Competitive Formation of Helical Cycloocta- and Cyclododecapyrroles

Jennifer A. Wytko,*,† Martin Michels,‡ Lars Zander,‡ Johann Lex,‡ Hans Schmickler,‡ and Emanuel Vogel‡,§

Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France, and Institut für Organische Chemie, Universität zu Köln, Greinstrasse 4, D-50939 Köln, Germany jwytko@chimie.u-strasbg.fr

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In connection with a study aimed at the evaluation of electronic effects in spiro-dicorrole (**1a**) and its binuclear Ni(II) complex (**1b**) we became interested in *gem*-dimethyl-substituted cyclotetrapyrrole (**2a**) and the corresponding Ni(II) complex (**2b**). Attempts to prepare **2a** as the 12,13,16,17-tetraethyl-2,3,7,8-tetramethyl derivative (**5**) by an acid-catalyzed (1 + 1) condensation of dimethyldipyrrylmethane **3** and diformylbipyrrole **4** resulted in the formation of the (2 + 2) and (3 + 3) condensation products, i.e., the cyclooctapyrrole **6** and the cyclododecapyrrole **7**, respectively, rather than in that of the desired *gem*-dimethyl cyclotetrapyrrole. The cyclododecapyrrole **7**, isolated as the major product, is among the largest cyclopolypyrroles known to date. These two new macrocycles have been structurally characterized by variable temperature 1D and 2D NMR experiments, as well as by single-crystal X-ray diffraction analysis. In solution both the cyclooctapyrrole **6** and cyclododecapyrrole **7** exhibit dynamic behavior. At 337 K **6** adopts a D_2-symmetric conformation, whereas at 196 K two equivalent C_2 conformers that interconvert through the D_2-symmetric intermediate are observed. The energy barrier for the interconversion process between these two degenerate conformers is found to be 10.6 kcal mol^{-1}. The solution dynamics of **7** could be described in an analogous manner, with the time-averaged conformation at 378 K displaying D_{3h} symmetry. X-ray analyses showed that for both macrocycles, **6** and **7**, the solid state structures were nearly identical to the low-temperature solution conformers.

Introduction

In 1995, while attempting to prepare a corrphycene derivative via a MacDonald condensation, the Cologne group discovered a new family of pyrrolic macrocycles, the cyclooctapyrroles (also known as octaphyrins).[1] This condensation reaction has been generalized, and a variety of cyclooctapyrroles, that differ by the number and/or type of spacers between each pyrrole moiety, have been prepared.[2−5] The octaphyrins adopt a helical figure-eight conformation[6] that seems well adapted for the formation of binuclear metal complexes. Although the number of expanded porphyrins capable of binding two metal ions is limited,[7−10] octaphyrins form a variety of bimetallic complexes.[4−6,11] During attempts to synthesize a bimetallic nickel(II) complex of diketo-octaphyrin-(1.1.1.0.1.1.1.0)[4,5,12] an unexpected chemical transformation occurred, generating the dicorrole bis-nickel(II) complex **1b**,[4,5] depicted in Figure 1. The spiro center linking two Ni(II) corroles renders this cyclooctapyrrole unique and poses the question of how the spiro carbon influences electronic interaction between the two halves. With the aim of better understanding this system and to establish the existence of spiro conjugation[13] in compound **1b**, we set out to prepare an appropriate reference compound. Cyclotetrapyrrole **2a** (Figure 1), in which the geminal (*gem*) dimethyl carbon replaces the spiro carbon of **1a**,**b**, represents an appropriate reference with respect to complex **1b**.

We assumed that a (1 + 1) condensation of diformylbipyrrole and a *gem*-dimethyl dipyrrylmethane (dpm) would be a successful synthetic strategy for the preparation of the free base **2a** as its 12,13,16,17-tetraethyl-

* To whom correspondence should be addressed. Fax: (33) 388-61-15-53.
† Université Louis Pasteur.
‡ Universität zu Köln.
§ E-mail: emanuel.vogel@uni-koeln.de. Fax: (49) 221-470-5057.

