N-Confused Expanded Porphyrin: First Example of a Modified Sapphyrin with an Inverted N-Confused Pyrrole Ring

Simi K. Pushpan,[†] Alagar Srinivasan,[§]
Venkataramanarao G. Anand,[†] Sundararaman Venkatraman,[†]
Tavarekere K. Chandrashekar,*[,†] Bhavani S. Joshi,[||]
Raja Roy,[||] and Hiroyuki Furuta[§]

Department of Chemistry, Indian Institute of Technology Kanpur, India- 208-016
NMR Division, Central Drug Research Institute Lucknow, India
Department of Chemistry, Graduate School of Science Kyoto University, Kyoto 606-8502, Japan

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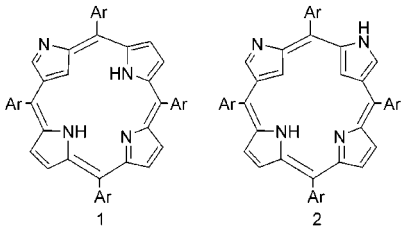
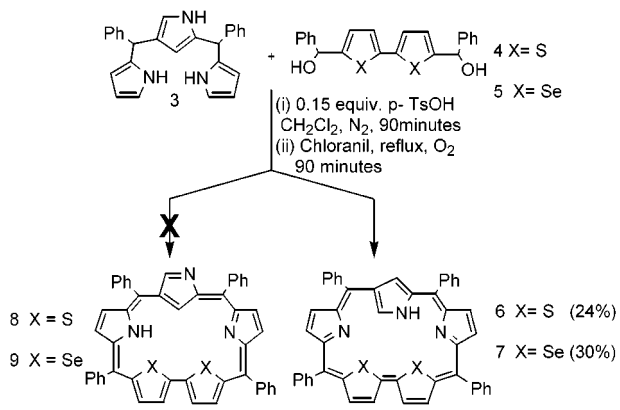
Research on synthesis of porphyrin isomers has gained momentum since the discovery of porphycene[1] by Vogel and co-workers and N-confused porphyrin[2] independently by Furuta et al. and Latos-Grazynski and co-workers. The other porphyrin isomers reported to date include, corrphycene,[3] hemiporphycene,[4] and isoporphycene[5] obtained by shuffling the four pyrrolic subunits and *meso*-carbon bridges. Extensive studies on N-confused porphyrin **1**[2] and doubly N-confused porphyrin **2**[6] have witnessed unusual metalation chemistry leading to the formation of a metal−carbon bond inside the porphyrin cavity, stabilization of unusual oxidation states of metals, and the existence of different tautomeric forms.[2a,6−8] Expanded porphyrins[9] bearing N-confused



pyrrole can not only complex 4d and 5d metals but also offer larger cavities for the formation of metal−carbon bonds. To the best of our knowledge there are no reports in the literature on the synthesis of expanded porphyrins bearing an N-confused ring. Herein, we wish to report the first successful synthesis of stable, aromatic modified sapphyrins bearing an N-confused pyrrole ring exhibiting an inverted structure.

Scheme 1



The first N-confused porphyrin was isolated as a side product in the Rothemund reaction.[2] We have recently reported rational syntheses of modified N-confused porphyrins by a 3+1 methodology incorporating an N-confused moiety as a part of the precursor.[8] We realized that a similar strategy could be used for the synthesis of N-confused sapphyrin by a 3+2 MacDonald-type condensation. Thus, condensation of 5,10-diphenyl-8-aza-16-carba-5,10,15,17-tetrahydrotripyrrane **3**[10] with 5,5′- bis (hydroxymethylphenyl)-2,2′-bithiophene **4**[11] in presence of 0.15 equiv of *p*-toluene sulfonic acid (*p*-TsOH) followed by chloranil oxidation gave **6** instead of expected **8** in 24% yield after chromatographic purification (**7** was isolated in 30% yield, instead of expected **9**, Scheme 1). It was observed that the concentration of the acid catalyst was very crucial for the formation of the desired N-confused sapphyrin.On increasing the acid concentration beyond 0.5 equiv tetrathia/tetraselena rubyrin was formed at the cost of the modified N-confused sapphyrin due to the acidolysis of precursor **3**.[11] The UV−vis spectra recorded for the compounds **6** and **7** in its freebase form shows that the Soret band was red-shifted by 14 and 8 nm, respectively, with respect to the normal dithia and diselena sapphyrin.[11] On protonation further redshifts of 12 and 16 nm, respectively, is consistent with changes observed in N-confused porphyrin on protonation.[8]

