Conjugated Macrocycles Related to the Porphyrins. 12.[1] Oxybenzi- and Oxypyriporphyrins: Aromaticity and Conjugation in Highly Modified Porphyrinoid Structures

Timothy D. Lash,* Sun T. Chaney, and Daniel T. Richter

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160

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The "3 + 1" route for porphyrinoid synthesis is an excellent methodology for preparing aromatic porphyrin analogues with six-membered ring subunits. Condensation of 5-formylsalicylaldehyde with tripyrranes **15**, **24**, and **25** in the presence of 5% TFA-dichloromethane, followed by neutralization and oxidation with DDQ, afforded a series of semiquinone-containing porphyrinoids **12**, **26**, and **27** in 35−52% yield. In these novel systems, the macrocycle achieves aromatization by undergoing a keto−enol tautomerization whereby the phenolic subunit is transformed so that the inner three carbon atoms become part of the 18 π-electron aromatic core, whereas the outer carbons generate an enone unit. The aromatic nature of these "oxybenziporphyrins" is evident from their porphyrin-like electronic spectra and the presence of powerful diamagnetic ring currents in their proton NMR spectra, where the inner CH is shifted upfield to $\delta = -7$ ppm, whereas the external *meso*-protons appear downfield between 8.8 and 10.3 ppm. The presence of a carbonyl unit is confirmed by IR and proton NMR spectroscopy. Addition of trace amounts of TFA give an aromatic monocation, but further protonation to the dication leads to the loss of macrocyclic aromaticity. Modified tripyrranes **15b**, **26**, and **27** were used to prepare oxybenziporphyrins with fused benzene, phenanthrene, and acenaphthylene ring systems, the former via a tetrahydrobenzo intermediate; and these compounds showed many of the same characteristics, including aromatic free bases and nonaromatic dications. The ring fusion gave rise to gradual bathochromic shifts from benzo- (**23**) to phenanthro- (**26**) to acenaphtho- (**27**) oxybenziporphyrins, which qualitatively followed the same trends observed for true porphyrins, although the influence of the acenaphthylene ring system was somewhat muted in this series. Condensation of isophthalaldehyde with tripyrrane **15a** gave the nonaromatic analogue "benziporphyrin" in 28% yield, and this species was thoroughly characterized and contrasted to oxybenziporphyrin **12a**. Reaction of 3-hydroxypyridine-2,6-dicarboxaldehyde with tripyrranes under the "3 + 1" conditions afforded exceptionally high yields of the corresponding azaoxybenziporphyrins (named "oxypyriporphyrins"; **35**, **47**−**49**), and these structures also exhibited porphyrinoid aromaticity. For this series, the dications retained their aromatic character as did the related nickel(II), copper(II), and zinc chelates. Ring fusion effects were investigated for the oxypyriporphyrins and their metal complexes, and again the major absorptions shifted to higher wavelength from benzo- to phenanthro- to acenaphthooxypyriporphyrins. However the effect of metalation on the oxypyriporphyrin chromophore differed considerably from the trends seen for metalloporphyrins. These results show that novel aromatic porphyrinoids are easily accessible via the "3 + 1" approach, and this work will facilitate in-depth studies on the chemical and physical properties of these exciting new bridged annulene structures.

Introduction

The remarkable stability of the porphyrin nucleus (**1a**,**b**; Chart 1) is well known and is caused partly by the aromatic nature of this macrocyclic system.[2,3] Porphyrins can be viewed as diaza-bridged annulenes (**1**; 18 π-electron delocalization pathways shown in **bold**)[4] and hence may be considered to be nature's [18]annulene.[5,6] However, unlike Sondheimer's synthetic system **2**,[7] the individual five-membered rings provide a framework that reinforces the near planar structure. Certainly the porphyrins demonstrate powerful diamagnetic ring currents by proton NMR spectroscopy[8] and possess a considerable resonance stabilization energy.[9] This representation of the porphyrin system is clearly an oversimplification, and other models for the aromatic nature

* E-mail: tdlash@ilstu.edu.

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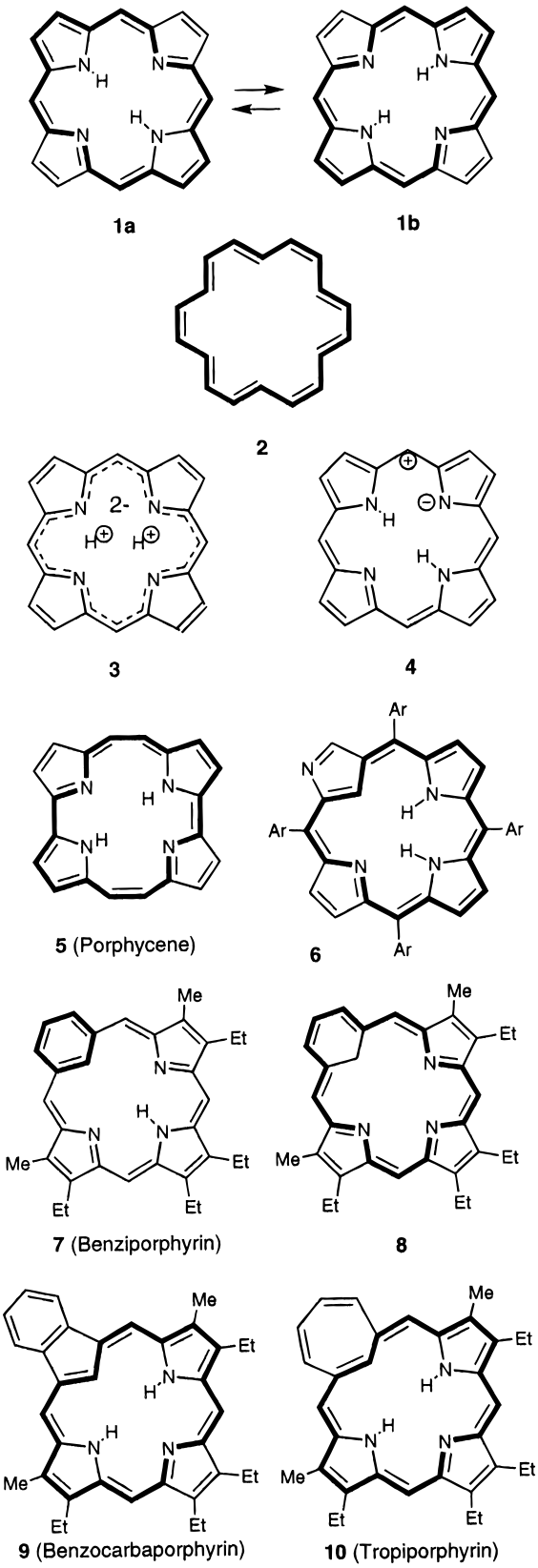
Chart 1



of these heterocyclic structures have been formulated. For instance, an "inner" 16-atom tetraazadianionic description **3** also allows 18 π-electron delocalization that could produce aromatic characteristics.[10] Further, to explain certain facets of porphyrin chemistry Woodward proposed that the individual pyrrole units could retain 6 π-electron aromatic character because of dipolar canonical forms such as **4**.[11] NMR spectroscopy demonstrates that free-base porphyrins exist as two rapidly interconverting tautomers **1a** and **1b**,[12] although these may not be present in equal proportions when substituents are present.[13] NMR[13] and X-ray crystallography[14] also support the 18-atom "inside−outside" view (i.e., structures **1a**,**b**) for aromaticity in free-base porphyrins, and the remaining pyrrolenic C═C units exhibit significant double-bond characteristics.[15] On the other hand, the symmetrically delocalized representation **3** provides a more realistic view of metalloporphyrins in which all four pyrrole rings are equivalent when substituent effects are discounted. The 18-atom delocalization rationale has been useful in predicting the aromaticity of related structures such as the porphyrin isomer porphycene[16,17] (**5**) and N-confused porphyrins **6**.[18] In much the same way, this approach can be applied to expanded porphyrinoid systems such as the sapphyrins[19] and the platyrins.[20]

During the past four years, our group[1,6,21−28] and others[29,30] have used a "3 + 1" methodology for the preparation of porphyrins and related conjugated macrocycles.[31] This approach was originally introduced by Broadhurst et al.[32] in the late 1960s for the synthesis of oxa- and thiaporphyrins, but its full potential was

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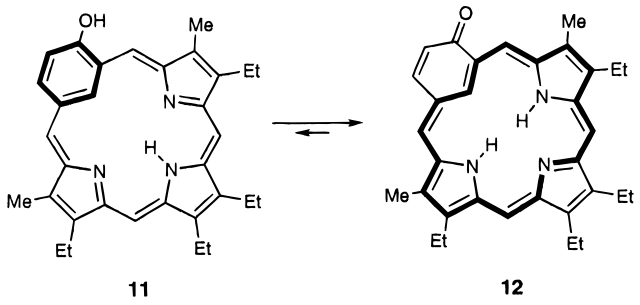
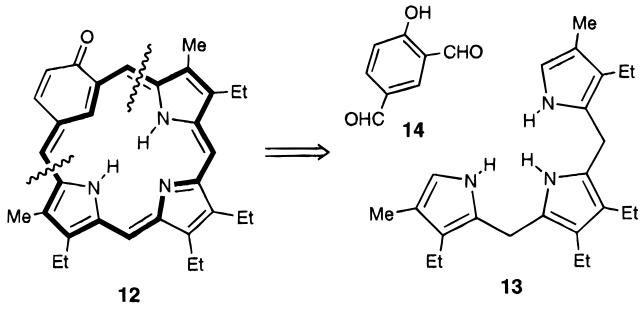
Scheme 1



Scheme 2



overlooked for more than two decades.[31] The "3 + 1" method was recently applied to the synthesis of a nonaromatic porphyrinoid **7**,[33] named "benziporphyrin", where a benzene ring effectively interrupts the macrocyclic delocalization pathway and NMR spectroscopy confirms the absence of a diamagnetic ring current over the whole structure. Although tautomer **8** potentially could obtain porphyrin-like aromaticity, albeit at the expense of losing the aromaticity of the benzene ring, there was no evidence for the formation of such a species. On the other hand, subsequent investigations demonstrated that five- or seven-membered carbocycles could be incorporated into porphyrinoid structures (e.g., carbaporphyrin **9**[25,30] and tropiporphyrin **10**[6]) while retaining overall aromaticity within the macrocyclic system. Clearly, much of the difficulty that benziporphyrin **7** has in attaining porphyrinoid aromaticity is related to its inability to give up the resonance stabilization for the 6 π-electron arene. We hypothesized that this barrier might be circumvented by the introduction of a suitably placed hydroxyl substituent (structure **11**, Scheme 1), because this would provide an alternative mode for tautomerization whereby a semiquinone porphyrinoid species **12**, which we named "oxybenziporphyrin", could be generated.[34] This "keto−enol" tautomerization would still result in the loss of the arene moiety, but the generation of a thermodynamically favorable carbonyl group in addition to the aza[18]annulene aromaticity would compensate for this. Furthermore, two pyrrole nitrogen "lone pairs" were also retained, which more closely resembles the situation in true porphyrins than in the hypothetical species **8**, and these most likely would further stabilize tautomer **12**. In this article, detailed synthetic and spectroscopic investigations of oxybenziporphyrins and related pyridone structures are reported.[34,35] These remarkable porphyrin analogues demonstrate completely new possibilities for modifying the porphyrin chromophore. These results are not only of theoretical significance in that they provide new insights into porphyrinoid aromaticity, but they may also open the door to practical applications.[36]

Results and Discussion

Oxybenziporphyrins. The "3 + 1" strategy for porphyrin synthesis involves the condensation of a monocyclic dialdehyde with a tripyrrane **13** under acid-catalyzed conditions.[31] Retrosynthetically we can envisage that the condensation of 5-formylsalicylaldehyde (**14**) with **13** would result in the formation of hydroxybenziporphyrin **11**, and subsequent tautomerization would lead to the aromatic macrocycle **12** (Scheme 2). Tripyrrane **13** is extremely unstable, but can be conveniently generated in situ from the corresponding dicarboxylic acid **15a**[28,37] (Scheme 3; this chemistry makes use of the principle that electron-rich pyrrole carboxylic acids readily decarboxylate under acidic conditions at ambient temperatures). Hence, tripyrrane **15a** was treated with TFA under nitrogen, diluted 20-fold with dichloromethane, and immediately reacted with 1 equiv of dialdehyde **14**. After neutralization with triethylamine and oxidation with DDQ, the crude product was extracted and chromatographed to give a deep-green fraction. Crystallization from chloroform-methanol afforded **15a** as lustrous purple needles in 35−44% yield. Readily available butanotripyrrane **15b**[28] similarly gave the related porphyrinoid **12b** in 39% yield.

