

Synthesis and Structural Characterization of the First Schiff-Base Macrocycles Containing Terpyrrole Subunits

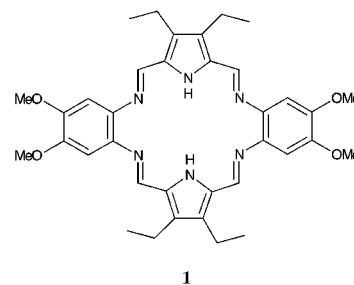
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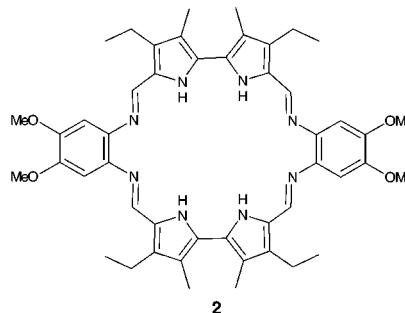
Received April 6, 1998

In recent years, increasing attention has focused on the study of so-called expanded porphyrins.^{1–4} Much of our own effort in the area, like that of others, has been devoted to the generation of ever larger π -conjugated polypyrrolic systems.^{1–4} This has led to the synthesis of macrocyclic compounds such as turcasarin,⁵ octaphyrin,^{6,7} vinylogous porphyrins,⁸ and torand-type expanded porphyrins⁹ as well as linear oligopyrroles¹⁰ and nonplanar polypyrrolic compounds.¹¹ Among the strategies currently employed to generate large polypyrrolic macrocycles, those predicated on the use of Schiff-base chemistry have a number of advantages, including versatility and ease of synthesis.^{12–18} Indeed, this approach has been used to prepare a range of interesting expanded porphyrin systems, including accordion porphyrins,¹⁶ texaphyrins,¹² and the [2 + 2] macrocycles **1** and **2**.¹⁴

Interestingly, however, Schiff-base macrocycles derived from terpyrrole¹⁹ subunits appear to be currently unknown.



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(1) Sessler, J. L.; Weghorn, S. J. Expanded, Contracted & Isomeric Porphyrins, *Tetrahedron Organic Chemistry Series*; Pergamon: New York, 1997; Vol. 15.

(2) Jasat, A.; Dolphin, D. *Chem. Rev.* **1997**, *97*, 2267–2340.

(3) Srinivasan, A.; Reddy, V. M.; Narayanan, S. J.; Sridevi, B.; Pushpan, S. K.; Ravikumar, M.; Chandrashekar, T. K. *Angew. Chem.* **1997**, *109*, 2710–2713; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2598–2601.

(4) Sessler, J. L.; Hoehner, M. C.; Gebauer, A.; Andrievsky, A.; Lynch, V. *J. Org. Chem.* **1997**, *62*, 9251–9260.

(5) Sessler, J. L.; Weghorn, S. J.; Lynch, V.; Johnson, M. R. *Angew. Chem.* **1994**, *106*, 1572–1575; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1509–1512.

(6) Vogel, E.; Bröring, M.; Fink, J.; Rosen, D.; Schmickler, H.; Lex, J.; Chan, K. W. K.; Wu, Y.-D.; Plattner, D. A.; Nendel, M.; Houk, K. N. *Angew. Chem.* **1995**, *107*, 2705–2709; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2511–2514.

(7) Bröring, M.; Jendryn, J.; Zander, L.; Schmickler, H.; Lex, J.; Wu, Y.-D.; Nendel, M.; Chen, J.; Plattner, D. A.; Houk, K. N.; Vogel, E. *Angew. Chem.* **1995**, *107*, 2709–2711; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2515–2517.

(8) Eickmeier, C.; Franck, B. *Angew. Chem.* **1997**, *109*, 2302–2304; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2213–2215.

(9) Bell, T. W.; Cragg, P. J.; Drew, M. G. B.; Firestone, A.; Kwok, A. D.-I.; Liu, J.; Ludwig, R. T.; Papoulis, A. T. *Pure Appl. Chem.* **1993**, *65*, 361–366.

(10) Morosini, P.; Scherer, M.; Meyer, S.; Lynch, V.; Sessler, J. L. *J. Org. Chem.* **1997**, *62*, 8848–8853.

(11) Sessler, J. L.; Dávila, R. M.; Král, V. *Tetrahedron Lett.* **1996**, *37*, 6469–6472.