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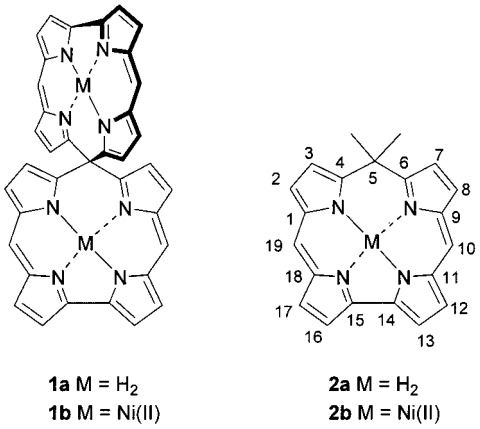


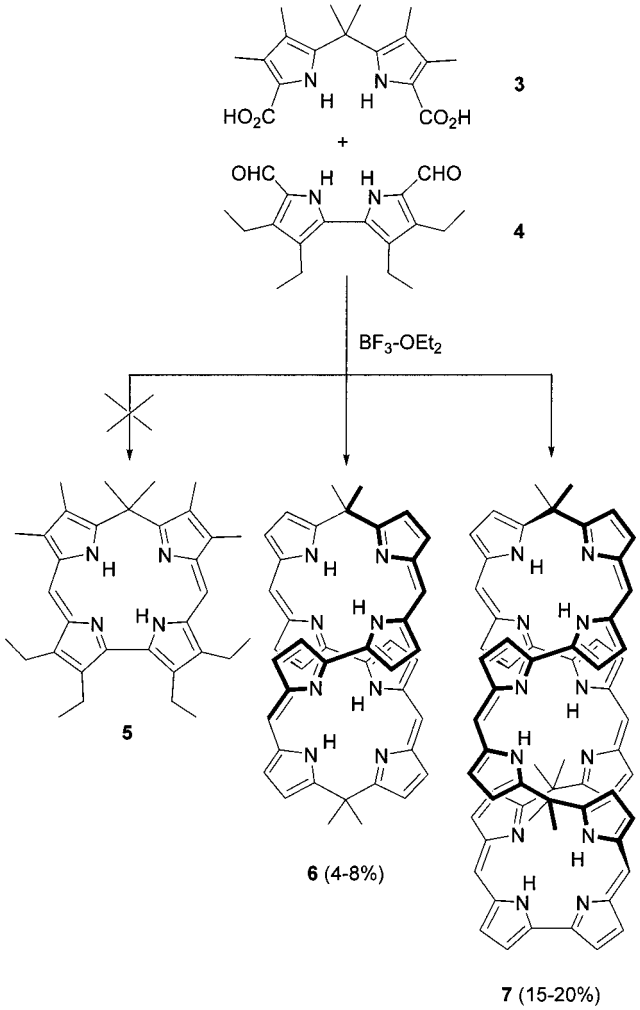
Figure 1. Spiro-dicorrole **1a**,**b** and an appropriate model compound **2a**,**b**.

2,3,7,8-tetramethyl derivative **5**. We reasoned that the introduction of *gem*-dimethyl groups at the dpm methylene carbon would result in compression of the internal angle C4−C5−C6 according to the *gem*-dimethyl or Thorpe−Ingold effect.[14,15] As a result, formation of the cyclotetrapyrrole might be favored over that of the cyclooctapyrrole (that is formed by condensation of unsubstituted dpm with diformylbipyrrole[1]). Despite this reasoning, this strategy fell short of our goal. Rather than affording the (1 + 1) condensation product (**5**), this synthetic route generated not only the commonly observed (2 + 2) product (**6**), but also yielded a higher order condensation product, namely the (3 + 3) product (**7**). Hereafter, we report the synthesis, characterization, and dynamic nature of *gem*-dimethyl-functionalized cyclooctapyrrole **6** and cyclododecapyrrole **7**.

Results and Discussion

Synthesis. Two key dipyrrolic precursors were necessary for the synthesis of the *gem*-dimethyl cyclotetrapyrrole **5** (Scheme 1). Compound **4** was readily available according to known procedures.[16] The dicarboxylic acid dipyrrylmethane derivative **3** was prepared by catalytic hydrogenation of its benzyl ester in the presence of 10% palladium on activated carbon.[17] The relatively unstable dicarboxylic acid **3** was used without isolation for the next step. The MacDonald condensation (Scheme 1) was carried out under strong acid conditions by successive addition of the diformylbipyrrole **4** and methanol to a tetrahydrofuran solution of the dicarboxylic acid **3**, followed by dropwise addition of boron trifluoride diethyl etherate at −10 °C. After 15 h of stirring at room temperature, the deep green solution was subjected to basic workup and then purified by column chromatography (alumina, hexane/toluene, 3/2). Three products, which eluted as a brick-red band, a violet band, and finally a deep blue band were isolated. Initially, ^{1}H NMR

Scheme 1. Synthesis of *gem*-Dimethyl Cyclopolypyrroles. *β*-Pyrrolic Alkyl Substituents Are Omitted from the Macrocycles 6 and 7 for Sake of Clarity.



spectra at 298 K were not helpful in characterizing these compounds, as the spectra of the red and violet fractions displayed an identical pattern and number of signals (for a more detailed discussion see the NMR section below). As expected, no conclusions could be drawn concerning the nature of the products based on their UV−visible spectra. The spectra of all three compounds showed similar features with several broad absorption bands between 300 and 600 nm. The most intense electronic transitions were progressively red-shifted in going from the red compound (λ_{max} = 435 nm) to the violet compound (λ_{max} = 544 nm) to the blue compound (λ_{max} = 598 nm).