The identity of these brightly colored compounds was confirmed by NMR, UV−vis and IR spectroscopy, mass spectrometry, and combustion analysis. Oxybenziporphyrins can exist as three nonequivalent aromatic tau-

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(36) Porphyrinoid chromophores with strong absorptions at longer wavelengths (>700 nm) have attracted considerable attention in recent years because of their intrinsic value in the development of novel optical materials with potential applications in optical recording technology, etc., and as superior photosensitizers for singlet oxygen formation in photodynamic therapy. See: Fabian, J.; Nakazumi, H.; Matsuoka, M. *Chem. Rev.* **1992**, *92*, 1197. Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19. Milgrom, L. R.; MacRobert, S. *Chem. Br.* **1998**, *34* (35), 45.

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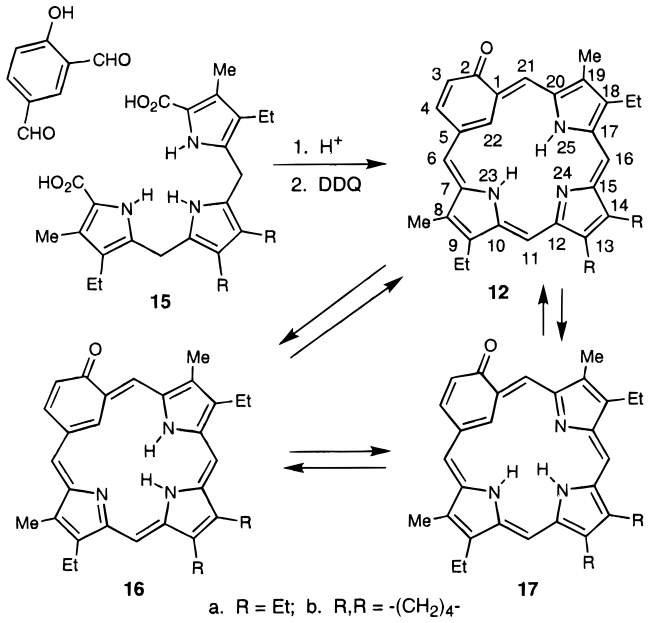
Scheme 3



tomers **12**, **16**, and **17**; and these appear to interconvert rapidly on the NMR time scale (Scheme 3). The methine bridge protons (*meso*-H) for **12a** appeared as a series of four singlets between 8.8 and 10.3 ppm where the *meso*-proton nearest to the carbonyl unit had undergone additional deshielding compared with the other three. More diagnostically the internal CH appeared as a weakly coupled doublet ($J = 2$ Hz) at −7.3 ppm, and the NH protons produced a broad resonance near −4 ppm, confirming the presence of the anticipated aromatic ring current. The enone unit produced a doublet at 7.35 ($J = 9$ Hz) and a doublet of doublets ($J = 2$ and 9 Hz) at 8.5 ppm. These values suggest that this unit is not part of the aromatic delocalization pathway; the downfield shift for the proton at 8.5 ppm is attributable to being β- to the carbonyl moiety and proximal to the porphyrinoid ring current. Nonetheless, the $\Delta\delta$ value for the most upfield and downfield protons on the six-membered ring is >15 ppm, providing further emphasis for the identity of oxybenziporphyrin **12a**. Carbon-13 NMR spectroscopy showed the presence of a carbonyl moiety at 188 ppm as well as resonances for all 21 of the other sp^2 hybridized carbons in this asymmetrical structure. The *meso*-carbons appeared at 93, 95, 106, and 111 ppm, compared with typical values of 95−100 ppm in regular porphyrins.[8] IR spectroscopy also showed the presence of a carbonyl unit, and the stretching frequency of 1624 cm^{-1} was consistent with a cross-conjugated enone moiety. EIMS showed a strong molecular ion, as expected for a stable aromatic structure, together with a small amount of benzylic fragmentation and significant M^{2+} peaks. Similar data were obtained for the butanooxybenziporphyrin **12b**.

The electronic spectra for porphyrins are particularly diagnostic, generally showing a strong Soret band ($\epsilon = 2 \times 10^5$) near 400 nm and a series of four weaker Q-bands between 490 and 625 nm. Bearing this in mind, the UV−vis spectrum for **12a** in chloroform was strikingly porphyrin-like showing two Soret bands at 428 and 456 nm and a series of four Q-bands at 548, 590, 636, and 698 nm (Figure 2). It is significant that these absorptions are red shifted compared with true porphyrins, a feature

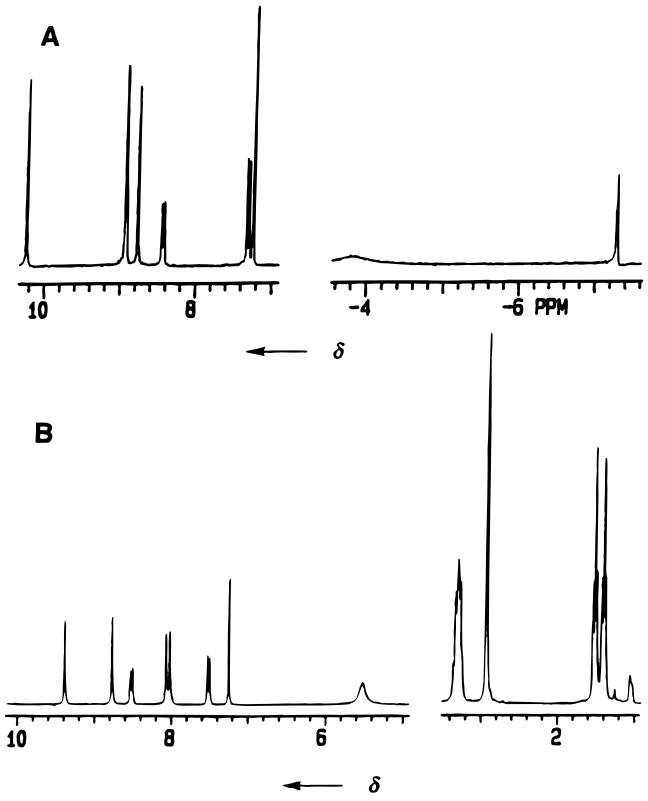


Figure 1. 300-MHz proton NMR spectra of oxybenziporphyrin **12a**. A, Partial spectrum showing the upfield and downfield regions for the free base in deuteriochloroform; B, Dication **20** in TFA-$CDCl_3$.

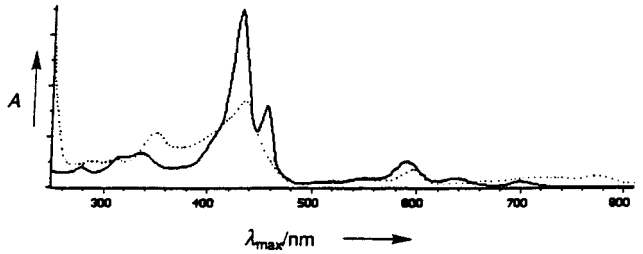
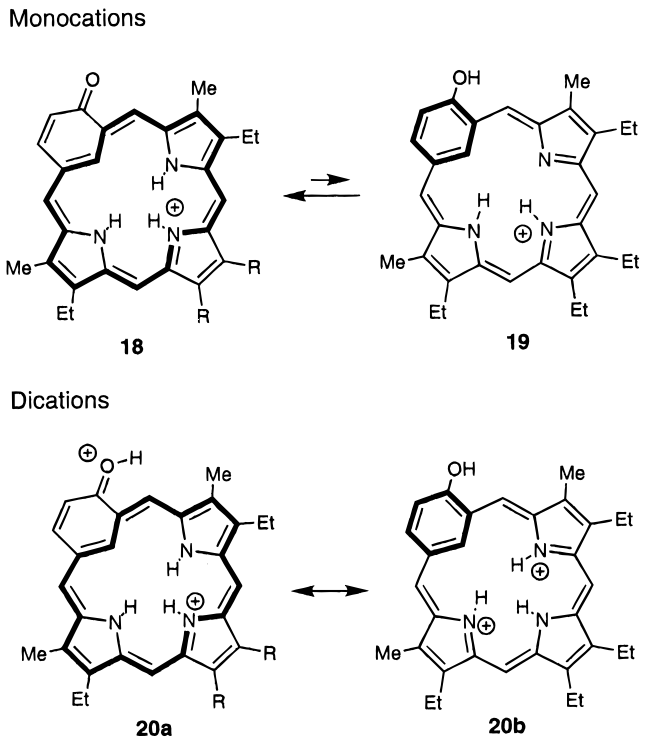


Figure 2. UV−vis spectra of oxybenziporphyrin **12a**. Free base in chloroform (solid line) and dication **20** in 5% TFA-chloroform (dotted line).

that is greatly valued in this area of research. Careful titration with TFA produced a second porphyrin-like chromophore that was attributed to a monoprotonated species (Chart 2). Again, the monocation might exist as an aromatic "keto" species **18**, or a nonaromatic phenolic structure **19**, but the retention of strong Soret absorptions at 428 and 468 nm suggests that **18** predominates. However, further addition of TFA results in a reduction in the intensity of the Soret band absorptions (Figure 2) and the production of a dication **20** (Chart 2). Although this dication can be represented by an aromatic resonance contributor with a protonated carbonyl moiety (**20a**), the data suggest that a diprotonated hydroxybenziporphyrin structure **20b** better describes this species. The proton NMR for this species in TFA-$CDCl_3$ also shows a much reduced ring current with the NH protons showing up at +5.5 ppm and the inner CH appearing near +1 ppm (Figure 1B). Similarly, in the carbon-13 NMR spectrum the C=O resonance was replaced by a peak at 171 ppm. Taken together, these results suggest

Chart 2



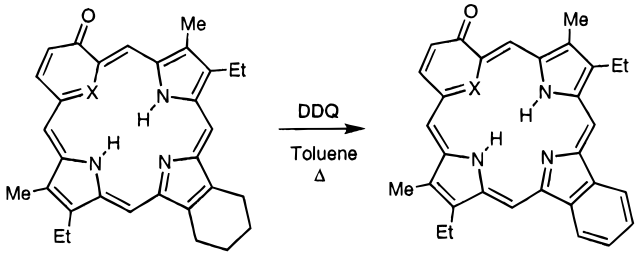
18 **19** **20a** **20b**

that **20a** contributes some aromatic characteristics to the dication, although this is much reduced compared with the free base or monocation. Similar data were obtained for the cyclohexenoporphyrinoid **12b**.

Most attempts to chemically modify oxybenziporphyrin **12** have not been fruitful, although these investigations are continuing. Although the system formally contains an enone unit, cycloaddition reactions (e.g., with cyclopentadiene under various conditions) have failed to give adducts, and hydride reductions were also unsuccessful. This high degree of thermodynamic stabilization also extends to the related pyridone systems (see below).

