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[30]Heptaphyrin(1.1.1.1.1.0.0): an aromatic expanded porphyrin with a 'figure eight' like structure

Christophe Bucher, Daniel Seidel, Vincent Lynch and Jonathan L. Sessler*

Department of Chemistry and Biochemistry, Institute for Cellular and Molecular Biology, The University of Texas at Austin, Austin, Texas 78712-1167, USA. E-mail: sessler@mail.utexas.edu

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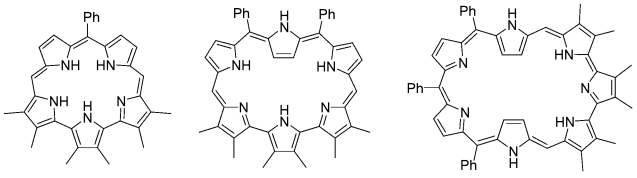
The synthesis, characterization, and X-ray structure of a heptapyrrolic macrocycle, [30]heptaphyrin(1.1.1.1.1.0.0) is reported; despite showing aromatic features, it exhibits a 'figure eight'-like structure in the solid state.

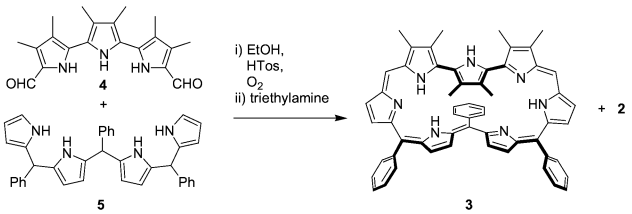
As a part of our general efforts to develop the chemistry of expanded porphyrins,[1] we recently reported the synthesis and characterization of [26]hexaphyrin(1.1.1.1.0.0) (**2**).[2,3] This macrocycle displayed the anticipated inversion of one particular pyrrolic subunit in its respective free base and protonated forms. Additionally, its smaller homologue, [22]pentaphyrin(1.1.1.0.0) (**1**), has also been studied and it was shown that it displays planarity without any apparent inversion under standard conditions.[3,4] The common feature of **1** and **2** is the presence of a terpyrrolic subunit that is linked to an oligopyrrane building block; a dipyrromethane unit in the case of **1** and a tripyrrane unit in the case of **2**. Because these building blocks are conveniently obtained by the condensation of pyrrole with benzaldehyde under appropriate conditions,[5] and higher homologues such as tetrapyrrane **5** are available as well, we were keen to attempt the synthesis of [30]heptaphyrin(1.1.1.1.1.0.0) (**3**) which would represent the next higher homologue in the series of pyrrane-terpyrrole containing expanded porphyrins.

In this paper we report the synthesis of the first example of such a system, namely **3**. Based on CPK-models we expected **3** to adopt a conformation with two pyrrolic subunits inverted. Further motivation to attempt the synthesis of **3** was given by the fact that heptaphyrins are still rather rare and only a few known expanded porphyrins containing seven pyrroles have been described in the literature. Very recently, Furuta and coworkers have reported on the synthesis of heptaphyrin(1.1.1.1.1.1.1) that was isolated as one product out of a mixture of various *meso*-aryl substituted expanded porphyrins.[6] However, its exact nature has yet to be determined. Chandrashekar *et al*. recently reported on the synthesis of three different types of *meso*-aryl substituted heptaphyrins that all displayed aromaticity while being partially inverted. In all of these heptaphyrins, however, several pyrrolic subunits have been substituted for either furan, thiophene or selenophene.[7] Thus far in only one instance, namely in the case of a [28]heptaphyrin(1.0.0.1.0.0.0), reported by our group, could solid state structural information be obtained.[8]



1 **2** **3**

The synthesis of compound **3** is summarized in Scheme 1. Briefly, it is obtained from the acid catalyzed condensation of a 1 : 1 mixture of the diformylhexamethylterpyrrole[9] (**4**) with the tetrapyrrane **5**.[5] Carrying out this condensation in ethanol at room temperature and open to air with a 4-fold molar equivalent excess of toluene-*p*-sulfonic acid, followed by chromatographic workup, provides **3** in 16% yield. Additionally, as a result of partial hydrolysis of the precursor tetrapyrrane **5** under the reaction conditions, [26]hexaphyrin(1.1.1.1.0.0) (**2**) was also isolated in approximately 15% yield. Such a finding, namely the formation of a smaller macrocycle due to a partial hydrolysis of starting material, is commonly observed in expanded porphyrin chemistry.[1]



