 mg) was added, and the mixture was stirred for an additional 1 h at room temperature. The solution was diluted with chloroform, washed with water, and evaporated under reduced pressure. The residue was chromatographed on grade 3 alumina eluting with dichloromethane. The product fraction was recrystallized from chloroform−methanol to give the title carbaporphyrin (13 mg, 12%) as purple crystals. Mp: >300 °C. UV−vis ($CHCl_3$): $\lambda_{max}$ (log $\epsilon$) 373 (4.47), 424 (4.96), 507 (4.13), 541 (3.97), 604 (3.60), 661 (3.26). UV−vis (0.01% TFA−$CHCl_3$, monocation): $\lambda_{max}$ (log $\epsilon$) 398 (4.63), 436 (4.76), 473 (4.27), 545 (3.96), 608 (3.77), 661 (3.14). UV−vis (50% TFA−$CHCl_3$, dication): $\lambda_{max}$ (log $\epsilon$) 347 (4.38), 424 (5.03), 615 (3.77), 671 (4.18). $^1$H NMR ($CDCl_3$): $\delta$ −6.77 (1H, s), −3.86 (2H, br s), 1.85 (6H, t, $J$ = 7.6 Hz), 3.75 (6H, s), 3.93 (4H, q, $J$ = 7.6 Hz), 7.75 (2H, m), 8.83 (2H, m), 8.99 (2H, s), 9.78 (2H, s), 10.14 (2H, s). $^1$H NMR (1 drop TFA−$CDCl_3$): $\delta$ −6.79 (1H, s), −4.98 (1H, br s), −3.54 (2H, br s), 1.84 (6H, t, $J$ = 7.6 Hz), 3.68 (6H, s), 4.07 (4H, q, $J$ = 7.6 Hz), 7.74 (2H, m), 8.70 (2H, m), 9.09 (2H, s), 10.08 (2H, s), 10.38 (2H, s). $^1$H NMR (50% TFA−$CDCl_3$): $\delta$ −5.57 (2H, s), −1.75 (2H, br s), 1.75 (6H, t, $J$ = 8 Hz), 3.74 (6H, s), 4.07 (4H, q, $J$ = 8 Hz), 9.02 (2H, m), 9.39 (2H, s), 10.25 (2H, m), 10.62 (2H, s), 11.25 (2H, s). $^{13}$C NMR (TFA−$CDCl_3$): $\delta$ 13.8, 17.5, 19.9, 96.8, 105.6, 119.2, 121.7, 126.5, 128.4, 137.6, 138.0, 138.8, 139.2, 141.3, 141.7, 142.2. EI MS: $m/z$ (rel intens) 443 (100, $M^+$), 428 (13), 413 (18), 221 (16, $M^{2+}$), 207 (11). HRMS (EI): $m/z$ calcd for $C_{31}H_{29}N_3$ 443.2361, found 443.2356.

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**Supporting Information Available:** UV−vis, $^1$H NMR, $^{13}$C NMR, and mass spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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