Benzo-, Phenanthro-, and Acenaphthooxybenziporphyrins. In unrelated studies, we investigated the influence of fused aromatic rings on the porphyrin chromophore. These studies showed that fused benzene,[38] naphthalene,[39] or phenanthrene[40] units had a surprisingly small effect on porphyrin UV−vis spectra. Solutions of 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) in organic solvents such as chloroform or benzene showed a strong Soret band at 400 nm,[41] and the longest wavelength Q absorption (band I) appeared at 622 nm. Monobenzoporphyrins showed the Soret band at 403 nm, whereas Q-band I was significantly enhanced and shifted to 628 nm.[38] Further extension of the π-system in phenanthroporphyrin **21**[40] gave absorptions of 417 nm (Soret) and 634 nm (Q-band I), λ_{max} values that fall far short of the bathochromic shifts that might have been anticipated. In complete contrast, acenaphthoporphyrin **22** exhibited a uniquely modified chromophore with a triply split Soret band (387, 431, and 454 nm) and an intense band I near 660 nm.[22,23,42] The "acenaphthylene effect" is intriguing and holds great promise in the modification of porphyrinoid chromophores.[22,23,42] Hence, it was of some interest to see whether the same trends were evident in the oxybenziporphyrin series. This aspect of the study was greatly aided by the mix-and-match nature of the "3 + 1" methodology.[22,23]

Scheme 4



12b X = CH
35b X = N

23 X = CH
47 X = N

Benzoporphyrins may be obtained from their tetrahydro analogues by dehydrogenation with DDQ in refluxing toluene,[38a] and the synthesis of benzo[*m*]oxybenziporphyrin **23** was accomplished analogously. The butanoporphyrinoid **12b**, which had been prepared for this purpose, was treated with 2.2 equiv of DDQ in refluxing toluene for 16 h to give the required benzo derivative **23** in 61% yield (Scheme 4). Modified tripyrranes **24** and **25** were available from the earlier studies,[22,23,31] and this allowed the synthesis of the extended oxybenziporphyrins **26** and **27** (Scheme 5). Pretreatment of the di-*tert*-butyl ester **24** with TFA, followed by condensation with **14** in 5% TFA-CH_2Cl_2, neutralization, and oxidation with DDQ gave the phenanthro[9,10-*m*]oxybenziporphyrin **26** in 52% yield. Similarly, acenaphthotripyrrane **25** condensed with **14** to afford oxybenziporphyrin **27** in 37% yield.

The UV−vis spectra for the free-base oxybenziporphyrins showed the same general trend of increasing bathochromic shifts from benzo- to phenanthro- to acenaphthoring fusion, but these shifts were more gradual in this series (Figure 3; Table 1). Hence, although the effect of one benzene or phenanthrene unit on the porphyrin chromophore was slight, and the acenaphthylene structure **22** showed profoundly modified UV−vis spectra,[22,23] the acenaphtho[1,2-*m*]oxybenziporphyrin was less of an outlier. The more intense Soret band shifted from 428 nm in **14a** to 434, 440, and 446 nm in **23**, **26**, and **27**, respectively, whereas the most red-shifted Q-band for the sequence was 698, 698, 713, and 724 nm (Table 1). The acenaphthylene clearly is exerting less influence than the

(38) Mono- and dibenzoporphyrins: (a) Lash, T. D. *Energy Fuels* **1993**, *7*, 166. (b) Clezy, P. S.; Fookes, C. J. R.; Mirza, A. H. *Aust. J. Chem.* **1977**, *30*, 1337. (c) Clezy, P. S.; Mirza, A. H. *Aust. J. Chem.* **1982**, *35*, 197. (d) Clezy, P. S.; Leung, C. W. F. *Aust. J. Chem.* **1993**, *46*, 6, 1705. (e) Bonnett, R.; McManus, K. A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2461. See also, May, D. A., Jr.; Lash, T. D. *J. Org. Chem.* **1992**, *57*, 4820. Lash, T. D. In *Advances in Nitrogen Heterocycles*; Moody, C. J., Ed.; JAI Press: 1995; Vol. 1, pp 19−69.

(39) Naphthoporphyrins: Lash, T. D.; Roper, T. J. *Tetrahedron Lett.* **1994**, *35*, 7715. Lash, T. D.; Denny, C. P. *Tetrahedron* **1995**, *51*, 59. Kopranenkov, V. N.; Vorotnikov, A. M.; Luk'yanets, E. A. *J. Gen. Chem. USSR* **1979**, *49*, 2467. Kopranenkov, V. N.; Vorotnikov, A. M.; Dashkevich, S. N.; Luk'yanets, E. A. *J. Gen. Chem. USSR* **1985**, *55*, 803. Rein, M.; Hanack, M. *Chem. Ber.* **1988**, *121*, 1601. Tomé, A. C.; Lacerdo, P. S. S.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. *Chem. Commun.* **1997**, 1199.

(40) Phenanthroporphyrins: Lash, T. D.; Novak, B. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 4, 683. Lash, T. D.; Novak, B. H. *Tetrahedron Lett.* **1995**, *36*, 4381. Novak, B. H.; Lash, T. D. *J. Org. Chem.* **1998**, *63*, 3998.

(41) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; pp 871−889.

(42) Lash, T. D.; Chandrasekar, P. *J. Am. Chem. Soc.* **1996**, *118*, 8767.

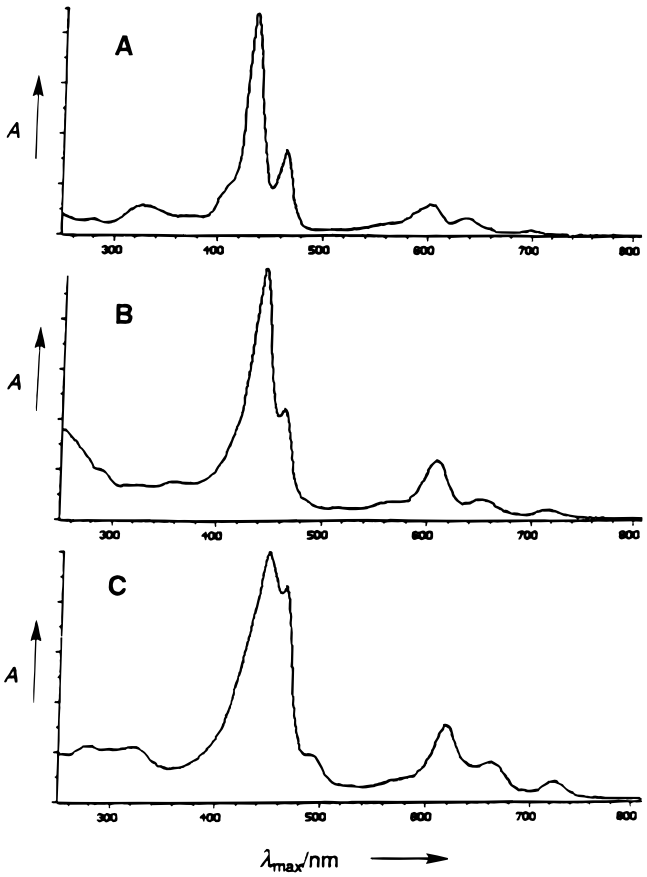
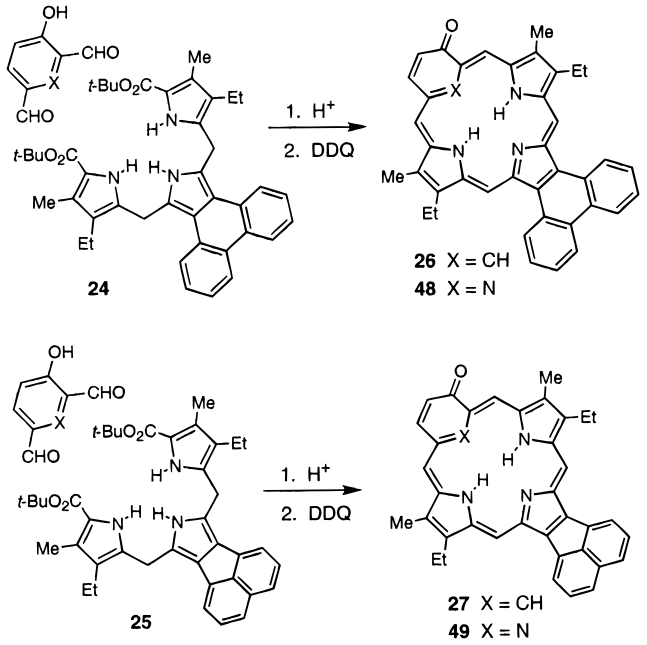


Figure 3. UV−vis spectra of benzo- (A), phenanthro- (B), and acenaphtho- (C) oxybenziporphyrins **23**, **26**, and **27**, repectively, in chloroform showing increasing bathochromic shifts down the series.

Scheme 5



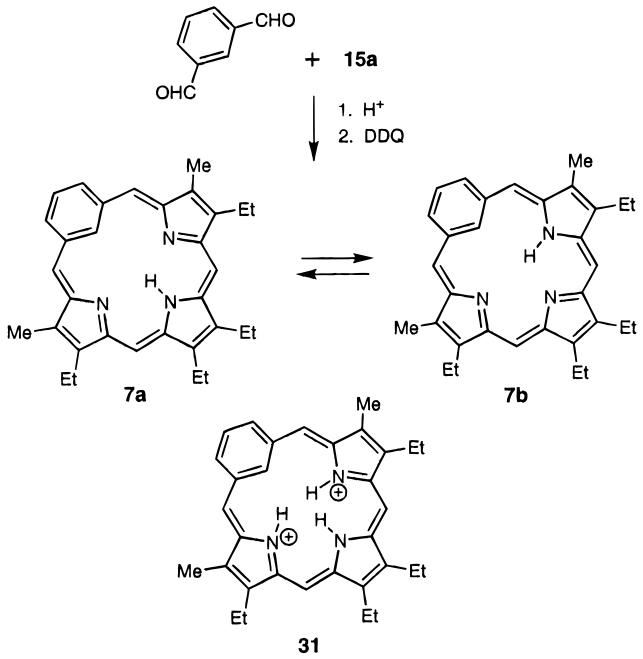
porphyrin series, but the phenanthrene unit in particular produces a much larger one. The monocation was not be observed for **23**, but spectroscopic data were obtained for the monocations of **26** and **27**. The dications for all three oxybenziporphyrins were also investigated, and again showed loss of porphyrinoid aromaticity by UV−vis and proton NMR spectroscopy. All these species showed the same general trends with the acenaphthylene-fused structures giving the largest red shifts. For instance, the strongest Soret-like bands for the dications shifted from 434 to 440 to 448 to 464 nm for **12a**, **23**, **26**, and **27**. The examination of these trends for other porphyrinoid systems is likely to be worthwhile (see also below).

Table 1. Electronic Spectra of Oxybenziporphyrin and Selected Porphyrinoids with One Fused Aromatic Ring System

porphyrinoid (solvent)	Soret bands[a]		Q bands IV	III	II	I
12a	428	456	548	590	636	698
($CHCl_3$)	(5.18)	(4.84)	(3.89)	(4.35)	(3.89)	(3.68)
23	434	464	565	602	634	698
($CHCl_3$)	(5.23)	(4.82)	(4.03)	(4.38)	(4.12)	(3.52)
26	440	462	568	608	650	713
($CHCl_3$)	(5.14)	(4.78)	(3.99)	(4.51)	(4.05)	(3.78)
27	446	464	570	618	658	724
($CHCl_3$)	(5.01)	(4.95)	(4.02)	(4.47)	(4.11)	(3.58)

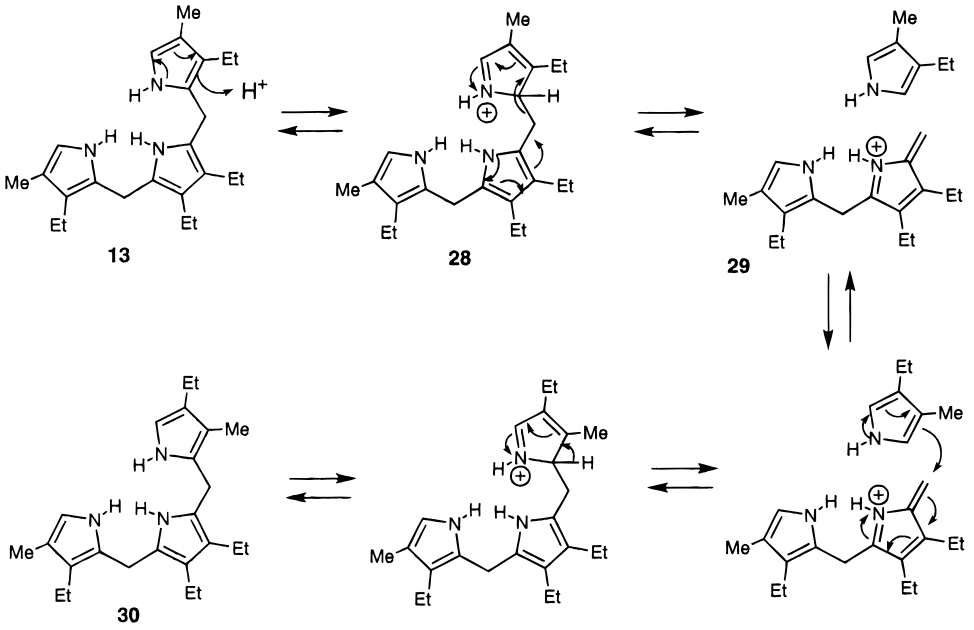
[a] λ_{max} values in nanometers ($\log_{10} \epsilon$).