4 + **5** **3**

Scheme 1

The structure of [30]heptaphyrin(1.1.1.1.1.0.0) (**3**), as it is shown in Scheme 1, was assigned based on NMR-spectroscopic observations. Namely, the ^{1}H-NMR spectrum in $CDCl_3$ displayed peaks that are not in agreement with the originally anticipated bis-inverted conformation. A peak observed at −4.2 ppm was correlated to a ^{13}C signal at 3.8 ppm by means of a HETCOR experiment. Based on this correlation and the integration of the peak, the signal was assigned to two methyl-groups pointing inward toward the center of an aromatic macrocycle. Two more singlets at 3.6 and 4.4 ppm, respectively, and integrating to six protons each, were assigned to two magnetically distinct methyl groups, establishing the partial inversion of the β-substituted terpyrrole. Another striking feature observed in the ^{1}H-NMR spectrum of **3** is the presence of three sets of multiplets at 0.48 (2H), 3.67 (2H) and 4.93 ppm (1H). Based on HETCOR and COSY experiments these signals were assigned to the respective *ortho*-, *meta*- and *para*-protons of one phenyl ring. The considerable upfield shift of these protons as compared to a 'normal' phenyl ring suggest that this particular phenyl-group experiences the strong ring current effect of the aromatic macrocycle, *e.g*. is placed 'inside' the ring. Additionally, the finding that the *ortho*-proton is subject to the strongest upfield shift led us to conclude that the overall conformation of **3** is likely to deviate substantially from planarity. All remaining signals in the ^{1}H-NMR spectrum of **3** are also in good agreement with the proposed structure as depicted in Scheme 1. Four sets of doublets between 8.43 and 8.94 ppm, integrating to two protons each, are assigned to the four magnetically distinct β-pyrrolic protons, providing further support for the assumption that none of the β-unsubstituted pyrrolic subunits is inverted. A singlet at 9.71 ppm is ascribed to the two *meso*-like C*H*-protons, while a broad singlet at 16.56 ppm is assigned to the N*H*-signal of the inverted pyrrole. Again, the position of these latter two signals supports the contention that **3** is aromatic. The signals corresponding to the two remaining phenyl groups are found to resonate as broad peaks between 7.81–8.03 and at 9.04 ppm. Unfortunately, the expected signals for the remaining inner N*H*-protons could not be detected.

Further characterization of [30]heptaphyrin(1.1.1.1.1.0.0) (**3**) was achieved from a single crystal X-ray diffraction analysis.†

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The resultant structure is shown in Fig. 1. To our surprise, it is characterized by the presence of a 'figure eight' motif as seen in several octa- and decapyrrolic expanded porphyrins.[11,12] The terpyrrolic subunit folds in the same way as in the decapyrrolic macrocycle turcasarin.[12] By contrast, the tetrapyrrane subunit, which completes the circle, adopts a conformation very similar to what has just been reported for octaphyrin(1.1.1.1.1.1.1.1).[6] In agreement with the chirality of **3** observed in the solid state as a result of the 'figure eight' motif, both enantiomeric forms of the macrocylce are seen in the crystal lattice (only one of which is shown in Fig. 1).

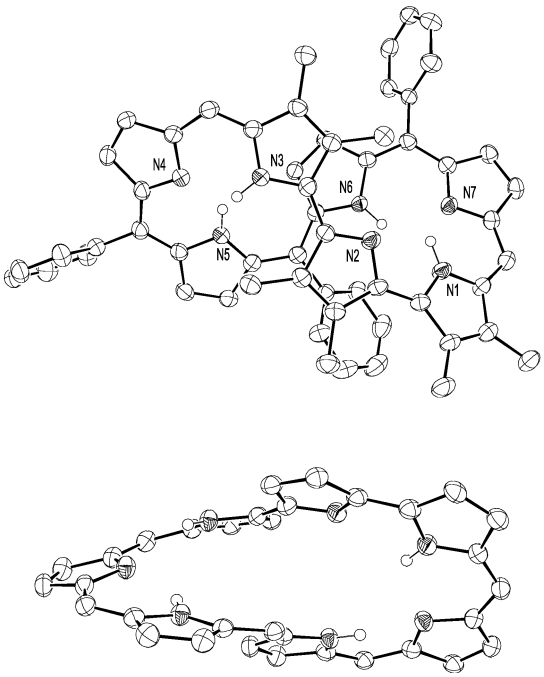

Fig. 1 Ortep views[10] of **3** with a partial atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale. For clarity, substituents have been removed in the side view.