By FAB$^+$ mass spectrometry the red and violet compounds were identified as a cyclooctapyrrole **6** (m/z = 988.7) and a cyclododecapyrrole **7** (m/z = 1484.9), respectively. The third (blue) compound displayed a series of mass peaks that correspond to higher polypyrrolic compounds with $(C_{33}H_{42}N_4)_n$ stoichiometry. It remains to be determined if the sample contains a whole series of higher cyclopolypyrroles or if the observed peak pattern is a result of fragmentation and recombination caused by the method. Variable temperature (190 to 370 K, toluene-d_8) proton NMR spectra of this blue sample are very complex and not helpful in characterization. Further investigations, in particular, attempts to grow monocrystals, are currently in progress.

(14) The terms "*gem*-dimethyl effect" and "Thorpe−Ingold effect" are often used interchangeably; however, the former more correctly refers to an overall acceleration of a cyclization, whereas the latter refers specifically to an angle change due to substitution.

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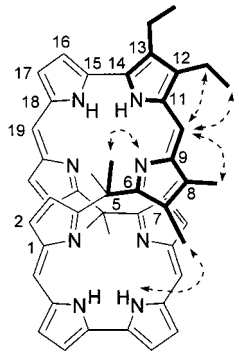

6

Figure 2. NOE interactions observed for **6** at both 378 K and 196 K. The β-pyrrolic alkyl substituents of one asymmetric unit are depicted to show the NOE interactions. All other alkyl groups have been omitted for clarity.

It is interesting to note that the main product of the condensation reaction in Scheme 1 is the cyclododecapyrrole **7**, typically obtained in 15−20% yields. This is one of the largest cyclopolypyrroles[18] known to date, being second only to the recently discovered cyclohexadecapyrrole[19] and closely followed by Sessler's turcasarin comprised of 10 pyrrole rings.[20] The cyclooctapyrrole **6** was consistently obtained as a secondary product in 4−8% yield. Despite all efforts, the target compound, cyclotetrapyrrole **5**, could not be located in the reaction mixture. Attempts to synthesize the reference ligand **5** by alternative methods are currently in progress.

NMR Studies. The ^{1}H NMR spectrum (500 MHz, toluene-d_8) of the cyclooctapyrrole **6** at 298 K displays broad peaks whereas at 337 K a sharp set of signals including a singlet (δ = 12.58 ppm) for the NH protons, one singlet (δ = 6.63 ppm) for the *meso* protons, and one singlet (δ = 1.31 ppm) for the *gem*-methyl groups is observed. At 337 K, the different β-pyrrolic alkyl groups appear as two singlets (methyl groups) and two ABX_3 spin systems (ethyl groups with diastereotopic CH_2 protons). This pattern is consistent with a D_2-symmetric loop conformation of **6** in Figure 2 in which the bold-faced dipyrrin moiety represents the smallest asymmetric unit. The position of the *gem*-dimethyl groups near the crossover point of the figure-eight conformation was confirmed by a 2D ROESY NMR experiment in which strong NOE interactions were observed between β-methyl protons and the imino protons (as shown in Figure 2 for the methyl substituent on C7 explicitly). Although in solution the NH protons are assumed to be tautomerically shared between neighboring pyrroles, ^{13}C NMR and carbon−proton correlation experiments provided evidence for only one tautomer. The α-bipyrrolic carbon atoms C14 and C15 at the pyrrole−pyrrole bond appear at 134.89 ppm, whereas the α-pyrrolic carbon atoms C4 and C6 located next to the *gem*-dimethyl carbon spacer appeared at 172.7 ppm. These chemical shifts can be accounted for by the electron-rich (pyrrolic) nature of the α-bipyrrolic carbon atoms and the electron-deficient (pyrrolenic) nature of the α-pyrrolic dpm carbon atoms.[21] Thus, the four imino protons are more highly localized on the bipyrroles, as depicted in Figure 2.