Scheme 6



Benziporphyrin Revisited. The nonaromatic benziporphyrin **7** originally was obtained in low yield (5.9%) by condensing the tripyrrane dicarboxylic acid **15a** with isophthalaldehyde under dilute conditions using HBr as a catalyst (Scheme 6).[33] In addition, unlike our investigations, dicarboxylic acid **15a** was not isolated, but instead the crude solution obtained from the hydrogenolysis of the related dibenzyl ester was used directly.[33] The compound was reported to exist as two nonequivalent tautomers **7a** and **7b** (ratio, 5:1) that did not interconvert on the NMR time scale. However, we speculated that the extra peaks might have arisen due to isomer contamination. It was important to know the spectroscopic properties of the nonaromatic species, because this provides a counterpoint to the structurally related aromatic systems. Using our standard conditions for the "3 + 1" chemistry, isophthalaldehyde was condensed with **15a**, and after careful chromatography and recrystallization from chloroform-methanol, benzipor-

Scheme 7



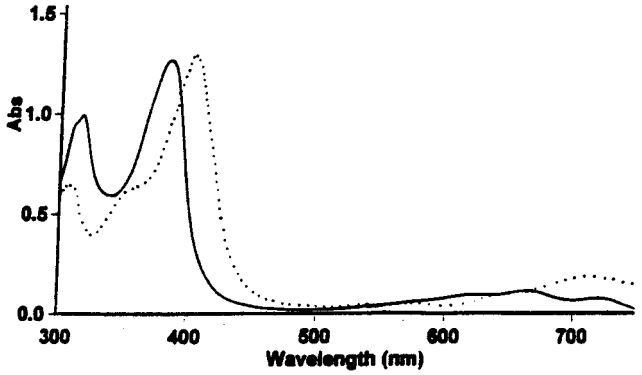


Figure 4. UV−vis spectra of benziporphyrin **7** in chloroform (solid line) and 1% TFA-chloroform (dotted line).

phyrin was obtained in 28% yield as dark-purple crystals. The product was somewhat unstable in solution and initially required considerable perseverance to obtain a pure sample. The 400-MHz proton NMR spectrum for **7** was in good agreement with the data reported for the "major tautomer" of this system,[33] but no further resonances were observed for the proposed "minor tautomer" (Figure 4). The inner CH appeared as an unresolved triplet at 7.96 ppm, whereas the external benzene protons were observed at 7.75 and 7.98 ppm. The *meso*-protons resonated at 6.6 and 7.3 ppm, the latter virtually coincident with the chloroform solvent peak, whereas the NH appeared near 8.9 ppm. These data confirm the absence of even a trace amount of porphyrinoid aromaticity in this structure. In addition, the internal CH did not exchange with D_2O, confirming that tautomer **8** (Chart 1) was not present in equilibrium at significant concentrations. Carbon-13 NMR spectroscopy showed the presence of 5 types of sp^3 and 12 types of sp^2 hybridized carbon atoms, as would be expected for a structure with a plane of symmetry. EIMS gave a strong molecular ion (also confirmed by high-resolution data), although abnormally large [M + 1] and [M + 2] were also noted.

The formation of isomers in "3 + 1" chemistry, as well as in other porphyrin syntheses, is a cause for concern and merits additional comments. Pyrrolic structures linked by methylene units, including dipyrrylmethanes,[43] tripyrranes, and bilanes,[44] are susceptible to acid-catalyzed rearrangements depending to a great extent on the reaction conditions used. In the present case, the electron-rich tripyrrane **13** (Scheme 7) may be reversibly protonated to generate intermediate **28**, and this may undergo a fragmentation to give the stabilized azafulvene cation **29** together with an α,α′-diunsubstituted pyrrole. Recombination then may occur in two different ways, one to re-form tripyrrane **13** but the other to give the isomeric structure **30**. Further fragmentation-recombination may lead to further isomeric or even nonisomeric tripyrranes (or other oligopyrroles). If the cyclization reaction is relatively fast, single porphyrinoid products are to be expected. However, if the acidolytic processes occur at a comparable rate, isomeric products will inevitably arise. In developing our conditions for the "3 + 1" methodology,[21,28] we sought to demonstrate rigorously the isomeric purity of our products, but the alternative HBr conditions clearly cannot be trusted for this type of chemistry.[45]

The UV−vis spectrum for **7** in chloroform (Figure 5) showed a moderately strong absorption at 384 nm ($\epsilon = 6.77 \times 10^4$) which was reminiscent of a weak Soret band but otherwise did not resemble the spectra for the aromatic oxybenziporphyrins. Our data differed considerably from the previous report,[33] raising additional questions about the purity of the original material. Given the problems that we encountered in purifying this compound, this is perhaps understandable. In 1% TFA-chloroform, a protonated species **31** was formed that showed bathochromically shifted UV−vis absorptions (Figure 5) but again no indications of overall aromaticity. The proton NMR spectrum for **7** in TFA-$CDCl_3$ showed mostly downfield shifts consistent with a protonated species, although the interior CH shifted to 5.2 ppm. This

(43) Jackson, A. H.; Lertwanawatana, W.; Pandey, R. K.; Rao, K. R. N. *J. Chem. Soc., Perkin Trans. 1* **1989**, 374.
(44) Jackson, A. H.; Kenner, G. W.; Smith, K. M. *J. Chem. Soc. (C)* **1971**, 502.
(45) For further commentary, see ref 25.

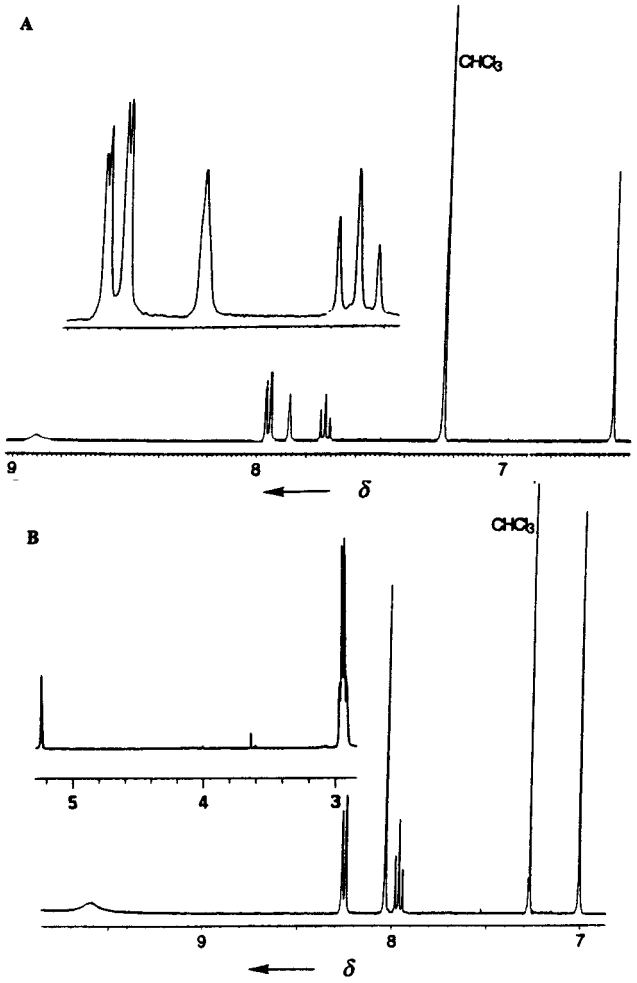
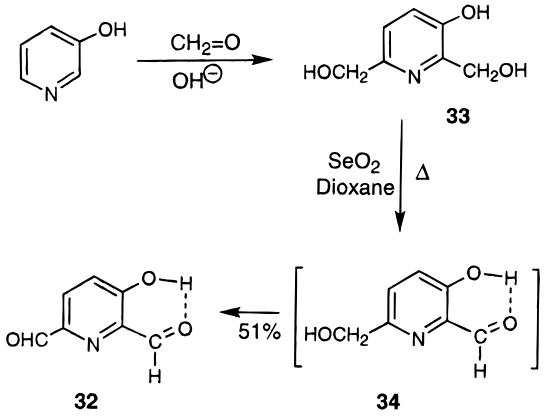


Figure 5. Partial 400-MHz proton NMR spectra of benziporphyrin **7**. A, Free base in $CDCl_3$; B, Dication in TFA-$CDCl_3$.

upfield shift could not be attributed to a weak diamagnetic ring current in **31** and presumably is caused by a conformational change in the macrocycle. The 22-H did not exchange with d-TFA even after several days at room temperature, confirming that protonated species related to structure **8** are not present under these conditions.

Oxypyriporphyrins. The success of these investigations quickly led us to investigate the synthesis of pyridone analogues of porphyrins.[24] For these studies, a 3-hydroxypyridinedialdehyde **32** was prepared by oxidation of the related dicarbinol **33** with selenium dioxide in refluxing dioxane (Scheme 8).[24] After 2 h, a mixture of mono- and dialdehydes was produced, but after further reaction the dialdehyde was formed in good yields. Only one of the two possible monoaldehydes was present by NMR spectroscopy in the 2-h reactions (assigned as isomer **34** due to the strong intramolecular hydrogen bonding exhibited in solution). The diformyl derivative is easily purified by steam distillation, an important consideration given the difficulties that can arise in removing selenium byproducts. The dialdehyde also shows strong intramolecular hydrogen bonding which persists even in d_6-DMSO. Condensation of **32** with tripyrrane **15** under the standard "3 + 1" conditions gave oxypyriporphyrin **35a** in excellent yields (60−86%).[24] This compound gave green solutions and was isolated as bluish-purple crystals. The structure and aromaticity for this system was confirmed by NMR, UV−vis and IR