(12) Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394–4397.

(13) Sessler, J. L.; Mody, T. D.; Ford, D. A.; Lynch, V. *Angew. Chem.* **1992**, *104*, 461–464; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 452–455.

(14) Sessler, J. L.; Mody, T. D.; Lynch, V. *J. Am. Chem. Soc.* **1993**, *115*, 3346–3347.

(15) Meyer, S.; Hoehner, M. C.; Lynch, V.; Sessler, J. L. *J. Porphyrins Phthalocyanines* **1998**, in press.

(16) Acholla, F. V.; Takusagawa, F.; Mertes, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 6902–6908.

(17) Johnson, M. R.; Slobodnick, C.; Ibers, J. A. *J. Porphyrins Phthalocyanines* **1997**, *1*, 87–92.

(18) Fernández-Lázaro, F.; Torres, T.; Hauschel, B.; Hanack, M. *Chem. Rev.* **1998**, *98*, 563–575.

Recently, we described a convenient synthesis of hexa- β -alkyl, α -free terpyrroles¹⁹ and showed that these oligopyrroles could be used to prepare a range of carbon-linked expanded porphyrins including turcasarin,⁵ amethyrin,¹⁹ and orangarin¹⁹ as well as some sapphyrin analogues.²⁰ Terpyrrole-like subunits have also been used to prepare core-modified expanded porphyrins.^{21–28} For instance, furan- and thiophene-containing macrocycles, known as ozaphyrins, were prepared by Johnson and Ibers et al.²¹ using a McMurry-type low-valent titanium-mediated coupling approach. An analogous strategy, explored independently by Johnson and Ibers,^{22,23} Cava,^{25–27} Merz and Neidlein,²⁸ and Johnson²⁴ also led to the preparation of hexaphyrin-type core-modified expanded porphyrins known as bronzaphyrins. In this paper, we describe the use of terpyrrole subunits as building units for the construction of Schiff-base macrocycles. Specifically, we report the synthesis and X-ray structural characteriza-

(19) Sessler, J. L.; Weghorn, S. J.; Hiseada, Y.; Lynch, V. *Chem. Eur. J.* **1995**, *1*, 56–67.

(20) Weghorn, S. J.; Lynch, V.; Sessler, J. L. *Tetrahedron Lett.* **1995**, *36*, 4713–4716.

(21) Johnson, M. R.; Miller, D. C.; Bush, K.; Becker, J. J.; Ibers, J. A. *J. Org. Chem.* **1992**, *57*, 4414–4417.

(22) Miller, D. C.; Johnson, M. R.; Becker, J. J.; Ibers, J. A. *J. Heterocycl. Chem.* **1993**, *30*, 1485–1490.

(23) Miller, D. C.; Johnson, M. R.; Ibers, J. A. *J. Org. Chem.* **1994**, *59*, 2877–2879.

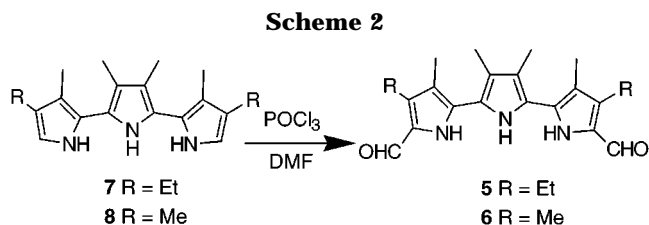
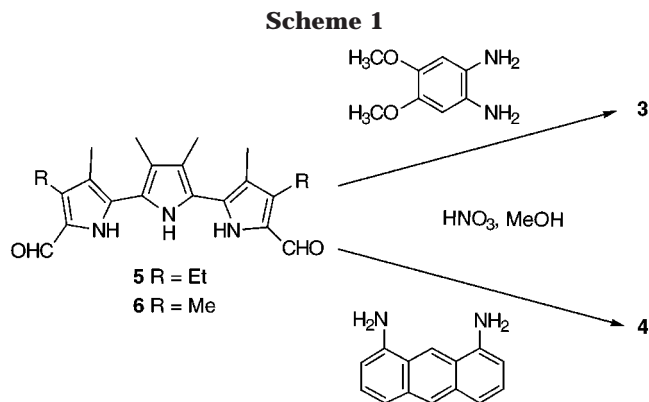
(24) Johnson, M. R. *J. Org. Chem.* **1997**, *62*, 1168–1172.

