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Synthesis and Characterization of Diaryl Sapphyrins Prepared under Lindsey-Type Conditions

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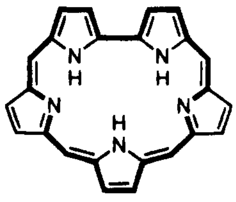
Sapphyrins (represented by parent structure **1**) are an interesting class of aromatic pentapyrrolic macrocycles related to porphyrins that were first described 29 years ago.[1a] Despite the intriguing structural features of this class of "expanded porphyrins", the chemistry of the sapphyrins has only recently begun to be explored in depth, due, in part, to the limiting nature of the original syntheses.[1b,c] This group has improved upon the Woodward sapphyrin synthesis by streamlining the synthesis of the two main acyclic precursors (e.g., **2** and **3**, Scheme 1) upon which it relies. This improved synthesis[2] has made possible investigations into the cation complexation behavior of sapphyrins,[3] a documentation of its unique anion-binding properties,[4,5] and a demonstration of its photosensitizing abilities.[6,7] Unfortunately, this now five-year-old strategy requires a multistep synthesis of a "tripyrrane" moiety (e.g., **3**) and does not permit placement of substituents on the *meso*-like positions of the final sapphyrin.



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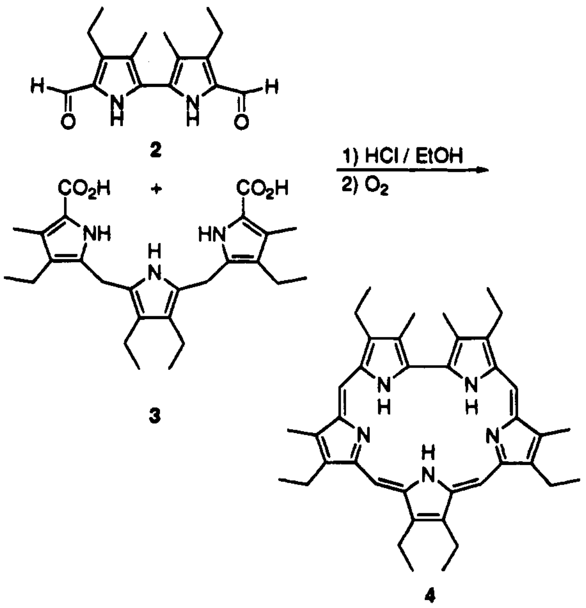
Here we present a powerful, new synthesis of sapphyrins, of general structure **7**, that allows substituents to be incorporated into two of the four *meso*-like methine positions. The advantage of this synthesis is that the need to prepare a tripyrrane intermediate is obviated; the sapphyrin macrocycle is obtained directly from bipyrrolic and monopyrrolic precursors *via* a Rothemund-type,[8] Lindsey-like[9] condensation.

Scheme 1



Discussion

The synthesis presented here avoids one of the more time-consuming aspects of the traditional sapphyrin synthesis, namely the preparation of the tripyrrane precursor **3**; this unit is effectively formed *in situ* from the acid-catalyzed condensation of a bipyrrole, a monomeric pyrrole and an aromatic aldehyde (cf Scheme 2).[10] Thus, this "all at once" synthesis bears analogy to the classic porphyrin synthesis of Rothemund[8] as well as to more recent syntheses of rosarin[11] and thiaporphyrin.[12]

In the specific case of the reaction involving bipyrrole **2**, benzaldehyde (**5a**), and pyrrole (**6**), the target compound **7a** is obtained in ca. 10% yield after chromatographic purification (silica gel column; methanol 8% in chloroform, eluent).[13] The material so obtained (λ_{max} = 452 nm) corresponds to the free-base form[14] but can be converted into its corresponding diprotonated salt (λ_{max} = 462 nm) by stirring with 10% HCl. A major byproduct of this reaction is 5,10,15,20-tetraphenylporphyrin, which

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(1) (a) First reported by R. B. Woodward at the Aromaticity Conference, Sheffield, U. K., 1966 (see ref 1b). (b) Bauer, V. J.; Clive, D. R.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429−6436. (c) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2111−2116.