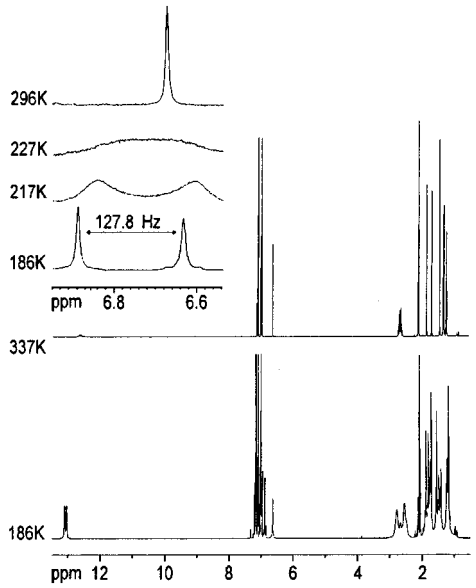

Figure 3. Representative spectra from variable temperature ^{1}H NMR experiments for **6** in toluene-d_8 (500 MHz). Insert: coalescence and splitting of H_{meso} peak. The energy barrier for the conversion of the D_2-symmetric and C_2-symmetric conformations is $\Delta G^{\ddagger} = 10.6$ kcal mol^{-1} with respect to a coalescence temperature of 227 K.

To investigate the dynamics of cyclooctapyrrole **6**, variable temperature NMR experiments were carried out. Representative spectra are shown in Figure 3. As mentioned above, at 337 K, one set of sharp signals is observed for the alkyl groups of the dpm unit, indicative of a D_2-symmetric conformation (Figure 4, structure b or e). The four *gem*-methyl groups (gray circles) are related by symmetry due to the presence of three perpendicular C_2 axes, one of which intersects the two *meso* sp^3 carbons. Upon lowering the temperature, the signals broaden and eventually split at 217K into two sets of signals of equal shape and intensity, indicating a new loop conformation of **6** with C_2 symmetry (Figure 4, structures a and c, or structures d and f). In this new conformation, two α−α linked tetrapyrrolic units that form the front and back strand of the figure-eight are symmetry-related by the remaining C_2 axis. This is confirmed by a 2D long range NMR experiment at 196 K which, compared to the spectrum at 298 K, still shows only one signal for the two symmetry-related sp^3 *meso* carbons.

In the C_2 symmetric conformation, the four *gem*-methyl groups are no longer equivalent but are divided into two pairs of equivalent methyl groups (white and black circles). The analysis of the low temperature 2D NMR ROESY spectra (500 MHz, 196K) shows identical nuclear Overhauser effects (NOE) for both sets of signals, a finding indicating an equilibrium between two identical C_2 conformers of **6**. As the examination of simple molecular models was taken into account, the mutual interconversion of the two C_2 conformers of **6** is achieved by partial rotation around the bonds between the sp^3 carbon C5 and α-pyrrolic carbon atoms C4 or C6 as

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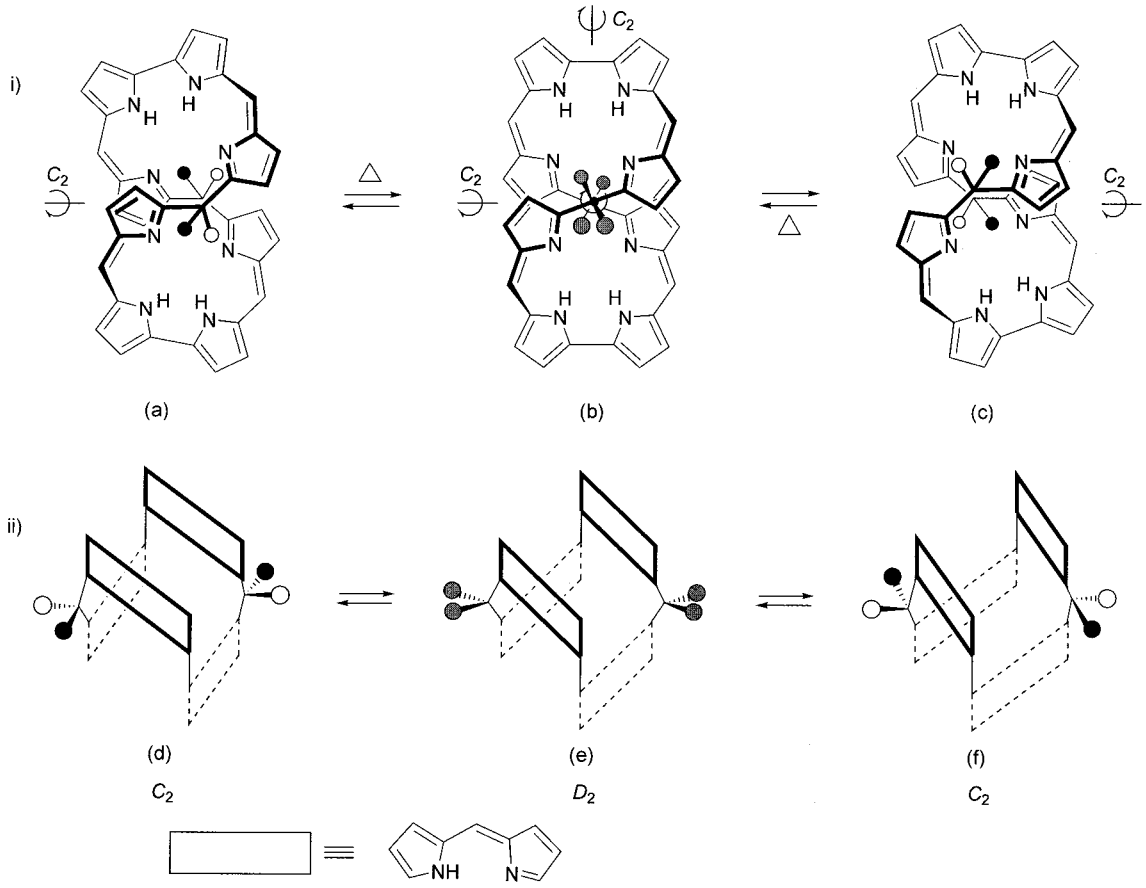