(25) Hu, Z.; Scordilis-Kelley, C.; Cava, M. P. *Tetrahedron Lett.* **1993**, *34*, 1879–1882.

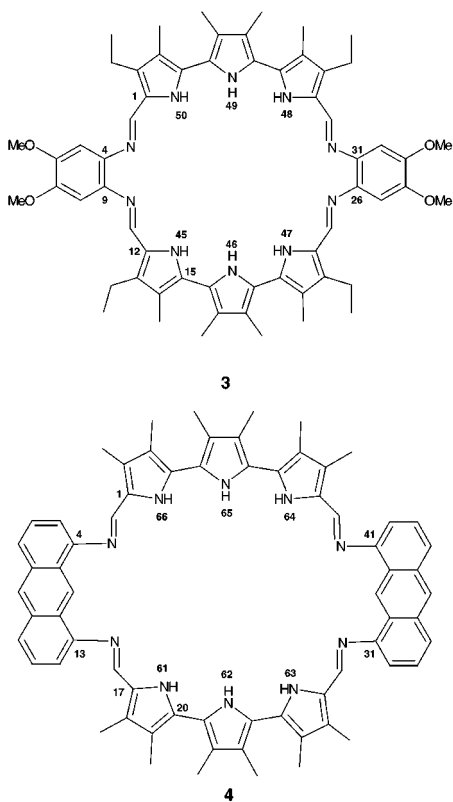
(26) Hu, Z.; Atwood, J. L.; Cava, M. P. *J. Org. Chem.* **1994**, *59*, 8071–8075.

(27) Kozaki, M.; Parrakka, J. P.; Cava, M. P. *J. Org. Chem.* **1996**, *61*, 3657–3661.

(28) Ellinger, F.; Gieren, A.; Hübner, Th.; Lex, J.; Lucchesini, F.; Merz, A.; Neidlein, R.; Salbeck, J. *J. Monats. Chem.* **1993**, *124*, 931–943.



tion of the [2 + 2] system **3**. We also report the preparation of its larger analogue **4**.



Compounds **3** and **4** were obtained from [2 + 2] condensations involving the use of the respective diformyl terpyrrole precursors **5** and **6** and the requisite diamines by an acid-catalyzed reaction¹² which involved the use of concentrated nitric acid as the proton source and methanol as the solvent (Scheme 1). Under these conditions, compounds **3** and **4** were isolated as the corresponding HNO_3 salts. Washing with aqueous NaHCO_3 then produced the corresponding free-base macrocycles. The key starting diformyl terpyrroles **5** and **6** were obtained from the known bis α -free terpyrroles **7** and **8**¹⁹

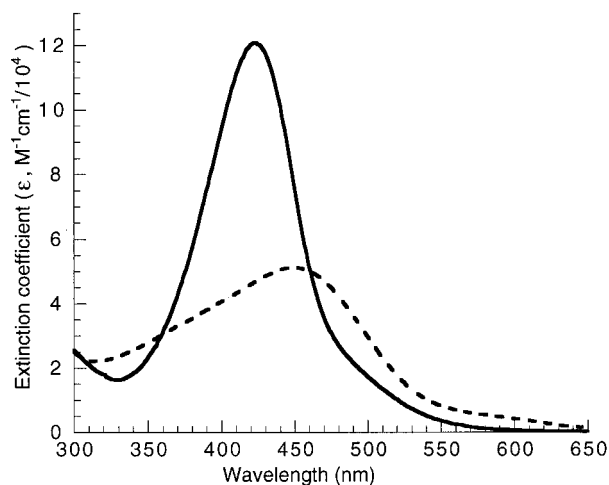


Figure 1. UV/vis absorption spectrum of the expanded porphyrins **3** (—) and **4** (---) recorded as the free-bases in dichloromethane/methanol (80/20).

by subjecting them to Vilsmeier–Haack formylation (Scheme 2).¹⁹ In carrying out this latter critical conversion, we found that we did not need to resort to the Clezy-modified Vilsmeier–Haack procedure²⁹ as (apparently) proved to be the case during the course of preparing a diformyl terpyrrole substituted by hexyl groups in the β positions of the outer pyrrole rings.²⁴ While this issue has not been probed in depth, the relative ease of this transformation in the case of **5** and **6** \rightarrow **7** and **8** could reflect the solubility advantages that accrue from using fully β -alkyl-substituted terpyrroles.