(2) Sessler, J. L.; Cyr, M. J.; Lynch, V.; McGhee, E.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 2810−2813. (b) Sessler, J. L.; Cyr, M. J.; Burrell, A. K. *Tetrahedron* **1992**, *48*, 9661−9672.

(3) Burrell, A. K.; Sessler, J. L.; Cyr, M. J.; McGhee, E.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 91−93.

(4) (a) Furuta, H.; Cyr, M. J.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 6677−6678. (b) Král, V.; Sessler, J. L.; Furuta, H. *J. Am. Chem. Soc.* **1992**, *114*, 8704−8705. (c) Iverson, B. L.; Shreder, K.; Král, V.; Sessler, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 11022−11023. (d) Sessler, J. L.; Ford, D. A.; Cyr, M. J.; Furuta, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1733−1735.

(5) Iverson, B. L.; Thomas, R. E.; Král, V.; Sessler, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2663−2664.

(6) Judy, M. L.; Matthews, J. L.; Newman, J. T.; Skiles, H.; Boriack, R.; Cyr, M.; Maiya, B. G.; Sessler, J. L. *Photochem. Photobiol.* **1991**, *53*, 101−107.

(7) Sessler, J. L.; Cyr, M.; Maiya, B. G.; Judy, M. L.; Newman, J. T.; Skiles, H.; Boriack, R.; Matthews, J. L.; Chanh, T. C. *Proc. SPIE Int. Opt. Eng.* **1990**, *1203*, 233−245.

(8) Rothemund, P. *J. Am. Chem. Soc.* **1936**, *58*, 625. Rothemund, P. *J. Am. Chem. Soc.* **1939**, *61*, 2912−2915.

(9) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. E.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827−836.

(10) The tripyrrane fragment is presumably formed during the reaction as the result of a condensation between 3 equiv of pyrrole and 2 equiv of benzaldehyde; however, one can imagine other reaction pathways comprising the attack of benzaldehyde on pyrrole or pyrrole derivatives, as in the case of the synthesis of tetraphenylporphyrins.

(11) Sessler, J. L.; Weghorn, S. J.; Morishima, T.; Rosingana, M.; Lynch, V.; Lee, V. *J. Am. Chem. Soc.* **1992**, *114*, 8306−8307.

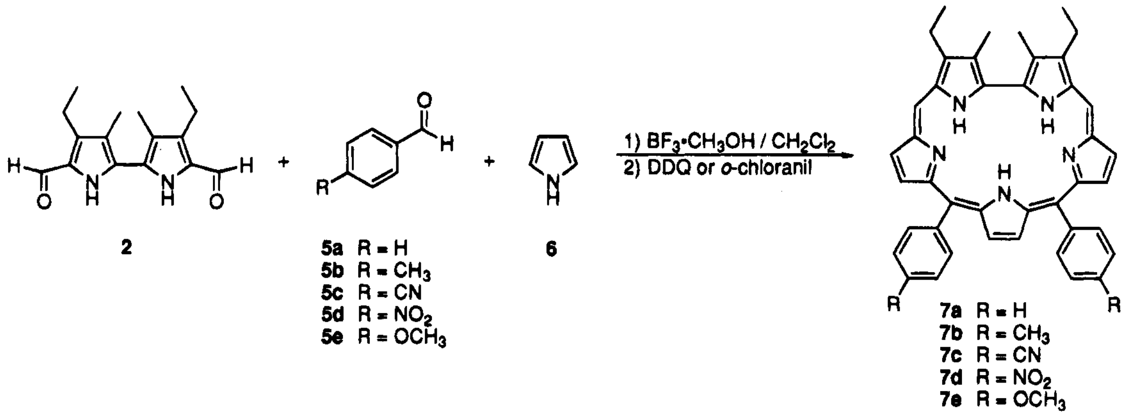
(12) Latos-Grazynski, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 4428−4429.

(13) Initial attempts to carry out the condensation of Scheme 2 under Adler−Longo conditions (Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. Kim, J. B.; Adler, A. D.; Longo, F. R. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Volume 1.) met with failure. This failure, however, was later understood in view of the fact that compound **7a** was found to undergo complete decomposition when heated in propionic acid at reflux.