Scheme 8

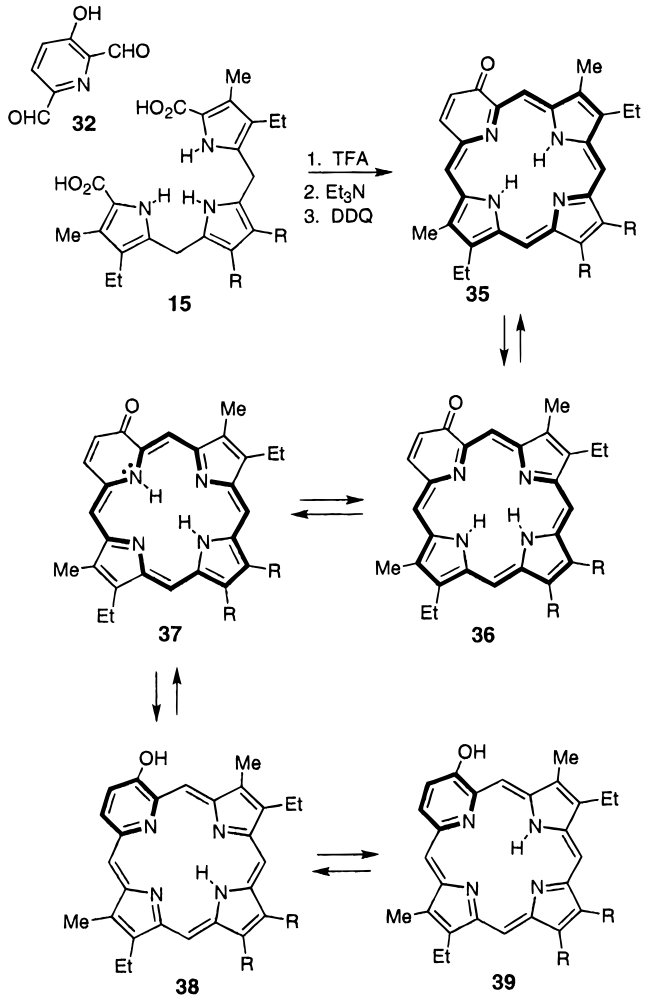


spectroscopy, as well as by MS and combustion analysis. The UV−vis spectrum showed a strong Soret band at 422 nm and several minor absorptions in the visible region. IR and carbon-13 NMR spectroscopy show the presence of the cross-conjugated carbonyl moiety that results from this chemistry. The proton NMR spectrum again demonstrated the presence of a strong diamagnetic ring current with the *meso*-protons showing up between 9.5 and 11 ppm, whereas the NHs were observed as two separate broad singlets near −3.6 ppm. Several aromatic tautomers can be envisioned for this system including **36** and **37**, as well as the nonaromatic hydroxypyriporphyrin species **38** and **39** (Scheme 9). Tautomers **38** and **39** do not seem to be favored, and we have previously argued that **35** would be preferred over **36** and **37** because of an unfavorable steric interaction between the internal hydrogens in the former and the loss of the pyridone unit in the latter.[24] This was subsequently confirmed by "gradient supported HMBC inverse CH correlation" NMR studies at high oxypyriporphyrin concentrations.[46] Trace TFA produced an aromatic monocation whose UV−vis spectrum was consistent with tautomers **40** and **41** but not with hydroxypyridine tautomers such as **42** (Chart 4). Further addition of TFA produced a new species (dication), but this remained fully aromatic as judged by the presence of a strong Soret band and the retention of a powerful ring current in proton NMR spectroscopy; this was consistent with the predominance of protonated pyridone structure **43** over hydroxypyridines such as **44**. This species persisted in 10% HCl-methanol, and triprotonated species such as **45** were not observed for this system. Oxypyriporphyrin readily formed nickel(II), copper(II), and zinc chelates **46**, and these also exhibited characteristics that were consistent with aromatic species.

The butanotripyrrane **15b** similarly condensed with **32** to give the new oxypyriporphyrin **35b** (Scheme 9) in 48% yield. Dehydrogenation with DDQ in refluxing toluene then gave the benzo derivative **47** (Scheme 4). In addition, by making use of the modified tripyrranes **24** and **25**, it was possible to produce the phenanthro[9,10-*m*]- and acenaphtho[1,2-*m*]oxypyriporphyrins **48** and **49** in 74% and 47% yield, respectively. Each of these extended structures were reacted with metal acetates to

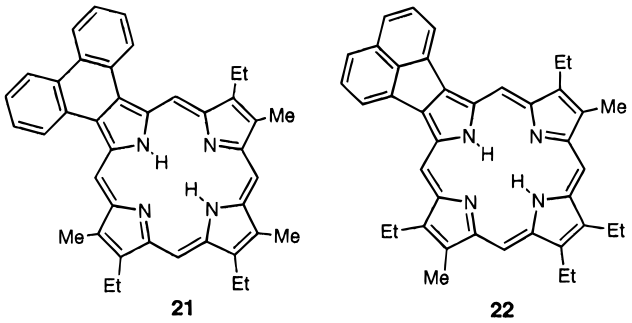
(46) Schönemeier, T.; Breitmaier, E. *Synthesis* **1997**, 273. The German group resynthesized oxypyriporphyrin **35a** under our conditions (5% TFA-CH_2Cl_2) using a crude preparation of diformylpyridine **32** and presumably for this reason isolated the product in relatively low yield (23%).

Scheme 9



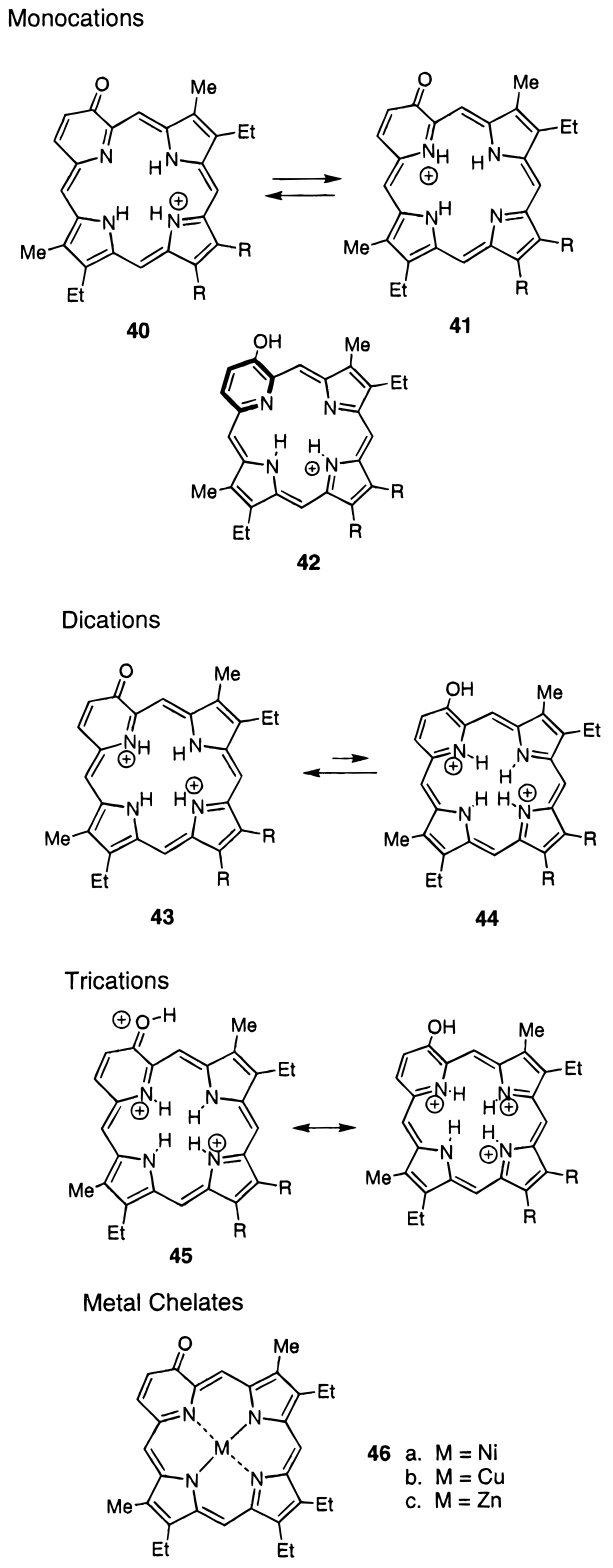
a. R = Et; b. R,R = -$(CH_2)_4$-

Chart 3



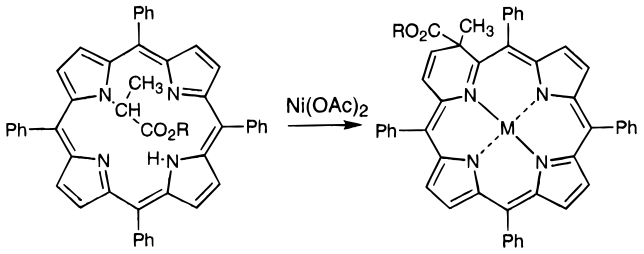
produce the related nickel(II), copper(II), and zinc chelates, and the UV−vis spectra for all of the species were investigated. The free bases, monocations, dications, and metal chelates all showed porphyrin-like (aromatic) characteristics by UV−vis and, where applicable, NMR spectroscopy. In terms of the red shifts anticipated, the series of values obtained for **35a**, **47**, **48**, and **49** showed many of the same trends discussed previously for the oxybenziporphyrin series. The larger Soret bands for the free bases were at 422, 424, 432, and 436 nm, whereas the dications gave values of 429, 442, 450, and 460 nm. The data for the metal chelates of oxypyriporphyrins did not correlate well with the trends observed for true metalloporphyrins. In particular, the λ_{max} values for the

Chart 4



major absorption bands of metalloporphyrins generally increased across the periodic table with zinc chelates given the longest wavelength absorptions, followed by Cu(II) and then Ni(II).[41] However, all the nickel(II) chelates in the oxypyriporphyrin series showed longer wavelength absorptions than the corresponding copper(II) complexes. Ni(II) and Cu(II) complexes gave one major Soret band for these structures, but the zinc chelates generally gave two strong bands in this region

Scheme 10



50 R = Me, Et

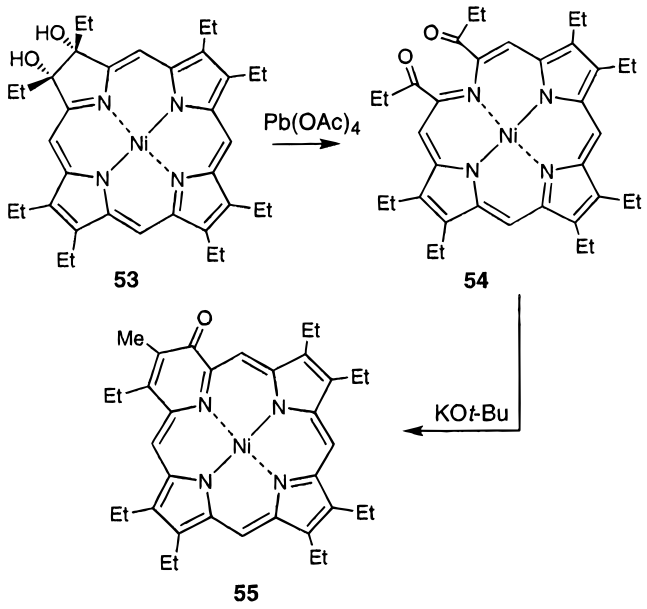
51 M = Ni a. R = Me
b. R = Et

52 M = 2H; R = Et

(these spectra were often run in the presence of trace pyrrolidine to inhibit aggregation, although this did not seem to be a factor). However, the zinc chelates still showed the largest bathochromic shifts in each case, although comparisons were difficult because of the varying number of bands that were present. The ring fusion affects for the metal chelates were similar to those discussed above, although the longest wavelength bands for the metalloacenaphthoporphyrinoids were disproportionally red shifted and intensified. For instance the longest wavelength band for the zinc complex of **48** appears at 650 nm ($\log \epsilon = 4.72$), whereas the zinc chelate of **49** shows the equivalent absorption at 670 nm ($\log \epsilon = 4.83$).

In our earlier articles,[24,34] we were unaware of any other reports on aromatic pyridine-containing porphyrinoids, but two separate examples have now been brought to our attention. In relation to their extensive studies on the synthesis of homoporphyrins, Callot and Schaeffer[47] showed that N-substituted tetraphenylporphyrin **50** rearranged in the presence of refluxing nickel(II) acetate in chloroform-methanol to give the ring-expanded nickel chelate **51** in 13% yield (Scheme 10). Demetalation afforded a tetraphenylporphyrinoid **52** that displayed a chlorin-like electronic spectrum with moderately strong absorptions at 535, 577, 627, and 687 nm and a strong Soret band at 430 nm. In model studies relating to chlorophyll catabolism, Adams et al.[48] reacted nickel(II) *vic*-dihydroxyoctaethylchlorin **53** with lead tetraacetate to give the secochlorin **54** and subsequent treatment with potassium *tert*-butoxide induced aldol cyclization to afford the nickel oxypyriporphyrin **55** (Scheme 11). This compound has essentially the same chromophore as **46a** and displayed a similar UV−vis spectrum with a Soret band at 437 nm and two weaker absorptions at 568 and 612 nm. Although these studies[47−49] had no influence on the development of our more extensive investigations, they nonetheless provided further information on the adaptability of the porphyrin macrocycle. The chemistry reported by Adams et al.[48] also potentially provides the means by which the new structures reported by our group could be further modified to give still more diverse porphyrinoid systems.

