Cyclic Oligofurans: One-Pot Synthesis of 30π and 40π Expanded Porphyrinoids
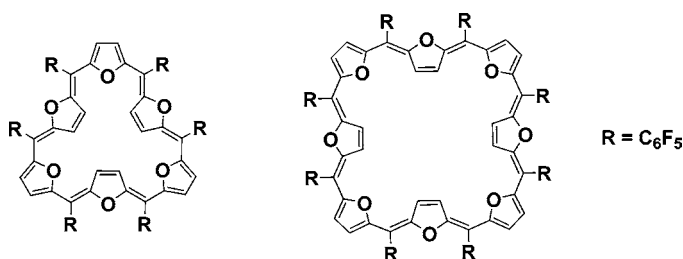
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Received September 26, 2006

ABSTRACT

Acid-catalyzed condensation of furan and pentafluorobenzaldehyde yielded conjugated macrocycles with six and eight furan rings. They represent systems similar to annulenes with 30π and 40π electrons. From their structural analyses, it was found that furan rings in both the molecules were inverted in an alternative fashion and displayed nontwisted conformations.

Porphyrins and expanded porphyrins represent model systems to understand the delocalization of π electrons in large cyclic conjugated systems. Electronic properties of such macrocycles are strongly dependent on their structural features and the nature of substituents.[1] Invariably, such macrocycles tend to twist and adopt nonplanar conformations due to their flexible nature.[2,3] Owing to this affinity for twisting, even $4n + 2\pi$ systems are devoid of aromatic features.[4] In a recent report, a spacer, such as benzene, has been employed in the center of 44π and 46π decapyrrolic systems to prevent the twisting of the macrocycle.[5] To date, 34π core-modified octaphyrins are the largest planar expanded porphyrins to be characterized in the solid and solution states.[6]

Reaction of pyrrole with pentafluorobenzaldehyde generates a series of expanded porphyrins.[2] Replacing the pyrrolic units with other heterocycles such as thiophene/furan/selenophene can be used to generate core-modified porphyrinoids, which are structurally similar to annulenes.[7] A dearth of straightforward synthetic methods to generate flat expanded porphyrinoids has hindered the study of such giant molecules. Herein, we report the one-pot synthesis of stable and neutral

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cyclo-hexa furans [1.1.1.1.1.1], **1**, and cyclo-octa furans [1.1.1.1.1.1.1.1], **2**, by direct condensation of furan with aryl aldehyde.

In a simple procedure (Scheme 1), $BF_3 \cdot O(Et)_2$ was added to an equimolar ratio of furan and pentafluorobenzaldehyde in methylene chloride, under an inert atmosphere, and was stirred in the dark followed by oxidation with $FeCl_3$. After workup and column chromatographic purification, two different products, cyclo-hexa furans **1** and cyclo-octa furans **2**, were isolated in 2% and 1% yield (Supporting Information). An uncharacterizable blue band was also isolated during chromatographic purification.

Scheme 1
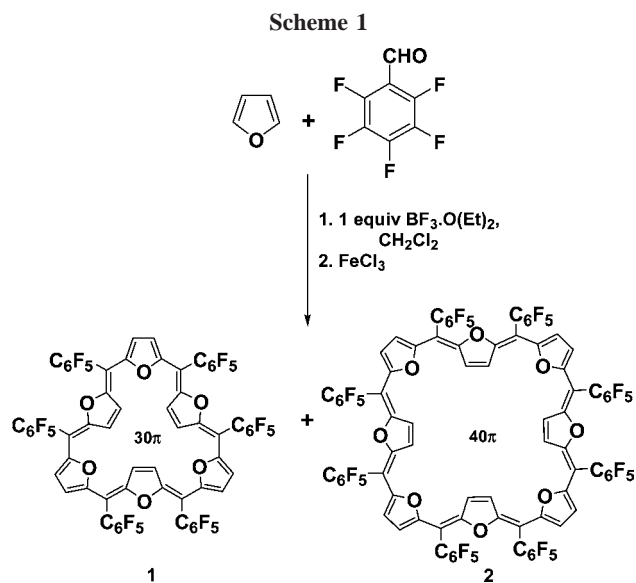
Varying the reaction conditions by long durations of stirring or by changing the acid catalysts did not have any profound effect on the yield of the products. The oxidation was successful only with $FeCl_3$, whereas other oxidizing agents such as chloranil or DDQ did not afford the conjugated macrocycles. Poor yields of the products formed can be attributed to the reduced reactivity of furan in comparison to pyrrole. Lack of formation of macrocycles with an odd number of furan subunits can be due to their unstable nature because they cannot form completely conjugated structures upon cyclization.[7]