(14) This is a qualitative indication that this diphenylsapphyrin is less basic than the β-decaalkyl sapphyrins; these latter elute as their diprotonated adducts.

0022-3263/95/1960-5975$09.00/0

Scheme 2



is easily removed from the sapphyrin during the chromatographic purification.

The NMR spectrum is consistent with the structure of the molecule and with its aromatic character. In particular, signals for the *meso*-like protons were observed at 11.81 ppm while those for the internal NH protons were found at −4.33, −4.21, and −3.70 ppm. However, the absorption bands of diphenylsapphyrin are bathochromically shifted compared to the all β-alkyl sapphyrin; this reflects, perhaps, partial overlap between sapphyrin- and *meso*-phenyl-derived π-orbitals.

An X-ray single crystal diffraction study of the bishydrochloride salt of **7a** was made.[22] It reveals the sapphyrin skeleton to be essentially flat (Figure 1) and also shows that the diphenylsapphyrins, like their β-alkyl-substituted analogs, can act as chloride anion receptors in the solid state. In **7a**·2HCl, the N-to-Cl distances for Cl1 are 3.256(3)° for N3 and 3.266(3)° for N5; for Cl2 they are 3.135(3)° for N1 and 3.235(3)° for N2. Thus, Cl2 is slightly closer to N1 and N2 than Cl1 is to N3 and N5. This has the effect of placing Cl1 1.848 Å out of the plane of the macrocycle, and Cl2 1.818 Å out of the plane. This is comparable to what is found in the case of **4**·2HCl; in this instance, the corresponding mean plane-to-chloride distance is ca. 1.8 Å.[15]

Extensions of the present procedure should allow a considerable range of diarylsapphyrins to be prepared. So far, we have prepared the tolyl (**7b**), 4-cyanophenyl (**7c**), 4-nitrophenyl (**7d**), and 4-methoxyphenyl (**7e**) derivatives of the original diphenylsapphyrin (**7a**). Using the nonracemic aldehyde **8**, derived from (1*R*)-(+)-nopinone,[16] we have also prepared what we believe to be the first chiral sapphyrin (**9**) to be reported in the literature (Scheme 3). It is currently being tested as a possible enantioselective anion-binding agent.