Scheme 11



53 **54** **55**

Conclusions and Future Outlook

The "3 + 1" route for porphyrinoid synthesis has been shown to be an ideal methodology for preparing unusual aromatic structures such as the oxybenzi- and oxypyriporphyrins. In fact oxybenziporphyrin **12** was the first example of a carbaporphyrinoid (i.e., a fully aromatic porphyrinoid with a carbocyclic ring in place of a pyrrole unit) and in part led the way toward the discovery of related structures such as **9** and **10**.[1,6,25,26,30] Oxypyriporphyrins are formed in particularly high yields using this method, and this will facilitate an extensive examination of their chemistry. By using further modified tripyrranes, structures with fused benzene, acenaphthylene, and phenanthrene rings are easily prepared, and important spectroscopic trends have been identified. These unusual porphyrinoid structures exhibit novel spectroscopic and chemical properties and are likely to garner considerable attention in the future.

Experimental Section

5-Formylsalicylaldehyde was purchased from TCI America; all other reagents were purchased from Aldrich Chemical Co. and used without further purification. Tripyrranes **15a**, **15b**, **24**, and **25** were prepared as described previously.[23,28] Chromatography was performed using grade 3 neutral alumina or 70−230 mesh silica gel. Metallooxypyriporphyrins were prepared under standard conditions by reacting the free-base porphyrinoid with nickel(II), copper(II), or zinc acetate in methanol-chloroform[50] or DMF.[51]

3-Hydroxy-2,6-pyridinedicarboxaldehyde (32): Prepared as white crystals, mp 145−146 °C as described previously.[24] ^{1}H NMR (d_6-DMSO): δ 7.60 (1H, d, J = 8.7 Hz, 4-H), 8.03 (1H, d, J = 8.7 Hz, 5-H), 9.88 (1H, s), 10.19 (1H, s) (2 × CHO), 11.85 (1H, br s, OH); ^{13}C NMR (d_6-DMSO): δ 126.89, 127.31, 138.74, 145.00, 160.12, 191.54, 191.66.

9,13,14,18-Tetraethyl-8,19-dimethyl-2-oxybenziporphyrin (12a): Tripyrranedicarboxylic acid **15a** (100 mg) was stirred with TFA (1 mL) under an atmosphere of nitrogen for 10 min. The solution was diluted with dichloromethane (19

(47) Callot, H. J.; Schaeffer, E. *Tetrahedron* **1978**, *34*, 2295.

(48) Adams, K. R.; Bonnett, R.; Burke, P. J.; Salgado, A.; Vallés, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1860; Adams, K. R.; Bonnett, R.; Burke, P. J.; Salgado, A.; Vallés, M. A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1769.

(49) In addition, secochlorins with six-membered ring anhydride or acetal units have been reported: Crossley, M. J.; King, L. G. *J. Chem. Soc., Chem. Commun.* **1984**, 920. Brückner, C.; Rettig, S. J.; Dolphin, D. *J. Org. Chem.* **1998**, *63*, 2094.

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(51) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

mL), followed immediately by the addition of 5-formylsalicylaldehyde (**14**; 36 mg), and the mixture was stirred under nitrogen, in the dark, for a further 2 h. After neutralization by the dropwise addition of triethylamine, DDQ (51 mg) was added and the resulting solution was stirred in the dark for an additional hour. The mixture was washed with water and chromatographed on grade 3 alumina, eluting first with dichloromethane and then with chloroform. A deep-green fraction was collected with chloroform and recrystallized from chloroform-methanol to give the porphyrin analogue (46 mg; 44%) as sparkling purple needles, mp 261−262 °C, dec; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 428 (5.18), 456 (4.84), 548 (3.89), 590 (4.35), 636 (3.89), 698 (3.68); UV−vis (0.005% TFA-$CHCl_3$; monocation): λ_{max} (log ϵ) 428 (5.22), 468 (4.74), 606 (4.17), 630 (4.11), 688 (3.68); UV−vis (5% TFA-$CHCl_3$; dication): λ_{max} (log ϵ) 352 (4.70), 434 (4.87), 554 (3.86), 598 (4.20), 696 (3.83), 768 (3.96); ^{1}H NMR ($CDCl_3$): δ −7.17 (1H, d, J = 2 Hz), −3.8 (2H, br s), 1.61−1.73 (12H, 4 overlapping triplets), 3.29 (3H, s), 3.65 (3H, s), 3.62−3.81 (8H, 4 overlapping quartets), 7.35 (1H, d, J = 9 Hz), 8.49 (1H, dd, ^3J = 9 Hz, ^4J = 2 Hz), 8.85 (1H, s), 8.98 (1H, s), 8.99 (1H, s), 10.29 (1H, s); ^{1}H NMR (10% TFA-$CDCl_3$): δ 1.05 (1H, br s), 1.42 (6H, t, J = 7.3 Hz), 1.54 (6H, t, J = 7.6 Hz), 2.95 (3H, s), 2.96 (3H, s), 3.27−3.38 (8H, m), 5.54 (2H, br s), 7.53 (1H, d, J = 8.5 Hz), 8.54 (1H, d, J = 8.5 Hz), 8.05 (1H, s), 8.10 (1H, s), 8.80 (1H, s), 9.41 (1H, s); ^{13}C NMR ($CDCl_3$): δ 11.39, 11.85, 17.08, 17.17, 18.25, 18.32, 19.31, 19.41, 19.74, 93.29, 94.92, 105.66, 111.07, 112.27, 121.35, 126.08, 130.15, 131.61, 134.14, 135.31, 136.28, 137.12, 137.90, 138.07, 140.07, 144.54, 145.07, 147.09, 154.64, 156.17, 187.94; ^{13}C NMR (TFA-$CDCl_3$): δ 10.98, 14.91, 15.00, 15.80, 15.85, 18.58, 18.77, 93.22, 94.33, 113.89, 119.38, 120.24, 121.69, 123.82, 126.97, 140.60, 140.96, 141.08, 141.64, 145.36, 146.02, 146.71, 147.61, 148.46, 148.74, 149.72, 154.85, 156.32, 171.43; EIMS (70 eV): m/z (%): 477 (100) [M^+], 462 (19) [$M^+ - CH_3$]; HRMS: Calcd for $C_{32}H_{35}N_3O$: m/z 477.2782; Found: 477.2774. Anal. Calcd for $C_{32}H_{35}N_3O \cdot {}^1/_2H_2O$: C, 78.98; H, 7.45; N, 8.63. Found: C, 79.04; H, 7.30; N, 8.61.

13,14-Butano-9,18-diethyl-8,19-dimethyl-2-oxybenziporphyrin (12b): Butanotripyrrane dicarboxylic acid **15b** (100 mg) and hydroxybenzenedialdehyde **14** (34 mg) were reacted under the conditions used for **12a**. Recrystallization from chloroform-methanol afforded the porphyrin analogue (41 mg; 39%) as purple crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 430 (5.21), 456 (4.84), 552 (3.92), 592 (4.32), 632 (3.93), 700 (3.69); UV−vis (0.005% TFA-$CHCl_3$; monocation): λ_{max} (log ϵ) 428 (5.22), 468 (4.75), 606 (4.17), 630 (4.16), 684 (3.67); UV−vis (5% TFA-$CHCl_3$; dication): λ_{max} (log ϵ) 350 (4.68), 434 (4.89), 552 (3.81), 596 (4.16), 696 (3.79), 762 (3.93); ^{1}H NMR ($CDCl_3$ + trace pyrrolidine): δ −6.53 (1H, s), 1.70−1.75 (6H, 2 overlapping triplets), 2.36−2.42 (4H, m), 3.40 (3H, s), 3.51 (3H, s), 3.75−3.80 (4H, m), 3.82−3.85 (4H, 2 overlapping quartets), 7.45 (1H, d, J = 9.9 Hz), 8.70−8.74 (1H, m), 9.08 (1H, s), 9.12 (1H, s), 9.20 (1H, s), 10.46 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ 1.37−1.42 (6H, 2 overlapping triplets), 2.20−2.21 (4H, m), 2.91 (6H, s), 3.21−3.27 (8H, m), 5.61 (3H, br s), 7.47 (1H, d, J = 8.7 Hz), 7.91 (1H, s), 7.95 (1H, s), 8.48 (1H, d, J = 8.4 Hz), 8.74 (1H, s), 9.35 (1H, s); ^{13}C NMR (TFA-$CDCl_3$): δ 11.05, 11.09, 14.97, 15.06, 18.62, 21.88, 22.16, 93.15, 94.24, 114.64, 119.59, 120.56, 121.89, 124.03, 127.17, 140.79, 141.16, 141.30, 141.84, 143.34, 144.01, 146.96, 147.82, 148.90, 150.15, 155.35, 156.83, 171.95; HRMS (FAB): Calcd for $C_{32}H_{33}N_3O$ + H: m/z 476.2702; Found: 476.2702. Anal. Calcd for $C_{32}H_{33}N_3O \cdot H_2O$: C, 77.86; H, 7.04; N, 8.30. Found: C, 77.86; H, 7.15; N, 8.51.

9,18-Diethyl-8,19-dimethylbenzo[*m*]-2-oxybenziporphyrin (23): Tetrahydrobenzooxybenziporphyrin **12b** (10 mg) was dissolved in toluene (5 mL), and DDQ (12 mg) was added. The mixture was refluxed 16 h, cooled to room temperature, and washed with water. The solvent was evaporated under reduced pressure and the residue chromatographed on grade 3 alumina, eluting first with chloroform and then with 1% triethylamine-chloroform. A deep-green fraction was collected and recrystallized from chloroform-methanol to give the benzoanalogue (6 mg; 61%) as a dark-blue powder, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 376 (4.17), 410 (sh, 4.61), 434 (5.23), 464 (4.82), 565 (sh, 4.03), 602 (4.38), 634 (4.12), 698 (3.52); UV−vis (5% TFA-$CHCl_3$): λ_{max} (log ϵ) 350 (4.52), 440 (4.98), 548 (3.89), 592 (4.19), 732 (3.90); ^{1}H NMR ($CDCl_3$): δ −6.61 (1H, s), −3.56 (2H, br s), 1.67−1.75 (6H, 2 overlapping triplets), 3.30 (3H, s), 3.41 (3H, s), 3.73−3.83 (4H, 2 overlapping quartets), 7.40 (1H, d, J = 9.6 Hz), 7.99−8.02 (2H, m), 8.59 (1H, d, J = 9.0 Hz), 8.90−8.95 (2H, m), 8.97 (1H, s), 9.23 (1H, s), 9.26 (1H, s), 10.23 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ 1.45−1.50 (6H, 2 overlapping triplets), 2.96 (3H, s), 2.98 (3H, s), 3.34−3.40 (4H, 2 overlapping quartets), 7.62 (1H, d, J = 7.2 Hz), 8.11−8.14 (2H, m), 8.37 (1H, s), 8.41 (1H, s), 8.48 (1H, d, J = 7.8 Hz), 8.71 (1H, s), 8.75−8.76 (2H, m), 9.40 (1H, s); HRMS (FAB): Calcd for $C_{32}H_{29}N_3O$ + H: m/z 472.2389; Found: 472.2390.