It is also worth noting that even if macrocycle **3** contains 36 π -electrons it cannot be formally considered as antiaromatic. For instance, compound **3** exhibits a rather strong absorption feature in the visible spectrum (e.g., $\lambda_{\text{max}} = 422 \text{ nm}$, $\epsilon = 120\,720 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 1) that is characteristic of a conjugated polypyrrolic species. The UV–vis spectrum of compound **4** exhibits a red shift relative to **3** ($\lambda_{\text{max}} = 449 \text{ nm}$). This is consistent with an increase in the π -conjugation pathway. Upon protonation with glacial acetic acid in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (80/20), a red shift is observed in the absorption spectrum of **3**. Also, the color of the solution changes from yellow to pink-red, and two absorption maxima at 441 and 488 nm appear. In the case of macrocycle **4**, the analogous protonation process induces an even larger spectral shift (λ_{max} moves from 449 to 523 nm), and the color of the solution changes from orange to pink. Taken together, the spectral properties of **3** are considered consistent with a nonaromatic, as opposed to antiaromatic, electronic formulation.

Systems **3** and **4** were found to be stable to both acidic and basic conditions. Exposure of **3** or **4** to protic acid (e.g. acetic acid) leads solely to protonation as evidenced by the fact that adding triethylamine serves to regenerate quantitatively the free-base macrocycle in both cases. This latter free-base form, was found to be remarkably stable with no decomposition of either **3** or **4** being observed over the course of months when either solid samples or dichloromethane/methanol solutions were left exposed to the atmosphere under ambient conditions.

Compound **3** was characterized by X-ray analysis in the solid state. It was found to cocrystallize with two

(29) Chong, R.; Clezy, P. S.; Liepa, A. J.; Nichol, A. W. *Aust. J. Chem.* **1969**, *22*, 229–238.

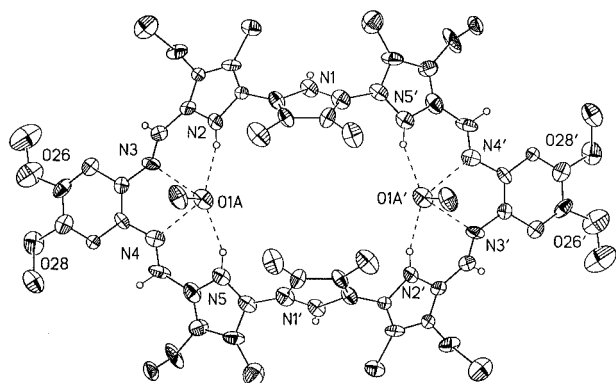


Figure 2. View of **3**·2CH₃OH showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale. The molecule lies around a crystallographic 2-fold rotation axis passing through $0, y, 1/4$. Atoms labeled by ' are related by $-x, y, 1/2 - z$. Hydrogen bonds are indicated by dashed lines. Two symmetry-related molecules of methanol are within H-bonding distance to the macrocycle. The relevant geometry of this interaction: N2–H2N···O1a, N···O 3.006(12) Å, H···O 2.131(12) Å, N–H···O 163.8(3)°; N5–H5N···O1a, N···O 2.949(12) Å, H···O 2.117(12) Å, N–H···O 153.3(3)°; O1A···N3 2.967(13) Å, O1A···N4 2.870(12) Å. The position of the hydrogen atom on the methanol oxygen atom could not be located in a ΔF map and was not calculated in the refinement model. The planes through the central pyrrole have dihedral angles of 42.7° and 50.8° with planes through the terminal pyrroles.

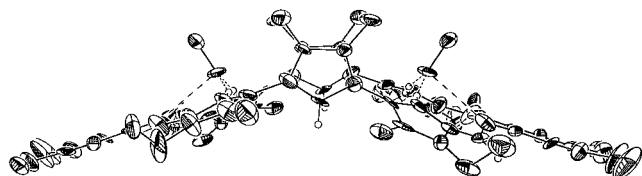


Figure 3. Side view showing the nonplanarity of the macrocycle **3** and the dome shape of the molecule. The disordered solvent molecule resides on the opposite side from the H-bound methanol molecules. The H-bonding interaction is illustrated by dashed lines.