Figure 4. Conformational changes occurring for **6** upon varying the temperature: (i) molecular representation, (ii) schematic representation. The *gem*-methyl groups are depicted as white, gray, or black circles. The β-alkyl substituents have been omitted for sake of clarity. The two degenerate C_2 conformers (a and c; or d and f) represent isomers that exchange slowly at low temperature via the D_2-symmetric conformation (b or e).

depicted in Figure 4, passing through the D_2-symmetric transition state described above as the high temperature conformation. The energy barrier calculated for this interconversion of the two identical C_2 conformers is $\Delta G^{\ddagger} = 10.6$ kcal mol^{-1} with respect to a coalescence temperature of 227 K. It is important to note that the C_2 conformer in solution at 196 K is also observed in the crystal structure[22] of **6**.

A similar yet more complex proton NMR behavior is observed for the cyclododecapyrrole **7**. At 298 K the proton spectrum (500 MHz, toluene-d_8) displays only broad signals, whereas at 378 K a sharp set of peaks corresponding to the smallest possible asymmetric unit, a dipyrrin moiety (shown in bold face in Figure 5a), is observed. In contrast to **6**, the ethyl protons of **7** appear as simple A_2X_3 patterns, indicating the presence of mirror planes. Thus, at 378 K, this molecule displays D_{3h} symmetry on the NMR time scale which is consistent with an apparent hexagonal conformation (Figure 5a). As the sample was cooled to 215 K, additional peaks appeared, out of which one set of signals could be correlated to a second conformer of **7**. The fifteen new singlets (three imino protons, three *meso* protons, three *gem*-methyl groups, and six β-pyrrolic methyl groups) and six new ABX_3 systems (ethyl groups) indicate an apparent C_2-symmetric conformation. In this conformation, two strands of six pyrroles are helically arranged around the 2-fold symmetry axis, which bisects one of the three *meso* sp^3 carbons at the top position (Figure 5b, middle structure). Thus the two remaining *gem*-dimethyl carbon spacers situated at the lower crossover point of the strands are divided into two different pairs of two equivalent methyl groups oriented up (black) and down (white). NOE and cross-peak analyses in the 2D ROESY spectra of **7** (500 MHz, toluene-d_8, 215 K) revealed a fast exchange between these two different up and down positions, indicating their mutual interconversion. To understand this conformational situation it is helpful to consider **7** as an asymmetric figure-eight composed of a tetra- and an octapyrrolic subunit as seen in the X-ray structure[22] of **7**. The latter substructure undergoes a dynamic process (Figure 5b, interconversion of the left and right conformers) very similar to that previously described for **6** (vide supra). As the temperature was lowered even further to 203 K, the signals became broad and can no longer be assigned. At this temperature the ethyl groups have partly fixed positions, as indicated by broadening of peaks, and symmetry may be completely lost.

In summary, NMR studies show that in solution both **6** and **7** demonstrate dynamic behavior in which their time-averaged conformations exhibit D_2 (337 K) and D_{3h} (378 K) symmetry, respectively. Variable temperature NMR experiments indicate that at lower temperatures

(22) Crystal structures of macrocycles **6** and **7** are available in Supporting Information. Crystallographic data (excluding structure factors) for the structures of **6** and **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-146223 (**6**) and CCDC 146224 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB21EZ (fax (+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