The first clue for the inversion of the N-confused pyrrolic ring came from the observed chemical shifts for the α- and *β*-CH signals of N-confused ring in the shielded and deshielded region, respectively. For example, these protons resonate at 2.73 and 9.79 ppm at 228 K for **6**. The pyrrole proton which resonates as a broad signal at 5.14 ppm (assigned on the basis of observed correlation in ^{1}H−^{1}H COSY) is localized on the nitrogen of the N-confused ring. This observation is in contrast to that reported for N-confused porphyrins where the pyrrole proton was localized on the normal pyrrole ring in the major tautomeric form.[8] The spectrum of **6** did not change upon recording the spectra in toluene-d_8 at 313 K, ruling out any ring inversion in high temperature. The $\Delta\delta$ values (difference in chemical shifts for *β*-CHs of inverted N-confused pyrrole moiety) of 7.06 and 8.79 ppm for the freebase and protonated forms of **6** suggests reduced aromaticity in **6** and **7** relative to all aza-*meso*-tetraaryl sapphyrin. Furthermore, the protonation does not lead to the dramatic 180° ring flipping observed for all aza-*meso*-tetraaryl sapphyrin.[12] The inner NH signals (26 and 28 NH) on protonation resonate as a

[†] Indian Institute of Technology.
[||] Central Drug Research Institute.
[§] Kyoto University.

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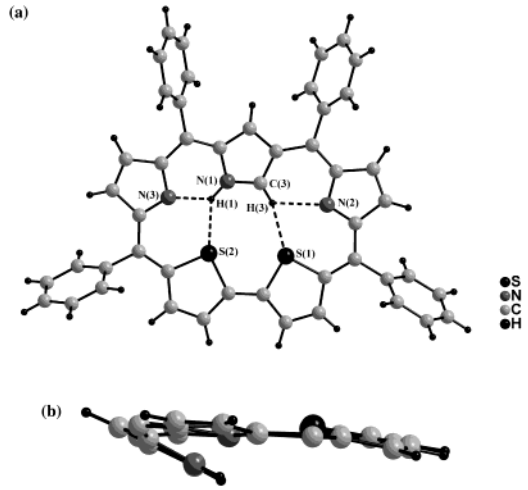

Figure 1. Crystal structure of **6**. (a) Top view (the dotted lines show the intramolecular hydrogen bonding); (b) side view showing the tilting away of the N-confused pyrrole ring from the plane of macrocycle (phenyl rings are omitted for clarity).

broad peak at −1.8 ppm at 298 K but splits into two sharp singlets at −1.57 and −2.08 ppm with intensity ratio 1:1 at 228 K, suggesting the inequivalence of these protons. The other protons for both freebase and the protonated derivative were assigned unequivocally with the help of 2D COSY (^{1}H−^{1}H), HMBC, HMQC, and NOESY.[13] The correlation observed between 13-CH of confused pyrrole and the inner 28-NH, 12-NH, and 26-NH in the protonated form further confirms the assigned structure.