symmetry related molecules of methanol being bound within H-bonding distance to the macrocycle. The relevant interactions, illustrated by dashed lines in Figure 2, are as follows: N2–H2N···O1a, N···O 3.006(12) Å, H···O 2.131(12) Å, N–H···O 163.8(3)°; N5–H5N···O1a, N···O 2.949(12) Å, H···O 2.117(12) Å, N–H···O 153.3(3)°; O1A···N3 2.967(13) Å, O1A···N4 2.870(12) Å. The position of the hydrogen atom on the methanol oxygen atom could not be located. The macrocycle lies around a crystallographic 2-fold rotation axis passing through $0, y, 1/4$. A methylene chloride solvent molecule lies around the 2-fold rotation axis in the depression at the center of the macrocycle. The molecule is nonplanar, and a side view shows the dome shape of the macrocycle (Figure 3). The disordered solvent molecule resides on the opposite side from the H-bound methanol molecules. As in the crystal structure of **5** (vide infra), the terpyrrole units are both found to adopt alternating planar–antiperiplanar–antiperiplanar conformations. Such a geometry is not unexpected in the absence of some strong substrate chelating interaction.

During the course of this study, the structure of the β -alkyl terpyrrolic species **5** was also elucidated via single-crystal X-ray diffraction analysis (Figure 4). This

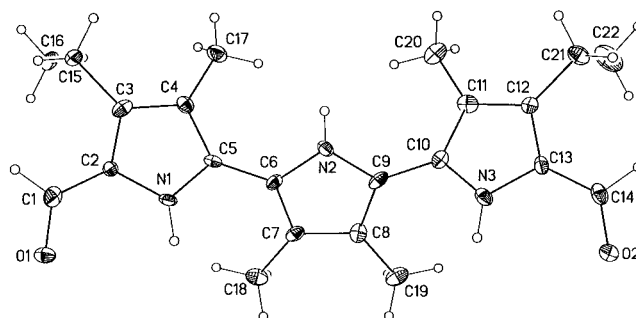


Figure 4. View of diformyl terpyrrole **5** showing the atom labeling and illustrating the planar–antiperiplanar–planar conformation of the polypyrrolic system. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

oligopyrrole adopts an alternating planar–antiperiplanar–antiperiplanar conformation similar to that observed for the simple unsubstituted 2,2',2''-terpyrrole.³⁰ Thus, this particular α, ω -disubstituted terpyrrole does not adopt the helical twist found for a previously characterized α, ω -disubstituted terpyrrole diethyl ester.¹⁹ On a different level, the X-ray structure of **5** reveals the presence of two crystallographically distinct molecules of **5** (in a 1:1 ratio) and of water (O1w and O1w'). These water molecules are involved in hydrogen bonding with the pyrrolic nitrogen atoms and the formyl group.

Conclusion

In summary, we have synthesized and characterized the first Schiff-base macrocycles based on the use of terpyrrole units. This result provides a further example of the utility of terpyrrole subunits in the construction of novel expanded porphyrins. Compounds **3** and **4** were found to be quite stable in solution and in the solid state. The X-ray structure of **3** revealed the binding of two molecules of methanol. It is thus reminiscent of the one reported for macrocycle **2**, a system that was also found to cocrystallize with two molecules of methanol in the solid state.¹⁴ However, in the present instance, the two bound methanol molecules were found to lie on the same side of the macrocycle, in contrast to what is seen in the case of **2**. Unfortunately, the poor solubility of **3** in most organic solvents precluded a study of whether the bound methanol molecules are complexed to any appreciated extent in nonprotic solvents such as CD₂Cl₂. Currently efforts are underway to prepare more soluble analogues of **3** that might allow us to address this issue more directly.

Experimental Section

General. Melting points, ¹H and ¹³C NMR spectra, UV–vis spectra, elemental analyses, and CI mass spectra were obtained using instrumentation described previously.¹⁹ Methanol was dried by distillation from calcium hydride under a nitrogen atmosphere whereas anhydrous DMF (Sure-Seal bottle) and phosphorus oxychloride were purchased from Aldrich Chemical Co. and used as received. All other solvents, acids, and bases were obtained commercially and used as received. Bis α -free terpyrroles **7** and **8** were prepared according to a published procedure.¹⁹ 1,2-Diamino-4,5-dimethoxybenzene was obtained by reduction of 1,2-dinitro-4,5-dimethoxybenzene with hydrazine