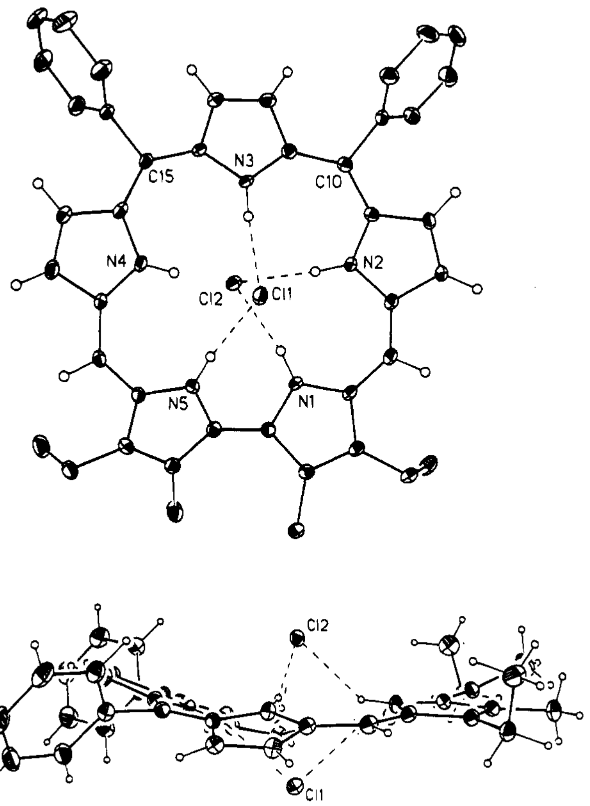


Figure 1. Top and side views of the molecular structure of the $[C_{42}H_{39}N_5]^{2+}·2Cl^-$ (**7a**·2HCl) cation showing the partial atom-labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary scale. The Cl^- ions are each within H-bonding distance to two pyrrole NH moieties. The relevant distances (Å) and angles (deg) are the following: N3−H3N ··· Cl1, N ··· Cl 3.256(3), H ··· Cl 2.401(3), N−H ··· Cl 158.6(3); N5−H5N ··· Cl1, N ··· Cl 3.266(3), H ··· Cl 2.423(3), N−H ··· Cl 155.9(3); N1−H1N ··· Cl2; N ··· Cl 3.135(3), H ··· Cl 2.347(3), N−H ··· Cl 146.2(3); N2−H2N ··· Cl2, N ··· Cl 3.235(3), H ··· N 2.368(3), N−H ··· Cl 161.6(3).

Experimental Section

General Information. All solvents and chemicals were of reagent grade quality except as noted below. Dichloromethane was distilled from anhydrous calcium chloride. Pyrrole (**6**) was distilled under reduced pressure prior to use. ICN SiliTech type 60 (32−63 mesh) silica gel obtained from ICN Biomedicals was used for column chromatography. Thin-layer chromatography (TLC) was performed on commercially prepared silica gel plates purchased from Analtech, Inc. Microanalysis on compound **7a** was performed by Atlantic Microlab, Inc.

3,22-Diethyl-2,23-dimethyl-10,15-diphenylsapphyrin (7a). Diformylbipyrrole (**2**; 250 mg; 0.918 mmol) was placed in a flask under an argon blanket. To it was then added 275 mL of dichloromethane (freshly distilled from CaH_2 and degassed with argon), 191 μL of pyrrole (**6**, 2.75 mmol), 187 μL of benzaldehyde (**5a**, 1.84 mmol) and 164 μL of $BF_3·CH_3OH$. The reaction was shielded from ambient light with aluminum foil. Upon addition of the catalyst, the reaction mixture immediately adopted a dark reddish-black hue. Reaction progress was followed by UV/vis spectroscopy. This was done by taking small (20 μL) aliquots of the reaction mixture, adding a small portion of DDQ, diluting with dichloromethane, and subjecting it to spectral analysis. The observation of increasingly intense Soret bands at 417 and 462 nm, corresponding to tetraphenylporphyrin and diphenylsapphyrin, respectively, was noted. At the point where no further

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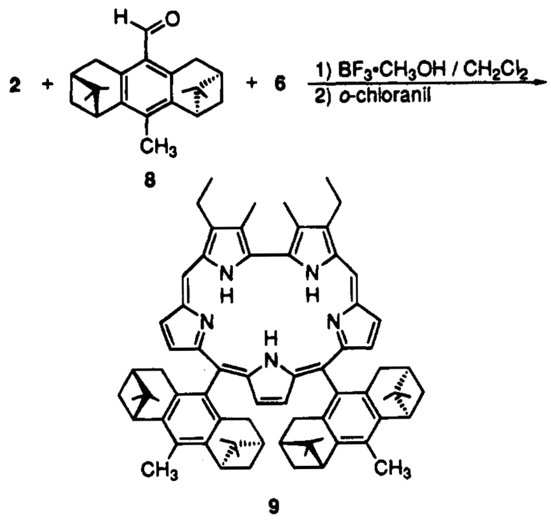
(15) Shionoya, M.; Furuta, H.; Lynch, V.; Harriman, A.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 5714−5722.

(16) Barry, J.; Kodadek, T. *Tetrahedron Lett.* **1994**, *35*, 2465−2468.