9,18-Diethyl-8,19-dimethylphenanthro[9,10-*m*]-2-oxybenziporphyrin (26): Phenanthrotripyrrane di-*tert*-butyl ester **24** (100 mg) and hydroxybenzenedialdehyde **14** (23 mg) were reacted in the manner described for **12a**. Recrystallization from chloroform-methanol yielded the title porphyrin analogue (45 mg; 52%) as dark-blue crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 358 (4.32), 440 (5.14), 462 (4.78), 568 (3.99), 608 (4.51), 650 (4.05), 713 (3.78); UV-vis (0.01% TFA-$CHCl_3$; monocation): λ_{max} (log ϵ) 448 (5.17), 482 (4.72), 628 (4.29), 648 (4.27), 708 (3.76); UV-vis (5% TFA-$CHCl_3$; dication): λ_{max} (log ϵ) 364 (4.60), 448 (4.83), 576 (4.06), 622 (4.34), 780 (3.96); ^{1}H NMR (d_5-pyridine): δ −5.57 (1H, s), −2.29 (2H, br s), 1.64−1.74 (6H, 2 overlapping triplets), 3.28 (3H, s), 3.33 (3H, s), 3.79−3.96 (4H, 2 overlapping quartets), 7.75 (1H, d, J = 9.6 Hz), 8.01−8.05 (2H, m), 8.23−8.26 (2H, m), 8.99 (1H, d, J = 9.6 Hz), 9.30−9.33 (2H, m), 9.58 (1H, s), 10.05−10.07 (2H, m), 10.43 (1H, s), 10.59 (1H, s), 10.75 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ 1.42−1.46 (6H, 2 overlapping triplets), 2.91 (6H, s), 3.30−3.34 (4H, 2 overlapping quartets), 6.43 (3H, br s), 7.46 (1H, d, J = 8.4 Hz), 8.05−8.08 (4H, m), 8.43 (1H, d, J = 8.4 Hz), 8.72 (1H, s), 8.89 (1H, s), 8.95 (1H, s), 9.06 (2H, d, J = 8.4 Hz), 9.14 (2H, d, J = 7.2 Hz), 9.24 (1H, s); ^{13}C NMR (TFA-$CDCl_3$): δ 11.06, 14.98, 15.08, 18.85, 95.98, 97.17, 113.51, 120.86, 121.96, 124.59, 125.12, 125.61, 126.66, 127.73, 129.69, 130.31, 130.39, 131.93, 132.40, 133.69, 133.80, 141.21, 141.30, 141.41, 142.45, 146.67, 146.74, 147.61, 147.72, 148.03, 155.49, 156.93, 170.95; HRMS (FAB): Calcd for $C_{40}H_{33}N_3O$ + H: m/z 572.2702; Found: 572.2702. Anal. Calcd for $C_{40}H_{33}N_3O \cdot {}^1/_2H_2O$: C, 82.73; H, 5.90; N, 7.23. Found: C, 83.12; H, 5.74; N, 7.03.

9,18-Diethyl-8,19-dimethylacenaphtho[1,2-*m*]-2-oxybenziporphyrin (27): Acenaphthotripyrrane di-*tert*-butyl ester **25** (100 mg) was stirred in TFA (7 mL) under nitrogen for 10 min. Dichloromethane (280 mL) was added, followed immediately by hydroxybenzenedialdehyde **14** (48 mg). The reaction was stirred in an atmosphere of nitrogen, in the absence of light, for 16 h. After neutralizing the mixture by the dropwise addition of triethylamine, DDQ (36 mg) was added to oxidize the reaction. The solution was stirred for a further hour. After washing with water, the solvent was removed in vacuo to give a dark residue. The residue was chromatographed on grade 3 alumina eluting with 1% methanol-chloroform. A dark-green fraction was collected and recrystallized from chloroform-methanol to give the porphyrin analogue (32 mg; 37%) as dark-blue crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 446 (5.01), 464 (4.95), 495 (sh, 4.31), 570 (sh, 4.23), 618 (4.50), 658 (4.29), 724 (3.92); UV−vis (0.1% TFA-$CHCl_3$; monocation): λ_{max} (log ϵ) 462 (5.01), 640 (4.45), 732 (3.92); UV−vis (5% TFA-$CHCl_3$; dication): λ_{max} (log ϵ) 350 (4.48), 396 (4.54), 464 (4.82), 584 (4.07), 636 (4.45), 720 (3.95), 798 (4.01); ^{1}H NMR ($CDCl_3$ + trace pyrrolidine): δ −7.62 (1H, s), 1.54−1.63 (6H, 2 overlapping triplets), 3.12 (3H, s), 3.28 (3H, s), 3.54−3.60 (4H, 2 overlapping quartets), 7.44 (1H, d, J = 9.3 Hz), 7.77−7.84 (2H, m), 7.94−7.97 (2H, m), 8.25−8.28 (2H, m), 8.55 (1H, d, J = 9.9 Hz), 8.63 (1H, s), 8.76 (1H, s), 8.80 (1H, s), 10.15 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ 1.48−1.53 (6H, 2 overlapping triplets), 2.99 (6H, s), 3.39−3.41 (4H, 2 overlapping quartets), 5.45 (3H, br s), 7.55 (1H, d, J = 9.0 Hz), 7.97 (2H, t, J = 7.5 Hz), 8.25 (2H, d, J = 7.8 Hz), 8.55−8.64 (5H, m), 8.85 (1H, s), 9.46 (1H, s); ^{13}C NMR (TFA-$CDCl_3$): δ 11.17, 15.16, 15.26, 18.86, 95.78, 96.99, 114.50,

119.57, 120.84, 122.23, 124.41, 127.14, 127.24, 127.26, 129.37, 130.35, 130.79, 132.22, 132.35, 135.54, 141.18, 141.58, 141.66, 142.21, 142.78, 143.98, 145.61, 146.25, 147.00, 147.94, 149.55, 154.54, 156.08, 172.46; HRMS (FAB): Calcd for $C_{38}H_{31}N_3O$ + H: *m/z* 546.2545; Found: 546.2544. Anal. Calcd for $C_{38}H_{31}N_3O\cdot H_2O$: C, 80.97; H, 5.90; N, 7.45. Found: C, 81.58; H, 5.35; N, 7.07.

9,13,14,18-Tetraethyl-8,19-dimethylbenziporphyrin (7): Tripyrrane dicarboxylic acid **15a** (100 mg) and 1,3-benzenedicarboxaldehyde (30 mg) were reacted under the conditions used for **12a**. The product was chromatographed on grade 3 alumina, eluting with dichloromethane and then on grade 2 alumina, eluting with chloroform. The product slowly "streaked" off the latter column as a blue fraction. Recrystallization from chloroform-methanol afforded the benziporphyrin (30 mg; 28%) as dark-purple crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 317 (4.725), 384 (4.83), 620 (3.70), 663 (3.785), 720 (3.60); UV−vis (1% TFA-$CHCl_3$): λ_{max} (log ϵ) 307 (4.54), 401 (4.84), 714 (4.00); ^{1}H NMR ($CDCl_3$): δ 1.28 (6H, t, J = 7.6 Hz), 1.36 (6H, t, J = 7.6 Hz), 2.43 (6H, s), 2.77 (4H, q, J = 7.6 Hz), 2.86 (4H, q, J = 7.6 Hz), 6.57 (2H, s), 7.27 (2H, s), 7.75 (1H, t, J = 7.5 Hz), 7.90 (1H, br t), 7.98 (2H, dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz), 8.93 (1H, br s); ^{1}H NMR (TFA-$CDCl_3$): δ 1.27−1.38 (12H, 2 overlapping triplets), 2.66 (6H, s), 2.90−2.97 (8H, 2 overlapping quartets), 5.24 (1H, br s), 7.00 (2H, s), 8.04 (2H, s), 7.96 (1H, t, J = 7.8 Hz), 8.25 (2H, dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz), 9.59 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 10.32, 15.25, 15.99, 18.07, 18.42, 93.12, 122.67, 125.16, 128.99, 134.26, 137.38, 140.67, 141.29, 141.48, 148.05, 157.33, 169.18; ^{13}C NMR (TFA-$CDCl_3$): δ 10.61, 14.19, 15.08, 18.10, 18.37, 94.37, 128.47, 132.07, 134.09, 140.62, 142.12, 143.89, 147.08, 149.01, 154.50, 162.76; HRMS: Calcd for $C_{32}H_{35}N_3$: *m/z* 461.2831; Found: 461.2832. Anal. Calcd for $C_{32}H_{35}N_3\cdot{}^1/_2H_2O$: C, 81.66; H, 7.71; N, 8.93. Found: C, 81.97; H, 7.64; N, 8.90.

13,14-Butano-9,18-diethyl-8,19-dimethyl-2-oxypyriporphyrin (35b): Butanotripyrranedicarboxylic acid **15b** (100 mg) was stirred with TFA (1 mL) under an atmosphere of nitrogen for 10 min. The solution was diluted with dichloromethane (19 mL), followed immediately by the addition of hydroxypyridinedialdehyde **32** (33 mg), and the mixture was stirred under nitrogen, in the dark, for a further 2 h. After neutralization by the dropwise addition of triethylamine, DDQ (51 mg) was added and the resulting solution was stirred in the dark for an additional hour. The mixture was washed with water and chromatographed on grade 3 alumina, eluting first with dichloromethane and then with chloroform. A deep-green fraction was collected with chloroform and recrystallized from chloroform-methanol to give the tetrahydrobenzoporphyrin analogue (51 mg; 48%) as dark bluish-purple crystals, mp > 300 °C; UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 422 (5.22), 438 (4.92), 548 (3.87), 586 (4.36), 600 (4.27), 608 (4.28); UV−vis (2% TFA-CH_2Cl_2): λ_{max} (log ϵ) 430 (5.32), 590 (4.03), 626 (4.06), 646 (4.20); ^{1}H NMR ($CDCl_3$ + 1 drop Et_3N): δ −3.60 (1H, br s), −3.52 (1H, br s), 3.53 (3H, s), 3.64 (3H, s), 3.89−4.01 (8H, m), 7.92 (1H, d, J = 9.6 Hz), 9.26 (1H, d, J = 9.3 Hz), 9.49 (1H, s), 9.57 (1H, s), 9.58 (1H, s), 10.96 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ −1.06 (4H, br s), 1.66−1.72 (6H, m), 2.53 (4H, m), 3.49 (3H, s), 3.53 (3H, s), 3.93−4.04 (8H, m), 8.59 (1H, d, J = 9.6 Hz), 9.73 (1H, d, J = 9.6 Hz), 10.08 (1H, s), 10.26 (1H, s), 10.27 (1H, s), 11.08 (1H, s); ^{13}C NMR ($CDCl_3$): δ 11.12, 11.66, 17.15, 19.29, 19.46, 23.27, 23.77, 95.33, 95.68, 103.22, 107.67, 131.25, 133.05, 134.75, 135.28, 137.06, 137.49, 137.80, 138.39, 138.68, 139.15, 142.54, 142.70, 144.23, 145.57, 154.90, 155.44, 185.29; HRMS (FAB): Calcd for $C_{31}H_{32}N_4O$ + H: *m/z* 477.2654; Found: 477.2656.