(30) Falk, H. *The Chemistry of Linear Oligopyrroles and Bile Pigments*; Springer-Verlag: New York, 1989; p 179.

monohydrate using 10% Pd/C as the catalyst and absolute ethanol as the solvent.³¹ 1,8-Diaminoanthracene was prepared as described previously.¹³

Synthesis. 13,22,35,44-Tetraethyl-6,7,28,29-tetramethoxy-14,17,18,21,36,39,40,43-octamethyl-3,10,25,32,45,46,47,48,49,50-decaazanacyclo[37.2.1.1^{12,15}.1^{16,19}.1^{20,23}.1^{34,37}.1^{38,41}.0⁴⁹.0^{52,51}]-pentaconta-2,4(9),5,7,10,12,14,16,18,20,22,24,26(31),27,29,32,34,36,38,40,42,44-dicontaene (3). 5,5'-Diformyl-4,4'-diethyl-3,3',4',3''-tetramethyl-2,2':5',2''-terpyrrole (5) (0.783 g, 2.14 mmol) along with methanol (300 mL) was placed in a three-necked 500 mL RBF equipped with an argon inlet and a reflux condenser. 1,2-Diamino-4,5-dimethoxybenzene (0.361 g, 2.14 mmol) was then added together with concd HNO₃ (about 20 drops). The solution immediately turned dark red. It was then heated under reflux for 1 h before being filtered through a fritted funnel. The blue-green solid collected in this way was washed with methanol (50 mL) to give product **3** in the form of the HNO₃ salt. Further product was also obtained by concentrating the filtrate. The free-base form of **3** was obtained quantitatively by washing a dichloromethane solution of this salt with an aqueous NaHCO₃ solution.³² This latter product was then purified using column chromatography (silica gel; CHCl₃/CH₃OH, eluent). After collecting the appropriate fraction (*R_f* = 0.30; silica gel TLC; 2% CH₃OH/CHCl₃, eluent) and evaporating to dryness, the free-base form of **3** was obtained as an orange solid (1.28 g; 60%): ¹H NMR (250 MHz, DMSO-*d*₆): δ 10.49 (s, 2H), 8.30 (s, 4H), 6.82 (s, 4H), 5.75 (s, 4H), 3.81 (s, 12H), 2.64 (q, *J* = 7.3, 8H), 2.03 (s, 12H), 1.98 (s, 12H), 1.10 (t, *J* = 7.2, 12H); ¹³C NMR (125 MHz, CDCl₃/CD₃OD): δ 147.6, 144.1, 138.5, 134.2, 128.3, 126.5, 121.5, 118.2, 116.1, 101.2, 56.2, 17.3, 16.2, 10.0; 9.5; HRMS (CI⁺) *m/z* calcd for C₆₀H₇₀N₁₀O₄: 994.5581, found: 994.5580; UV-vis (CH₂Cl₂/CH₃OH, 80/20) λ_{max} [nm] (ε) (yellow color): 422 (120 720); IR (KBr) ν(C=N) 1605 cm⁻¹. Anal. Calcd for C₆₀H₇₀N₁₀O₄·CHCl₃·CH₃OH: C, 64.94; H, 6.59; N, 12.21. Found: C, 65.01; H, 6.78, N, 12.28.