Scheme 3



gain in Soret band spectral intensity was noted (ca. 1 h), DDQ (198 mg; 0.872 mmol) was added and the reaction stirred at room temperature under argon for an additional 1 h.[17] After evaporative removal of the solvent, the residue was subjected to column chromatography on silica gel. The column was first eluted with chloroform in order to remove tetraphenylporphyrin, followed by chloroform containing gradually increasing percentages of methanol (1−8%). The green, sapphyrin-containing fraction with a characteristic absorption at 452 nm was collected and concentrated under reduced pressure. This crude material was then subject to three more rounds of chromatographic purification using the same procedure. The pure sapphyrin product obtained in this way is largely unprotonated, in contradistinction with what would be found for other sapphyrins.[2,4] Still, for ease of characterization it was converted to its corresponding diprotonated derivative. This was done by washing a dichloromethane solution of this crude product with 10% HCl, separating off the green organic layer, taking it to dryness, and recrystallizing from dichloromethane/hexanes. This yields 59.5 mg of **7a**·2HCl (overall yield, 9.5%): ^{1}H NMR (CDCl$_3$) δ −4.33 (s, 2H), −4.21 (s, 2H), −3.70 (s, 1H), 2.16 (t, 6H), 4.25 (s, 6H), 4.57 (q, 4H), 8.02 (m, 6H), 8.72 (d, 4H), 9.41 (s, 2H), 9.66 (d, 2H, J = 4.4 Hz), 10.21 (d, 2H, J = 4.5), 11.81 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 15.8, 17.6, 20.7, 29.5, 101.9, 114.5, 126.6, 128.1, 128.4, 129.9, 130.2, 130.3, 130.6, 131.0, 134.6, 135.9, 139.2, 139.3, 143.0, 145.8; $\lambda_{\max}$ (log ϵ) 462.0 (5.58), 625.0 (4.00), 706.0 nm (4.17); mass spectrum (FAB) m/z (relative intensity) 612 (M$^+$, 100), 613 ([M + H]$^+$, 57); exact mass (CI) for C$_{42}$H$_{38}$N$_5$ ([M + H]$^+$) calcd 612.3127, found 612.3126. Anal. Calcd for C$_{42}$H$_{37}$N$_5$·3HCl: C, 70.07; H, 5.60; N, 9.73. Found: C, 70.07; H, 5.52; N, 9.55. Salt **7a**·2HCl was also characterized by X-ray diffraction.

10,15-Bis(4-methylphenyl)-3,22-diethyl-2,23-dimethylsapphyrin (7b). This compound was prepared in a fashion similar to that used to prepare **7a**, but starting with *p*-tolualdehyde (**5b**), rather than benzaldehyde, to yield 30.5 mg (7.8%) of **7b**·2HCl. ^{1}H NMR (CDCl$_3$) δ −4.41 (s, 2H), −4.31 (s, 2H), −3.75 (s, 1H), 2.24 (t, 6H), 2.91 (s, 6H), 4.22 (s, 6H), 4.57 (q, 4H), 7.80 (d, 4H, J = 7.8 Hz), 8.43 (d, 4H, J = 7.8 Hz), 9.32 (s, 2H), 9.62 (d, 2H, J = 4.2 Hz), 10.20 (d, 2H, J = 4.3 Hz), 11.78 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 15.9, 17.7, 20.8, 21.7, 101.9, 114.8, 127.4, 128.2, 130.0, 130.2, 130.4, 130.6, 131.2, 134.8, 136.3, 138.4, 139.6, 139.9, 143.1, 143.3; $\lambda_{\max}$ (log ϵ) 464.0 nm (5.36), 625.0 nm (3.81), 709.0 nm (3.97); mass spectrum (FAB) m/z (relative intensity) 640 (M$^+$, 25); exact mass (FAB) for C$_{44}$H$_{40}$N$_5$ ([M − H]$^+$) calcd 640.3425; found 640.3429.

10,15-Bis(4-cyanophenyl)-3,22-diethyl-2,23-dimethylsapphyrin (7c). This compound was prepared analogously from 4-cyanobenzaldehyde (**5c**) to yield 25.2 mg (6.2%) of **7c**·2HCl. ^{1}H NMR (CDCl$_3$) δ −4.35 (s, 2H), −4.28 (s, 2H), −3.73 (s, 1H), 2.19 (t, 6H), 4.20 (s, 6H), 4.56 (q, 4H), 8.29 (d, 4H, J = 7.9 Hz), 8.74 (d, 4H, J = 7.8 Hz), 9.23 (s, 2H), 9.47 (d, 2H, J = 4.7 Hz), 10.26 (d, 2H, J = 4.7 Hz), 11.85 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 15.9, 16.0, 17.7, 20.9, 103.2, 112.3, 113.0, 118.8, 128.9, 129.7, 129.9, 130.7, 130.9, 131.5, 131.7, 134.9, 136.3, 138.0, 138.3, 144.1, 150.1; $\lambda_{\max}$ (log ϵ) 462.0 nm (5.52), 633.0 nm (3.96), 703.0 nm (4.06); mass spectrum (FAB) m/z (relative intensity) 662 ([M + H]$^+$, 19), 663 ([M + 2H]$^+$, 10); exact mass (FAB) for C$_{44}$H$_{36}$N$_7$ ([M + H]$^+$) calcd 662.3032, found 662.3049.