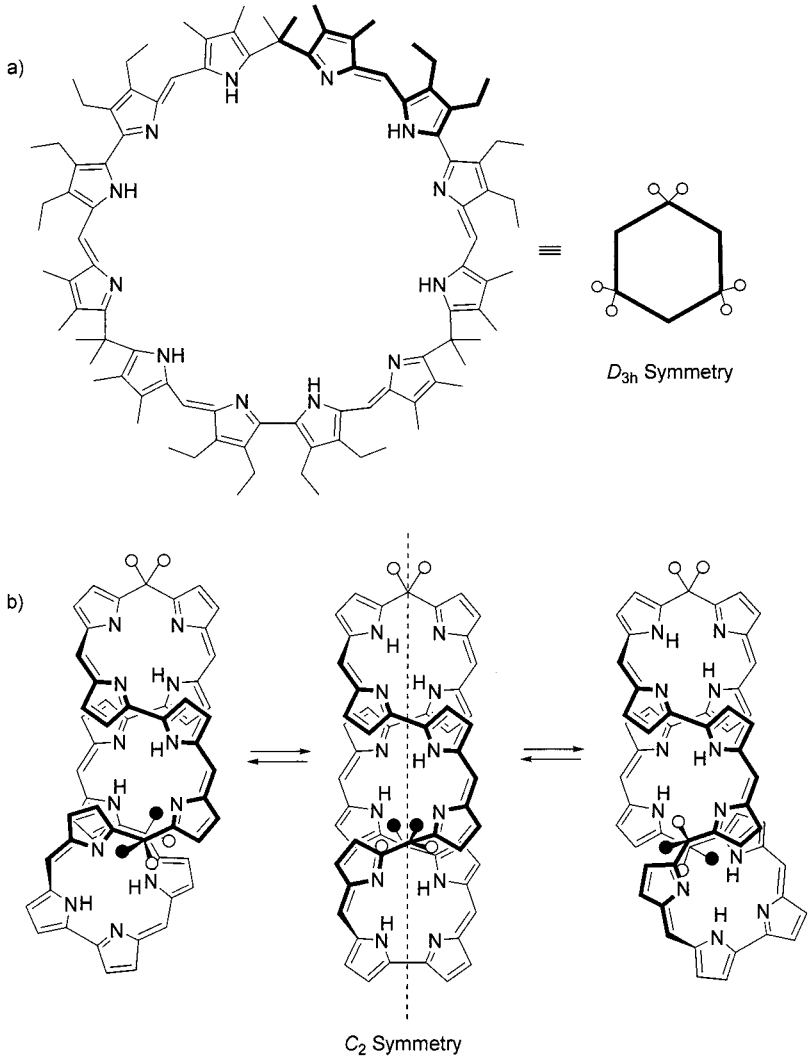

Figure 5. Conformations of **7** as observed by variable temperature NMR studies. The *gem*-methyl groups are depicted as white or black circles. (a) 378 K: hexagonal conformation; (b) 215 K: two helical conformations with C_2 symmetry are in fast exchange (interconversion of black and white methyl groups). The β-alkyl substituents have been omitted for sake of clarity.

each of these ligands adopts two degenerate conformations of lower symmetry in which the *gem*-methyl groups are in exchange via the higher symmetry D_2 or D_{3h} conformations. The interconversion processes in both macrocycles most likely occur by rotations around the bonds linking the sp^3 *meso* carbons and the α-pyrrolic carbons.

Solid State Structures. In agreement with the ^{1}H NMR data at 196 K, X-ray analysis of the cyclooctapyrrole **6** at 298 K shows that in the solid state, **6** displays a helical conformation in which the imino protons are located on the bipyrrole nitrogen atoms N3, N4, N7, N8.[22] One of the *gem*-methyl groups is aligned with one side of the cavity and the other points outside of the cavity. In the *gem*-dimethyl dpm units, the internal bond angle opposite the *gem*-methyl substituents C4−C5−C6 is 111.0°. Compared to the crystal structures of other octaphyrins,[1−5] **6** adopts a more folded figure-eight or tub-like conformation. Each of the four dipyrrin subunits is nearly planar with torsion angles between 1 and 5°. The bipyrrole moieties, on the other hand, are rotated around the pyrrole−pyrrole bond with a torsion angle of 38.1° (N7−C33−C34−N8). The torsion of the bipyrroles combined with the presence of two sp^3 carbons within the macrocyclic framework are mainly responsible for the conformation of the macrocycle.

Upon close inspection of the crystallization of **6**, two types of crystals were identified. X-ray diffraction analysis revealed that identical molecules of **6** crystallized in two distinct space groups depending on whether toluene was present within the lattice. A triclinic space group $P\bar{1}$ was observed in the presence of toluene, and orthorhombic space group P_{ccn} was observed in the absence of toluene. In the latter case, the tub-shaped molecules are packed in alternating stacks of all up and all down orientations. In the toluene-containing crystals, the tub-like molecules are arranged in face-to-face pairs, with the left side of the face-down conformation pointing into the central cavity of its face-up counterpart. The toluene molecules are organized in stacks intercalated between every two columns of cyclooctapyrrole **6**.