18,19,22,23,26,27,45,46,49,50,53,54-Dodecamethyl-3,15,30,42,61,62,63,64,65,66-decaazanacyclo-[42.2.1.1^{17,20}.1^{21,24}.1^{25,28}.1^{44,47}.1^{48,51}.0^{4,14}.0^{31,41}]-hexahexaconta-2,4(55),5,7,9,11,13,15,17,19,21,23,25,27,29,31(58),32,34,36,38,40,42,44,46,48,50,52,54,56,59-tricontaene (4). In a three-necked 500 mL RBF equipped with a reflux condenser was placed diformyl terpyrrole (**6**) (0.075 g, 0.22 mmol) along with methanol, 1,8-diaminoanthracene (0.046 g, 0.22 mmol), and concd HNO₃ (2 drops) under an argon atmosphere. The dark red reaction mixture was then heated at reflux for 1 h and then stirred at room-temperature overnight. The resulting nitrate salt whose stoichiometry was not investigated was washed with an aqueous NaHCO₃ solution. The product **4** (*R_f* = 0.25; silica gel TLC; 2% MeOH/CH₂Cl₂, eluent) was purified by column chromatography (silica gel; CH₂Cl₂/CH₃OH gradient until 98:2 v/v). The product was further purified by dissolving in dichloromethane and precipitating out with hexanes. In this way, compound **4** was obtained in the form of a brown red solid (70 mg; 62%): ¹H NMR (250 MHz, CD₂Cl₂): δ 9.26 (s br, 4H), 8.44 (s, 4H), 8.36 (s, 4H), 8.23 (br, 2H), 7.83 (d, *J* = 8.5, 4H), 7.48 (t, *J* = 7.3, 4H), 6.97 (d, *J* = 6.7, 4H), 2.19 (s, 12H), 2.09 (s, 12H), 2.00 (s, 12H); ¹³C NMR (125 MHz, CD₂Cl₂): δ 151.5, 148.1, 133.1, 128.5, 128.1, 128.0, 127.8, 126.5, 126.1, 125.1, 122.3, 119.9, 119.1, 118.1, 112.3, 10.4(2), 9.1; HRMS (CI⁺) *m/z* calcd for C₆₈H₆₃N₁₀: 1019.5237, found: 1019.5240; UV-vis (CH₂Cl₂/CH₃OH, 80/20) λ_{max} [nm] (ε) (orange color): 449 (51 250); IR (KBr) ν(C=N) 1596 cm⁻¹. Anal. Calcd for C₆₈H₆₂N₁₀·CH₂Cl₂·CH₃OH: C, 73.99; H, 6.03; N, 12.33. Found: C, 73.89; H, 5.98, N, 12.11.

5,5'-Diformyl-4,4'-diethyl-3,3',4',3''-tetramethyl-2,2':5',2''-terpyrrole (5). In a three-necked 50 mL RBF equipped with a reflux condenser and a rubber septum was cooled anhydrous DMF (2.00 mL, 25.83 mmol) with stirring for about 15 min in an ice-water bath under an argon atmosphere. At this point, phosphorus oxychloride (0.6 mL, 6.44 mmol) was added via syringe over the course of 10 min. The reaction mixture was then stirred at room temperature for 20 min. 1,2-Dichloroethane

(3 mL) was then added and the solution cooled in an ice bath for 10 min. The bis-α-free terpyrrole **7** (0.816 g, 2.64 mmol), dissolved in 1,2-dichloroethane (4 mL), was then added dropwise to the POCl₃-DMF complex via syringe over 1 min. A brown yellow precipitate formed. Nonetheless, the mixture was stirred at room temperature for another 20 min. At this point, a saturated aqueous NaOAc solution (20 mL) was added and the mixture heated at 90–100 °C (reflux) for about 10 min. The reaction mixture was then allowed to cool to room temperature with vigorous stirring over the course of roughly 30 min. It was filtered through a fritted funnel. The brown solid collected in this way was washed with water (20 mL) and hexanes (20 mL). This gave compound **5** in the form of a yellow brown solid (0.945 g; 98%): mp 286–288.5 °C; ¹H NMR (250 MHz, DMSO-*d*₆): δ 11.34 (s br, 2H), 10.65 (s, 1H), 9.54 (s, 2H), 2.70 (q, *J* = 7.1, 4H), 2.00 (s, 6H), 1.97 (s, 6H), 1.13 (t, *J* = 7.2, 6H); ¹³C NMR (62.5 MHz, DMSO-*d*₆): δ 176.6, 130.5, 128.0, 120.8, 117.9, 117.5, 16.9, 16.1, 10.3, 9.3; HRMS (CI⁺) *m/z* calcd for C₂₂H₂₇N₃O₂: 365.2103, found: 365.2113. Anal. Calcd for C₂₂H₂₇N₃O₂·2H₂O: C, 65.81; H, 7.78; N, 10.47. Found: C, 66.11; H, 7.46; N, 10.32.