10,15-Bis(4-nitrophenyl)-3,22-diethyl-2,23-dimethylsapphyrin (7d). This compound was prepared analogously 4-nitrobenzaldehyde (**5d**) to give 17.5 mg (6.2%) of **7d**·2HCl: ^{1}H NMR (CDCl$_3$) δ −4.27 (s, 2H), −4.24 (s, 2H), −3.65 (s, 1H), 2.21 (t, 6H), 4.22 (s, 6H), 4.58 (q, 4H), 8.81 (d, 2H, J = 8.6 Hz), 8.88 (d, 2H, J = 8.6 Hz), 9.25 (s, 2H), 9.49 (d, 2H, J = 4.2 Hz), 10.29 (d, 2H, J = 4.2 Hz), 11.87 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 15.9, 17.7, 20.9, 30.9, 103.2, 103.3, 111.8, 122.0, 129.0, 129.6, 129.9, 131.0, 131.5, 131.7, 134.9, 136.4, 137.9, 138.2, 144.2, 148.3, 151.8, 206.8; $\lambda_{\max}$ (log ϵ) 463.0 (5.67), 634.0 (4.15), 703.0 nm (4.24); mass spectrum (FAB) m/z (relative intensity) 702 ([M + H]$^+$, 100), 703 ([M + 2H]$^+$, 38); exact mass (FAB) for C$_{42}$H$_{36}$N$_7$O$_4$ ([M + H]$^+$) calcd 702.2829, found 702.2834.

10,15-Bis(4-methoxyphenyl)-3,22-diethyl-2,23-dimethylsapphyrin (7e). This compound was prepared analogously from 4-methoxybenzaldehyde (**5e**) to give 25.0 mg (9.1%) of **7e**·2HCl: ^{1}H NMR (CDCl$_3$) δ −4.38 (s, 2H), −4.34 (s, 2H), −3.62 (s, 1H), 2.24 (t, 6H), 4.20 (s, 6H), 4.26 (s, 6H), 4.56 (q, 4H), 7.52 (d, 4H, J = 8.5 Hz), 8.57 (d, 4H, J = 8.5 Hz), 9.26 (s, 2H), 9.59 (d, 2H, J = 4.6 Hz), 10.18 (d, 2H, J = 4.5 Hz), 11.75 (s, 2H); ^{13}C NMR (CDCl$_3$): δ 15.9, 17.7, 20.8, 30.9, 55.8, 101.7, 112.3, 114.5, 128.3, 129.8, 129.9, 130.3, 130.4, 131.2, 134.9, 137.6, 138.9, 140.0, 140.5, 143.0, 160.1, 206.9; $\lambda_{\max}$ (log ϵ) 465.0 (5.37), 625.0 (4.00), 714.0 nm (4.07); mass spectrum (FAB) m/z (relative intensity) 672 ([M + H]$^+$, 100), 673 ([M + 2H]$^+$, 42); exact mass (FAB) for C$_{44}$H$_{42}$N$_5$O$_2$ ([M + H]$^+$) calcd 672.3339, found 672.3328.