Solid-state structural information was also obtained for the cyclododecapyrrole **7** at 298 K.[22] This macrocycle displays an asymmetric figure-eight conformation in which four pyrroles form the top of the asymmetric figure-eight and the remaining eight pyrroles form a larger bottom loop. In the bottom loop the dpm subunits zigzag from front to back, giving a helical appearance to the molecule when viewed from a different angle. As in the case of the cyclooctapyrrole **6**, this conformation arises mainly because of the torsion angles around the

C−C bond connecting the two pyrroles in the bipyrrole moieties. The bipyrrole located at the bottom of the larger loop is twisted 48.7° (N11−C52−C53−N12) around the pyrrole−pyrrole bond with both imino groups oriented toward the macrocyclic cavity. The two bipyrroles situated near the top of the larger loop (at the crossing point) are both anti-periplanar; the bipyrrole of the front strand of the loop is nearly planar (torsion angle of 176.1°, N7−C33−C34−N8) whereas the bipyrrole of the back strand of the loop has a torsion angle of 155.3° (N3−C14−C15−N4). Each of the six dipyrrin units displays nearly coplanar pyrrole rings, with torsion angles ranging from −5.6° to 5.4°. For two of the three sets of *gem*-methyl groups, the internal angles opposite the *gem*-methyl substituents, C4−C5−C6 (110.7°) and C23−C24−C25 (110.9°), are compressed compared to the third internal angle C42−C43−C44 (113.0°) that is a rather wide angle for a *gem*-dimethyl-substituted carbon.

In agreement with ^{1}H NMR data, the six imino protons of **7** are located on the bipyrrole nitrogen atoms N3, N4, N7, N8, N11, N12. Due to the orientation of the two *gem*-methyl groups at the bottom of the loop that point into the macrocyclic cavity and that of the two bipyrroles located at the crossing point, the lower cavity is quite large and does not appear to be well suited for metal coordination.[23] The cavity defined by the bottom loop is much wider near the crossing point with a *meso* carbon−*meso* carbon distance of 10.59 Å (C10−C38) compared to the 7.76 Å separating the remaining two unsubstituted *meso* carbons (C48−C57) at the bottom. The total length of the molecule, from the top *gem*-dimethyl *meso* carbon (C24) to a bottom α bipyrrole carbon (C52), is 17.77 Å, with the larger loop spanning 11.40 Å (C31−C52).

Conclusion

Although our initial objective to synthesize a *meso-gem*-dimethyl cyclotetrapyrrole **5** via a (1 + 1) acid-catalyzed condensation was not reached, this reaction led to the serendipitous discovery of a dodecapyrrolic macrocycle **7**. The cyclooctapyrrole **6**, the (2 + 2) product commonly observed under these reaction conditions, is merely a side product in this case. Formation of the larger cyclododecapyrrole may be a result of the *gem*-dimethyl effect. Rationalization of the factors governing the size of the pyrrolic macrocycle produced during condensation is currently being studied.

The helical structures of both **6** and **7** observed in the low temperature ^{1}H NMR spectra correlate very well with those seen in their respective crystal structures. Whereas the figure-eight conformation of **6** appears to be well suited for the complexation of two metal cations, the conformation of cyclododecapyrrole **7** seems better suited to coordinate only one metal ion within a tetrapyrrolic loop. Investigations of the binding properties of **7** with both metal ions and neutral or charged substrates are currently in progress.

Experimental Section

General. Compounds **3** and **4** were prepared according to refs 17 and 16, respectively. Reagents and solvents of reagent-grade were purchased and used without further purification. Tetrahydrofuran was distilled under argon over sodium/benzophenone. Methanol was distilled under argon over magnesium. Anhydrous Na_2SO_4 was used as drying agent after aqueous workup. Evaporation and concentration in vacuo were carried out at H_2O-aspirator pressure. Column chromatography was performed with aluminum oxide 90 (0.063−0.200 mm) from Merck. Melting points are uncorrected. Mass spectra were recorded using a nitrobenzyl alcohol matrix.

Cyclooctapyrrole (6) and Cyclododecapyrrole (7). To a solution of dipyrrylmethane **3** (prepared in situ by hydrogenation of the corresponding benzyl ester (548 mg, 1.1 mmol) in the presence of 10% Pd/C (100 mg)) in dry THF (75 mL) were added 3,3′,4,4′-tetraethyl-5,5′-diformyl-2,2′-bipyrrole **4** (300 mg, 1.00 mmol) and MeOH (70 mL). The solution was cooled to −10 °C, and then $BF_3{\cdot}OEt_2$ (15 mL) was added dropwise over 30 min. The resulting deep green solution was allowed to warm to room temperature and stirred for 20 h. Toluene and dilute $NaOH_{(aq)}$ were added until the color changed to blue followed by an aqueous workup. The organic layer was dried, filtered, and concentrated in vacuo. Column chromatography over alumina (hexane/toluene, 3/2) afforded **6** (21 mg, 21 μmol, 4%) as a dark red solid, and **7** (80 mg, 54 μmol, 16%) as a violet solid. Each compound was recrystallized from CH_2Cl_2/MeOH.