9,18-Diethyl-8,19-dimethylbenzo[*m*]-2-oxypyriporphyrin (47): Tetrahydrobenzooxypyriporphyrin **35b** (50 mg) was dissolved in toluene (15 mL) with DDQ (72 mg), and the mixture was heated under reflux for 16 h. After cooling to room temperature, the solution was washed with water and the solvent evaporated under reduced pressure. The residue was chromatographed on grade 3 alumina, eluting with a solution of 1% Et_3N and 1% methanol in chloroform. A deep-green fraction was collected and recrystallized from chloroform-methanol to yield the oxidized porphyrin analogue (44 mg; 89%) as dark-blue microcrystals, mp > 300 °C; UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 402 (sh, 4.70), 424 (5.33), 442 (4.94), 575 (sh, 4.15), 594 (4.41), 614 (4.47), 662 (3.56); UV−vis (2% TFA-CH_2Cl_2): λ_{max} (log ϵ) 428 (5.04), 442 (5.11), 540 (3.65), 582 (4.13), 656 (4.27), 706 (3.83); ^{1}H NMR ($CDCl_3$): δ −3.97 (1H), −3.95 (1H) (2 overlapping singlets), 1.76−1.84 (6H, 2 overlapping triplets), 3.46 (3H, s), 3.58 (3H, s), 3.93−4.00 (4H, 2 overlapping quartets), 7.89 (1H, d, J = 9.3 Hz), 8.06−8.08 (2H, m), 9.11−9.17 (3H, m), 9.29 (1H, s), 9.73 (1H, s), 9.77 (1H, s), 10.79 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ −1.05 (4H, br s), 1.55 (3H, t, J = 7.5 Hz), 1.65 (3H, t, J = 7.6 Hz), 3.02 (3H, s), 3.13 (3H, s), 3.61−3.93 (4H, 2 overlapping quartets), 8.07−8.10 (2H, m), 8.61 (1H, d, J = 8.4 Hz), 8.66 (1H, s), 8.68 (1H, s), 8.74−8.81 (2H, m), 8.84 (1H, s), 9.12 (1H, d, J = 8.1 Hz), 9.67 (1H, s); HRMS (FAB): Calcd for $C_{31}H_{28}N_4O$ + H: *m/z* 473.2341; Found: 473.2341. Anal. Calcd for $C_{31}H_{28}N_4O\cdot{}^1/_2H_2O$: C, 77.32; H, 6.07; N, 11.63. Found: C, 77.46; H, 5.38; N, 12.12. Nickel(II) complex: as sparkling blue crystals from chloroform-petroleum ether, mp > 300 °C; UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 442 (5.10), 628 (4.55). Copper(II) complex: as dark-purple crystals from chloroform-methanol, mp > 300 °C; UV−vis (CH_2Cl_2 − trace pyrrolidine): λ_{max} (log ϵ) 436 (5.27), 582 (4.04), 628 (4.59). Zinc complex: as sparkling-blue crystals from chloroform-hexanes, mp > 300 °C; UV−vis (CH_2Cl_2 − trace pyrrolidine): λ_{max} (log ϵ) 446 (5.30), 460 (4.99), 588 (4.09), 640 (4.52); ^{1}H NMR ($CDCl_3$ + 1 drop pyrrolidine): δ 1.79−1.84 (6H, 2 overlapping triplets), 3.46 (3H, s), 3.55 (3H, s), 3.96−4.00 (4H, 2 overlapping quartets), 8.09−8.13 (3H, m), 9.28−9.29 (2H, m), 9.39 (1H, d, J = 9.3 Hz), 9.43 (1H, s), 9.97 (1H, s), 9.98 (1H, s), 10.94 (1H, s).

9,18-Diethyl-8,19-dimethylphenanthro[9,10-*m*]-2-oxypyriporphyrin (48): Phenanthrotripyrrane di-*tert*-butyl ester **24** (100 mg) and **32** (23 mg) were reacted in the manner described for **35b**. The residue was chromatographed on grade 3 alumina eluting with 10% methanol-chloroform. A dark-green band was collected and recrystallized from chloroform-methanol to give the title porphyrin analogue (64 mg; 74%) as dark navy-blue crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 432 (5.29), 585 (sh, 4.25), 602 (4.50), 626 (4.58), 670 (3.71); UV−vis (1% TFA-$CHCl_3$; monocation): λ_{max} (log ϵ) 454 (5.15), 602 (4.19), 666 (4.39); UV−vis (20% TFA-$CHCl_3$; dication): λ_{max} (log ϵ) 450 (5.05), 596 (4.00), 614 (4.05), 672 (4.51); ^{1}H NMR ($CDCl_3$ + 1 drop TEA): δ −4.68 (2 H, br s), 1.65−1.70 (6H, 2 overlapping triplets), 3.35 (3H, s), 3.47 (3H, s), 3.79−3.82 (4H, 2 overlapping quartets), 7.88−7.96 (3H, m), 8.05−8.11 (2H, m), 9.06−9.14 (3H, m), 9.18 (1H, s), 9.52−9.58 (2H, m), 10.09 (1H, s), 10.10 (1H, s), 10.67 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ −0.12 (4H, br s), 1.58−1.64 (6H, 2 overlapping triplets), 3.45 (3H, s), 3.49 (3H, s), 3.98−4.05 (4H, 2 overlapping quartets), 8.18−8.23 (2 H, 2 overlapping triplets), 8.30−8.36 (2H, 2 overlapping triplets), 8.69 (1H, d, J = 9.9 Hz), 9.26−9.28 (2H, 2 overlapping doublets), 9.73−9.75 (2H, 2 overlapping doublets), 9.79 (1H, d, J = 9.3 Hz), 10.10 (1H, s), 10.97 (1H, s), 11.16 (2H, s); ^{13}C NMR (TFA-$CDCl_3$): δ 11.74, 11.92, 16.10, 16.13, 20.15, 101.71, 101.88, 102.11, 105.65, 125.34, 127.04, 127.19, 127.30, 130.03, 130.38, 131.09, 131.24, 132.48, 133.99, 134.95, 135.63, 139.68, 140.75, 140.95, 142.01, 144.05, 144.59, 144.76, 144.96, 145.58, 145.81, 179.82; HRMS (EI): Calcd for $C_{39}H_{32}N_4O$: *m/z* 572.2576; Found: 572.2576; HRMS (FAB): Calcd for $C_{31}H_{28}N_4O$ + H: *m/z* 573.2654; Found: 573.2652. Anal. Calcd for $C_{39}H_{32}N_4O$: C, 81.79; H, 5.63; N, 9.78. Found: C, 81.65; H, 5.57; N, 9.97. Nickel(II) complex: as dark-blue crystals from chloroform-hexanes, mp 250−252 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 448 (5.13), 640 (4.52); ^{1}H NMR ($CDCl_3$): δ 1.61−1.67 (6H, 2 overlapping triplets), 3.13 (3H, s), 3.18 (3H, s), 3.60−3.65 (4H, 2 overlapping quartets), 7.84−8.01 (5H, m), 8.44 (1H, s), 8.99−9.01 (4H, m), 9.15 (1H, d, J = 8.1 Hz), 9.55 (1H, s), 9.72 (1H, s), 9.82 (1H, s). Copper(II) complex: as green crystals from chloroform-methanol, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 348 (4.33), 442 (5.32), 598 (4.06), 642 (4.68). Zinc complex: as shiny metallic-blue crystals from chloroform-methanol, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 350 (4.22), 446 (5.36), 460 (4.99), 602 (4.02), 650 (4.72); ^{1}H NMR ($CDCl_3$ + 1 drop pyrrolidine): δ 1.85−1.90 (6H, 2 overlapping triplets), 3.48

(3H, s), 3.58 (3H, s), 4.03−4.07 (4H, 2 overlapping quartets), 7.93 (2H, d, J = 7.5 Hz), 8.09−8.12 (3H, m), 9.11 (2H, d, J = 8.4 Hz), 9.40 (1H, d, J = 9.3 Hz), 9.46 (1H, s), 9.99 (2H, t, J = 7.8 Hz), 10.71 (1H, s), 10.73 (1H, s), 10.91 (1H, s).

9,18-Diethyl-8,19-dimethylacenaphtho[1,2-*m*]-2-oxypyriporphyrin (49): Acenaphthotripyrrane di-*tert*-butyl ester **25** (100 mg) and **32** (24 mg) were reacted in the manner described for **35b**. The residue was chromatographed on grade 3 alumina, eluting with 4% methanol-chloroform. A green fraction was collected and recrystallized from chloroform-methanol to give the title porphyrin analogue (41 mg; 47%) as green crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 436 (5.23), 454 (5.04), 595 (4.26), 610 (4.47), 640 (4.69), 680 (3.49); UV−vis (1% TFA-$CHCl_3$; monocation): λ_{max} (log ϵ) 462 (5.25), 594 (4.06), 618 (4.09), 678 (4.56); UV−vis (20% TFA-$CHCl_3$; dication): λ_{max} (log ϵ) 460 (5.08), 596 (4.07), 624 (4.11), 684 (4.63); ^{1}H NMR ($CDCl_3$ + 1 drop TEA): δ −4.59 (1H, br s), −4.48 (1H, br s), 1.65−1.77 (6H, 2 overlapping triplets), 3.38 (3H, s), 3.58 (3H, s), 3.80−3.91 (4H, 2 overlapping quartets), 7.86−7.92 (3H, m), 8.02−8.05 (2H, m), 9.15 (1H, d, J = 9.9 Hz), 9.23 (1H, s), 9.46 (2H, s), 10.74 (1H, s); ^{1}H NMR (TFA-$CDCl_3$): δ −0.82 (4H, br s), 1.73−1.78 (6H, 2 overlapping triplets), 3.52 (3H, s), 3.57 (3H, s), 4.05−4.12 (4H, 2 overlapping quartets), 8.15 (2H, t, J = 7.7 Hz), 8.37 (2H, d, J = 7.8 Hz), 8.69 (1H, d, J = 9.3 Hz), 9.11 (2H, d, J = 6.9 Hz), 9.81 (1H, d, J = 9.3 Hz), 10.14 (1H, s), 10.85 (2H, s), 11.08 (1H, s); ^{13}C NMR (TFA-$CDCl_3$): δ 11.80, 11.99, 16.35, 16.37, 20.16, 102.41, 102.63, 106.15, 127.66, 127.70, 129.64, 130.92, 131.19, 132.08, 132.76, 135.06, 135.73, 136.69, 137.64, 137.80, 140.01, 141.14, 142.80, 143.89, 144.75, 144.86, 145.07, 145.16, 145.22, 145.39, 180.20; HRMS (EI): Calcd for $C_{37}H_{30}N_4O$: m/z 546.2420; Found: 546.2418; HRMS (FAB): Calcd for $C_{37}H_{30}N_4O$ + H: m/z 547.2498; Found: 547.2500. Anal. Calcd for $C_{40}H_{33}N_3O\cdot H_2O$: C, 78.70; H, 5.71; N, 9.29. Found: C, 78.40; H, 5.14; N, 9.26. Nickel(II) complex: as dark-green crystals from chloroform-petroleum ether, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 456 (5.02), 562 (3.92), 610 (4.05), 662 (4.60); ^{1}H NMR ($CDCl_3$): δ 1.63−1.69 (6H, 2 overlapping triplets), 3.15 (3H, s), 3.19 (3H, s), 3.63−3.68 (4H, 2 overlapping quartets), 7.77 (1H, d, J = 9.0 Hz), 7.82−7.86 (2 H, m), 7.98 (2H, d, J = 8.4 Hz), 8.42 (1H, s), 8.51−8.57 (2H, m), 8.99 (1H, d, J = 9.3 Hz), 9.37 (1H, s), 9.43 (1H, s), 9.50 (1H, s). Copper(II) complex: as sparkling-green crystals from chloroform-methanol, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 448 (5.02), 562 (3.23), 612 (3.90), 646 (sh, 4.24), 662 (4.53). Zinc complex: as a dark-blue powder from chloroform-methanol, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 454 (5.12), 462 (5.12), 564 (3.82), 616 (4.00), 670 (4.83); ^{1}H NMR ($CDCl_3$ + 1 drop pyrrolidine): δ 1.78−1.85 (6H, 2 overlapping triplets), 3.40 (3H, s), 3.53 (3H, s), 3.89−3.96 (4H, 2 overlapping quartets), 7.85−7.96 (4H, m), 8.07 (1H, d, J = 9.0 Hz), 8.65−8.72 (2H, m), 9.32−9.39 (2H, m), 9.92 (1H, s), 9.97 (1H, s), 10.84 (1H, s).

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Supporting Information Available: Copies of UV−vis, proton NMR, and carbon-13 NMR spectra, for porphyrinoids **7**, **12**, **23**, **26**, **27**, **35**, and **47**−**49** and some related metal chelates are provided (82 pages). This material is contained in many libraries on microfiche, immediately follows the article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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