1 and **2** represent unsaturated cyclic structures purely through an sp^2 carbon framework that bears a close resemblance to annulenes. **1** accounts for a formal 30π electron count in its conjugated pathway, and **2** is a 40π system. Because of their extensive conjugation, they absorb in the visible region of the electronic absorption spectrum (Figure 1). **1** exhibits a strong absorption at 551 nm followed by a
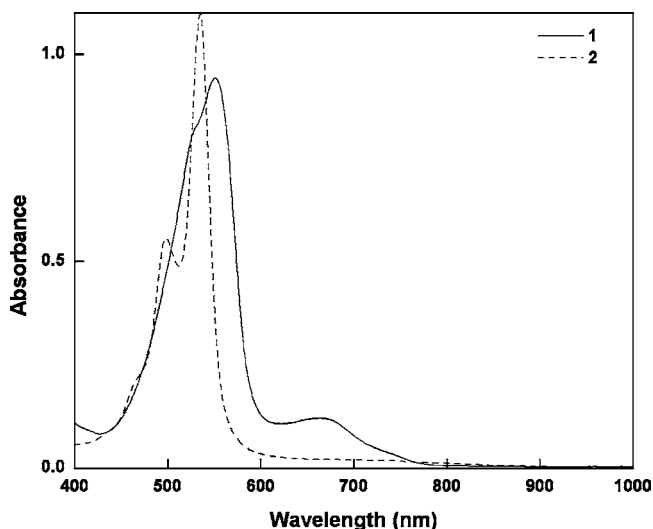
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Figure 1. Electronic absorption spectra of **1** and **2** ($\sim 10^{-6}$ M) in methylene chloride at room temperature.

weaker band at 663 nm. In spite of its extended conjugation, **2** exhibits absorptions at 535 nm and 498(sh) nm with no low-energy absorptions. The lack of a red shift in the absorption spectrum for **2** with respect to **1** reveals an antiaromatic character, as expected for a $4n\pi$ system. The molar extinction coefficients of both the macrocycles are comparable to 18π porphyrin systems, indicative of strong absorption in the visible region. Protonation of macrocycles **1** and **2** could not be observed upon addition of trifluoroacetic acid, as evidenced by no change in their absorption spectra.

^{1}H NMR spectra revealed a symmetrical structure for both **1** and **2**. In the case of **1**, two singlets were observed at δ 7.85 and 2.5 ppm corresponding to an equal number of (six) protons. Two discrete singlets are possible only if three rings are inverted in an alternate fashion such that the protons of the inverted and the noninverted furan rings are different from each other. Because **1** is a 30π system, the protons toward the center of the macrocycle experience diatropic ring current effects and are hence upfield shifted, whereas protons on the periphery are downfield shifted justifying the aromatic nature of the macrocycle. In a similar fashion, **2** displayed two singlets corresponding to an equal number of (eight) protons at δ 9.4 and 5.85 ppm. Such anisotropy in chemical shifts for $4n\pi$ expanded porphyrins has been reported in the literature.[8] The difference in the chemical shift values, $\Delta\delta$, for furan ring protons calculated from the ^{1}H NMR spectrum was found to be 5.35 and 3.55 for **1** and **2**, respectively. Neither molecule exhibited fluxional behavior, as studied by low-temperature measurements. The chemical shift values do not vary, and still two distinct singlets were observed even upon lowering the temperature to -40 °C (Supporting Information). This clearly illustrates the absence of any rotational dynamics as detected in *meso*-aryl sapphyrin.[9] The