2,3,5,5′,7,8,21,22,24,24′,26,27-Dodecamethyl-12,13,16,-17,31,32,35,36-octaethyl-39,40,41,42,43,44,45,46-octa-aza-nonacyclo[34.2.1.1(6,9).1(11,14).1(15,18).1(20,23).1(25,28).1(30,33).1(34,37)]-hexatetraconta-2,4(39),6(40),7,9,-11,13,15,17,19,21,23(43),25(44),26,28,30,32,34,36,38-icosene (6): mp = >270°. ^{1}H NMR (500 MHz, 337 K, toluene-d_8): 12.58 (br. s, 4 H), 6.63 (s, 4 H), 2.67 (m, ABX_3-system, AB part, 8H), 2.65 (m, ABX_3-system, AB part, 8H), 1.84 (s, 12H), 1.68 (s, 12H), 1.44 (s, 12H), 1.31 (m, ABX_3 system, X_3 part, 12H), 1.23 (m, ABX_3 system, X_3 part, 12H). ^{13}C NMR (125 MHz, 337 K, toluene-d_8): 172.70, 145.41, 138.91, 135.28, 134.89, 133.03, 127.92, 125.88, 115.06, 42.98, 25.99, 18.97, 18.51, 17.27, 15.66, 12.24, 9.63. UV/Vis (CH_2Cl_2): 219 (32400), 253 (24300), sh 345 (24700), sh 409 (45100), 435 (47500), 523 (25300). FAB^+ MS, calcd for $C_{66}H_{84}N_8$: 989.4, found: 988.7 (M^+, 23%). The hydrochloride salt (**6**·4HCl) was prepared by washing a CH_2Cl_2 solution of **6** with 1 M $HCl_{(aq)}$ (3 × 25 mL), drying the organic phase, and recrystallization from CH_2Cl_2/hexane: UV/vis (CH_2Cl_2) of **6**·4HCl: 219 (30400), 270 (19800), sh 332 (15600), 451 (74100), 591 (65600), sh 662 (28900). Anal. Calcd for **6**·4HCl: $C_{66}H_{84}N_8{\cdot}4HCl$ (1135.27 g mol^{-1}): C: 69.83, H 7.81, N 9.87. Found: C 69.75, H 7.91, N 9.63.

12,13,16,17,31,32,35,36,50,51,54,55-Dodecaethyl-2,3,5,5′,7,8,21,22,24,24′,26,27,40,41,43,43′,45,46-octadecamethyl -58,59,60,61,62,63,64,65,66,67,68,69-dodeca-aza-tridecacyclo[53.2.1.1(6,9).1(11,14).1(15,18).1(20,23).1(25,28).1(30,33).1(34,37).1(39,42).1(44,47).1(53,56)]-nonahexaconta-1,3,6(59),7,9,11,13,15(61),16,18,20,22,25,27,29,-31,33(64),34,36,38,40,42(66),44(67),45,47,49,51,53(69),54,56-triacontaene (7): mp = 246−247°. ^{1}H NMR (500 MHz, 378 K, toluene-d_8): 10.00 (br. s, 6H), 6.68 (s, 6H), 2.57 (q, 12H), 2.63 (q, 12H), 1.98 (s, 18H), 1.89 (s, 18H), 1.87 (s, 18H), 1.13 (t, 18H), 0.97 (t, 18H). ^{13}C NMR (125 MHz, 378 K, toluene-d_8): 168.00, 142.87, 138.00, 137.96, 134.87, 130.04, 127.14, 116.09, 42.58, 28.78, 18.91, 18.35, 17.19, 15.54, 11.20, 9.67. UV/Vis (CH_2Cl_2): 258 (20300), 342 (18300), 429 (26000), 544 (53000), sh 608 (35300). FAB^+ MS, calcd for $C_{99}H_{126}N_{12}$: 1484.1, found: 1484.9 (M^+, 100%). Anal. Calcd for $C_{99}H_{126}N_{12}$ (1484.20 g mol^{-1}): C: 80.12, H 8.56, N 11.32. Found: C 79.84, H 8.84, N 11.09.

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Supporting Information Available: Crystal structures and tables of X-ray crystallographic data for compounds **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Preliminary complexation studies indicate that only mononuclear complexes are formed even when a large excess of the metal salt is employed. (Zinc(II), copper(II), and nickel(II) acetates have been tried.)