5,5'-Diformyl-3,4,3',4',3'',4''-hexamethyl-2,2':5',2''-terpyrrole (6). Compound **6** was obtained as a green powder (yield 89%) using a procedure similar to that used to prepare **5** but starting from the bis-α-free terpyrrole **8**: mp 286–288.5 °C; ¹H NMR (250 MHz, DMSO-*d*₆): δ 11.33 (s br, 2H), 10.65 (s, 1H), 9.55 (s, 2H), 2.25 (s, 6H), 1.98 (s, 6H), 1.97 (s, 6H); ¹³C NMR (62.5 MHz, DMSO-*d*₆): δ 176.7, 130.5, 128.8, 120.8, 118.3, 118.0, 10.3, 9.5, 9.1; HRMS (CI⁺) *m/z* calcd for C₂₀H₂₃N₃O₂: 337.1790, found: 337.1789. Anal. Calcd for C₂₀H₂₃N₃O₂·0.5H₂O: C, 69.34; H, 6.98; N, 12.13. Found: C, 69.94; H, 6.75; N, 11.99.

X-ray Diffraction Analysis. Crystals of 3·2CH₃OH·CH₂Cl₂ grew as orange prisms by slow evaporation from CH₃OH/CH₂Cl₂. The data crystal was a prism of approximate dimensions: 0.17 × 0.34 × 0.34 mm. Crystals were monoclinic, space group *C2/c*, with *a* = 28.375(13) Å, *b* = 10.231(2) Å, *c* = 21.248(8) Å, β = 102.85(3)°, *V* = 6014(5) Å³, ρ_{cal} = 1.26 g·cm⁻³ for *Z* = 4. The data were collected at -90 °C on a Siemens P4 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The structure was solved and refined using the Shelxtl-Plus (Siemens Analytical X-ray Instruments, Inc., Madison, WI) software package. One ethyl group was found to be disordered about two orientations of nearly equal occupancy. The hydrogen atom on the methanolic oxygen atom could not be located in a Δ*F* map and was not included in the final refinement model. The macrocycle lies around a crystallographic 2-fold rotation axis passing through 0, *y*, 1/4. The macrocycle is slightly concave and an indeterminate solvent molecule resides in this depression. The best fit to the data was found using two-half-weight chlorine atoms as if one molecule of methylene chloride resided in the concave region. This area of electron density was not well defined and was complicated by its close proximity to the crystallographic 2-fold rotation axis. No carbon atom position was included in the model for the methylene chloride molecule. The structure was refined on *F*² to a *R_w* = 0.232 using 4258 unique reflections and 379 parameters (conventional *R(F)* = 0.132 for 1132 reflections with *F* > 4(σ(*F*))). Full details of the structure determination, along with tables of atomic coordinates, bond lengths and angles, and thermal parameters, as well as supplementary figures, are given in the Supporting Information.

Crystals of 5·H₂O grew as pale green plates by slow evaporation from CH₂Cl₂/CH₃OH. The data crystal was of approximate dimensions 0.07 × 0.14 × 0.42 mm. Crystals were monoclinic, space group *P2₁/n*, with *a* = 13.314(3) Å, *b* = 16.401(4) Å, *c* = 19.956(5) Å, β = 103.07(2)°, *V* = 4245(2) Å³, ρ_{cal} = 1.20 g·cm⁻³ for *Z* = 8. Data were collected at -85 °C on a Siemens P4 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The structure was solved and refined using the Shelxtl-Plus (Siemens Analytical X-ray Instruments, Inc., Madison, WI) software package. The structure was refined on *F*² to a *R_w* = 0.247 using 7467 unique reflections and 506 parameters (conventional *R(F)* = 0.116 for 2180 reflections with *F* > 4(σ(*F*))). There are two crystallographically unique molecules of 5 per asymmetric unit, each with one molecule of water. The

(31) Sessler, J. L.; Mody, T. D.; Ramasamy, R.; Sherry, A. D. *New J. Chem.* **1992**, *16*, 541–544.

(32) It was found that the free-base form could also be obtained by using either an aqueous 10% concd NaOH solution or triethylamine as the base.

two unique molecules are H-bound via the terminal pyrrole and aldehyde moieties. The H-bound molecules form an infinite chain parallel to the *b* axis. The H₂O molecules connect adjacent chains via H-bonds involving the central pyrrole of one chain and the aldehyde oxygen of the second chain. Full details of the structure determination, along with tables of atomic coordinates, bond lengths and angles, and thermal parameters, as well as supplementary figures, are given in the Supporting Information.

Acknowledgment. This work was supported by the National Science Foundation (grant CHE 9725399 to J.L.S.). S.M. thanks the French Ministère des Affaires

Etrangères (Lavoisier Program) for a postdoctoral research fellowship.

Supporting Information Available: X-ray structural data for **3** and **5**, including X-ray experimental, summaries of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (55 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO980628G