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observation of two distinct singlets for **2** is possible only if the molecule is planar with a C_4 axis of symmetry. This was further confirmed from single-crystal X-ray analysis of **2** (Figure 2).[10]
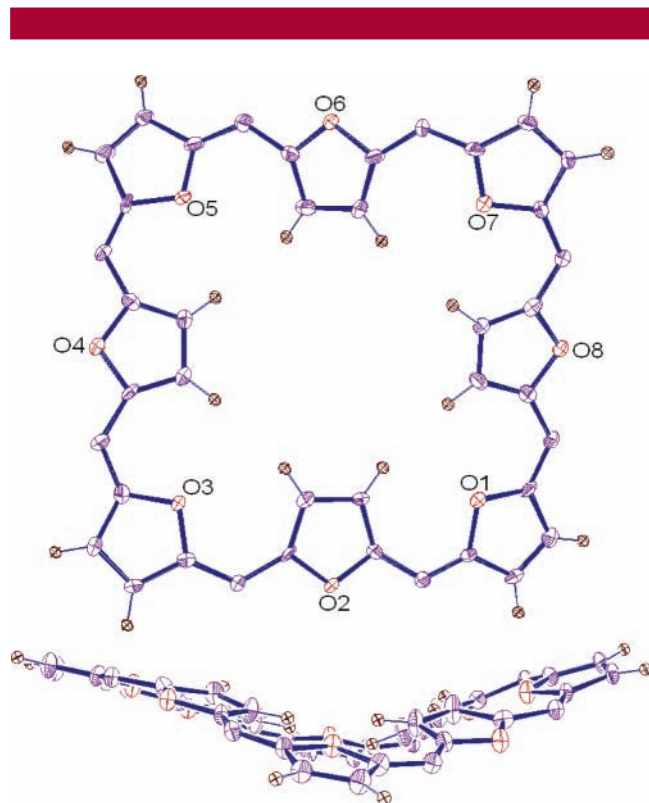

Figure 2. X-ray crystal structure of **2** with partial labeling. (Top) Front and (Bottom) side view. *meso*-Pentafluorophenyl rings are omitted for clarity. Thermal ellipsoids were scaled to 50% probability level.

The remarkable feature of the crystal structure lies in the near-planar conformation for a $(4n)$ 40π macrocycle. The shape resembles that of a square, with all the four sides having a length of 11.55 Å. The nontwisting of **2** can be attributed to the symmetrical multiple ring inversions which can reduce the bulk strain of the molecule. As seen along the molecular plane defined by the eight *meso*-carbons, it shows a deviation from the absolute planar conformation. The two arms that arise from the trifuran subunits ([O1, O2, O3] and [O5, O6, O7]), tend to come toward the center of the macrocycle. The angle between the two trifuran planes was found to be 40°. Carbon–carbon (C–C) bond lengths were in between single bond and double bond distances, with the maximum and minimum being 1.454 and 1.342 Å, respectively, substantiating the delocalization of π electrons. The distance between the oxygens of noninverted furans (O1, O3, O5, and O7) was found to be 7.5 Å. This distance is sufficient to accommodate two β-CH protons inside the macrocyclic core. A similar trend has already been observed in core-modified expanded porphyrins.[11]

Cyclic voltammetric studies were helpful to understand the ring current effects in both macrocycles. **1** showed a typical porphyrinoid-like voltammogram with two reversible oxidations and reductions, confirming its aromatic behavior. The Δ_{redox} calculated from the first oxidation and reduction potential was found to be 1.57 V. On the other hand, **2** exhibits only a single oxidation and reduction peak with a Δ_{redox} of 1.38 V. Cyclo-octa furans, **2**, represent a novel example of an expanded porphyrin, useful to study anti-aromatic planar $4n\pi$ systems.

In summary, we have described a one-pot synthesis of cyclo-hexa furan [1.1.1.1.1.1] and cyclo-octa furan [1.1.1.1.1.1.1.1]. **1** and **2** are the first examples of expanded porphyrins bearing six or eight furan subunits. To the best of our knowledge, **2** is the largest cyclic oligofuran system to be characterized in the solid state. Structural features in terms of four ring inversions in an alternate fashion in expanded porphyrins are reported for the first time. A similar synthetic methodology is being explored with other hetero-cyclic systems such as thiophene, selenophene, and *N*-methyl pyrrole.

Supporting Information Available: Experimental procedures and characterization including FAB-Mass, variable-temperature ^{1}H NMR, UV–vis, and cyclic voltammetric studies for **1** and **2**. CIF for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystals were grown by slow evaporation of *n*-hexane into a chloroform solution of **2**. Observation of several electron density peaks in the difference Fourier map indicated disordered solvent molecules. They were eliminated using the SQUEEZE/BYPASS program and ignored in further refinement cycles (Supporting Information). Crystallographic data of **2**: $C_{88}H_{16}F_{40}O_8$, M_w = 1961.01, monoclinic, space group *P*2(1)/*c* (No. 14), *a* = 16.871(5) Å, *b* = 22.045(6) Å, *c* = 22.462(6) Å, β = 103.148(6)°, *V* = 8135.0(4) Å,[3] *Z* = 4, D_{calcd} = 1.601 g/cm^{-3}, *T* = 125 K, R1 = 0.1468, wR2 = 0.1934 for all data, R1 = 0.0995, wR2 = 0.1754 for 14 846 observed data ($I > 2\sigma(I)$) for 1225 parameters.

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