Final confirmation of the inverted structure came from the single-crystal X-ray analysis of **6** (Figure 1).[14] The structure indicates that N-confused pyrrole opposite the bithiophene unit is inverted and makes a dihedral angle of 25.17° with respect to the mean plane containing four *meso* carbons. Four *meso* carbons are almost planar (deviations from the mean plane shown by *meso* carbons are C(5) 0.03, C(10) −0.02, C(20) 0.02, and C(24) −0.03 Å). The dihedral angles for the other heterocyclic rings are 5.03°, 7.7°, 3.07°, and 4.76°. These angles are comparable to that of normal modified sapphyrin reported earlier.[11] There are two independent molecules present in the asymmetric unit cell, and a closer look into the packing revealed the presence of inter- and intramolecular hydrogen bonds. Specifically there are four intramolecular hydrogen-bonding interactions in each molecule involving C−H···N (2.82 Å, 110.57° and 2.74 Å, 112.93°), C−H···S (3.35 Å, 121.42° and 3.38 Å, 120.25°), N−H···N (2.69 Å, 114.74° and 2.8 Å, 111.54°) and N−H···S (3.36 Å, 120.47° and 3.35 Å, 122°), giving rise to an eight-membered ring in chair conformation. A further closer look at the packing diagram reveals the presence of two types of intermolecular hydrogen bonds:[15] (a) one β-CH of the thiophene ring of one molecule with one of the core nitrogens of the pyrrole ring of the other molecule present in the unit cell (3.42 Å, 113.78°), (b) the aromatic CH group of the *meso*-phenyl ring are involved in hydrogen bonding with the heteroatom (S/N) present in the core of the other molecule(C(36)−H(21)···S (3) 3.94 Å, 164.29°; C(80)−H(48)···S(1) 4.03 Å, 154.57°; C(26)−H(12)···N (2) 3.67 Å, 135.30°; C(96)−H(62)···N(6) 3.36 Å, 121.24°). These interactions are responsible for holding the molecule in a supramolecular array[16] (refer to the Supporting Information for the complete structure). The torsion angle involving C(23)−C(24)−C(1)−N(1) is 12.5° and C(23)−C(24)−C(1)−C(2) is −160.1° for one molecule, while the similar torsion angles for the other is 15.8° and −163.4°. The differences in two types of pyrrole rings (confused and normal) are also reflected in bond distances; the $C_\alpha-C_\beta$, $C_\beta-C_\beta$ distances of confused pyrrole ring are significantly lower and higher, respectively, than those of normal pyrroles present in the macrocycle, suggesting the modified electron delocalization pathway.[17] The aromatic nature of **6** was evident from the observation that $C_\alpha-C_\beta$ is greater than $C_\beta-C_\beta$ distances (1.46 Å vs 1.35 Å for one pyrrole ring).

The sapphyrin **6** reported here undergoes two quasi-reversible reductions and two irreversible oxidations. Comparison of **6** with modified sapphyrins suggests that it is easier to reduce than others by about 100 mV, and the Δ_{redox} value 1.49 V explains the red-shift in the absorption spectra and again ascertains the aromaticity of the compound. The Δ_{redox} value for **7** is 1.45 V, which explains its red-shift in absorption spectra with respect to **6.** The triplet lifetime of **6** in its freebase and protonated form was found to be 0.13 and 0.36 μs. Upon protonation, the triplet excited-state absorption bands were red-shifted compared with the freebase form which can be explained by invoking the resonance participation of triplet spin density on the sapphyrin π-plane with the *meso*-substituted phenyl rings. The short-lived triplet suggests that the rate of internal conversion from the singlet excited state is much more efficient in this compound compared to that in the sapphyrin dication. The preliminary spectroscopic studies on **6** and **7** indicate that they bind metals in free base form and anions in its protonated state. Thus, in conclusion, we have successfully synthesized the first N-confused modified sapphyrin and have shown that these molecules are stable and aromatic and display an inverted structure in both freebase and protonated form.

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Supporting Information Available: Table 1 shows all ^{13}C and ^{1}H chemical shift values of freebase and protonated forms of **6**; the numbering, COSY, NOESY, HMBC, and HMQC correlation (S1);^{1}H NMR at 298 and 228 K, ^{1}H−^{1}H COSY, NOESY, HMQC, and HMBC for **6** (S2−S5); UV−vis spectra for **6** and **7** (S6); CV for **6** and **7** (S7); mass spectra for **6** and **7** (S8); crystal packing diagram of **6** showing the intermolecular hydrogen bonding (S9); intramolecular hydrogen bonding leading to eight-membered chair conformation (S10); triplet absorption spectra for **6** ((S11); crystallographic information files (CIF) for compound **6** and experimental procedure(S12) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) X-ray data of **6** (23 °C): violet prismatic, $C_{48}H_{31}N_3S_2$, MW = 713.91, triclinic, space group *P*-1 (no. 2), a = 16.9197(7) Å, b = 19.477(1) Å, c =12.7815(5) Å, α = 96.889(2)°, β = 101.353(5)°, γ = 75.100(9)°, V = 3980.1(4) Å^3, Z = 4, D_{calcd} = 1.191 g/cm^3, R = 0.075, R_w = 0.124, GOF = 0.44. In the unit cell, two pairs of enantiomers were present, and the analysis of electron density map clearly indicated the location of N in the confused ring. The positions of N(1) and C(3) of **6** were unambiguously determined by the peak heights obtained from the Fourier synthesis.

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