10,15-Bis{9-(1*S*,4*R*,5*R*,8*S*)-bis[2,4,5,7]pinyl-10-methylanthacenyl}-3,22-diethyl-2,23-dimethylsapphyrin (9). This compound was prepared analogously using the chiral aldehyde **8**. The product was recrystallized from dichloromethane/petroleum ether to yield 34.3 mg of **9**·2HCl (4.7%). Assignments of protons in the ^{1}H NMR spectrum were made from the COSY, APT, and C−H correlation spectra. For **9**·2HCl: ^{1}H NMR (CDCl$_3$) δ −4.20 (s, 2H), −3.92 (s, 2H), −3.77 (s, 1H), 1.00 (s, 6H), 1.05 (s, 6H), 1.38 (s, 6H), 1.39 (s, 6H), 1.48 (d, 2H, J = 8.6 Hz), 1.58 (d, 2H, J = 8.6 Hz), 1.73 (m, 4H), 2.21 (t, 6H), 2.27 (d, 4H, J = 0.1 Hz), 2.31 (m, 4H), 2.54 (s, 6H), 2.64 (m, 4H), 3.51 (q, 4H), 4.16 (s, 6H), 4.51 (q, 4H), 9.42 (d, J = 1.0 Hz, 2H), 9.65 (d, J = 4.6 Hz, 2H), 10.13 (d, J = 4.6 Hz, 2H), 11.63 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 14.4, 15.9, 17.7, 20.8, 21.9, 22.0, 26.6, 32.1, 32.2, 34.1, 38.8, 38.8, 40.3, 40.3, 43.8, 101.7, 111.3, 127.9, 128.3, 129.6, 130.0, 130.1, 131.0, 131.5, 134.4, 134.5, 134.7, 138.7, 138.8, 141.1, 142.1, 143.0; $\lambda_{\max}$ (log ϵ) 466.0 (5.63), 627.0 (4.05), 708.0 nm (4.20); mass spectrum (FAB) m/z (relative intensity) 1016 (M$^+$, 32), 1017 ([M + H]$^+$, 100), 1018 ([M + 2H]$^+$, 74); exact mass (FAB) for C$_{72}$H$_{81}$N$_5$ (M$^+$) calcd 1015.6492, found 1015.6470.

X-ray Experimental for [C$_{42}$H$_{39}$N$_5$]$^{2+}$·2Cl$^-$·(C$_4$H$_{10}$O) (7a·2HCl). Crystals of this bishydrochloride salt of **7a** grew as very dark, thin plates by vapor diffusion of diethyl ether into a CHCl$_3$ solution of [C$_{42}$H$_{39}$N$_5$]$^{2+}$·2Cl$^-$. The datum crystal, space group $P2_{1/c}$, had approximate dimensions of 0.22 × 0.41 × 0.54 mm and contains a molecule of diethyl ether in the lattice. The data were collected at 183 K on a Nicolet P3 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). Data reduction, decay correction, and figure production was performed using the SHELXTL-*Plus* software package.[18] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares[19] with anisotropic thermal parameters for the non-H atoms. The hydrogen atoms were calculated in idealized positions with U_{iso} set to 1.2 × U_{eq} of the appropriate atom. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the Interna-

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[17] The oxidation may also be performed by adding *p*-chloranil to the reaction mixture and stirring for two days in the presence of air; both methods seem to be equally effective.

[18] Sheldrick, G. M. SHELXTL-*PLUS* (Version 4.1); Siemens Analytical X-ray Instruments, Inc.; Madison, 1990.

[19] Sheldrick, G. M. SHELXL93. *J. Appl. Cryst.* **1995**, in preparation.

tional Tables for X-ray Crystallography (1992).[20] Other computer programs used in this work are listed elsewhere.[21,22]

Note Added in Proof: Subsequent to the submission ofthis work, the synthesis in ca. 1.1% yield of a fully *meso*-substituted analog of **7** was reported: Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K. *Chem. Eur. J.* **1995**, *1*, 68–73.

Acknowledgment. Support for this work came from grants from the Texas Advanced Technology Program (3658-280 to J.L.S.), the NIH (AI-33577 to J.L.S.), and the NSF (CHE-9122161 to J.L.S. and CHE-9202931 to T.K.). This paper is dedicated to Prof. Richard Neidlein on the occasion of his 65th birthday.

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[20] International Tables for X-ray Crystallography; Wilson, A. J. C., Ed.; Kluwer Academic Press: Boston, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

[21] Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607–1613.

[22] The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.