The solid state structure thus appears to differ from the more symmetric structure observed in solution. One rationale for this discrepancy could be dynamic motion. If one takes into account the presence of two different enantiomeric 'figure eight' forms of this macrocycle, then what is seen in solution could be just the result of a rapid equilibrium between these two forms with the structure depicted in Scheme 1 representing a time averaged conformation. However, low temperature ^{1}H-NMR spectroscopic analyses, carried out in $CDCl_3$ at 213 K, revealed little change in the spectral features as compared to the room temperature spectrum.§ On the other hand, substantial differences would be expected were the two enantiomeric 'figure eight' forms being frozen out. We thus propose that the 'flat' conformation is really the preferred structure in solution, and what is seen in the solid state is simply the result of crystal packing effects.

Two other possible explanations for the disparity between the solid state structure and what is inferred on the basis of the NMR spectroscopic studies were also considered and ruled out. First, we were concerned that in $CDCl_3$ compound **3** was undergoing protonation as the result of adventitious solvent-borne impurities. This possibility, which would have the effect of having the species studied in solution being different from that in the crystalline phase, was discounted on the basis of the fact that an ^{1}H-NMR spectrum recorded in DMSO-d_6 proved concordant with that recorded in $CDCl_3$. Further, the addition of either K_2CO_3 or solid NaOH to the DMSO-d_6 solution resulted in little qualitative change in the spectrum (other than a significant reduction in the signal to noise level).

The second possibility involved the idea that facile oxidation or reduction of **3** would result in a different heptaphyrin-(1.1.1.1.1.0.0) being present in solution. This possibility, however, was ruled out based on the structure itself; four pyrrolic N*H*-hydrogens have been located, supporting the contention that **3** is indeed a 30 π-electron macrocycle.

The UV–vis spectrum of **3** further supports the assumption that **3** is aromatic.‡ Specifically, one Soret-type band is seen at 640 nm, with less intense Q-type bands being seen at 834, 919 and 1077 nm, respectively. The shape of the spectra and the intensity of the Soret-type bands are similar in the case of both **2** and **3**, with the bands for the larger heptapyrrolic system (**3**) being red shifted as compared to the smaller macrocycle (**2**).

In summary, the approach reported here provides access to a new class of heptapyrrolic macrocycles, namely [30]heptaphyrin-(1.1.1.1.1.0.0) (**3**). Probably the most striking feature of **3** is the inversion of a β-substituted pyrrolic subunit observed in solution. While β-unsubstituted pyrroles are commonly found to be inverted in expanded porphyrins,[1–3,7,13] to the best of our knowledge such behavior has not yet been reported for their substituted congeners. Additionally, the finding that one phenyl group is 'pointing inward' toward the center of the macrocyclic ring is rather unique for molecules of this type. Finally it is worth noting that **3** is the smallest oligopyrrolic macrocyclic system reported to date that displays a 'figure eight' structure, at least in the solid state.

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Notes and references

† *Crystallographic summary* for $C_{57}H_{47}N_7$ (**3**): Crystals were grown by slow evaporation of a solution of **3** in dichloromethane–ethylacetate. Black needles, triclinic, $P\bar{1}$, μ = 0.075 mm^{-1}, Z = 2 in a cell of dimensions: a = 11.1246(2), b = 13.1607(2), c = 15.7093(3) Å, α = 96.337(1)°, β = 105.570(1)°, γ = 95.214(1)°, 2184.51(7) Å^3, ρ_{calc} = 1.262 Mg m^{-3}, F(000) = 876. A total of 9874 unique reflections were measured on a Nonius Kappa CCD using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) at −120 °C. The structure was refined on F^2 to an R_W = 0.159, with a conventional R = 0.0722, and a goodness of fit = 1.083 for 593 refined parameters using the SHELX-97 package (ref. 14). CCDC 173526. See http://www.rsc.org/suppdata/cc/b1/b109877b/ for crystallographic data in .cif format.

§ Two signals of equal intensity were observed at −0.45 and −0.96 ppm in the low temperature spectrum of **3**; these are ascribed to the two tautomeric forms in fast exchange.

‡ UV–vis summary for **3**: λ_{max} [nm] (ε in mol^{-1} L^{-1}) 317 (28200), 402 (32200), 640 (75200), 689 (27100), 834 (9400), 919 (9000), 1077 (13600).

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