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A Porphyrin with a C=C Unit at Its Center

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Supporting Information

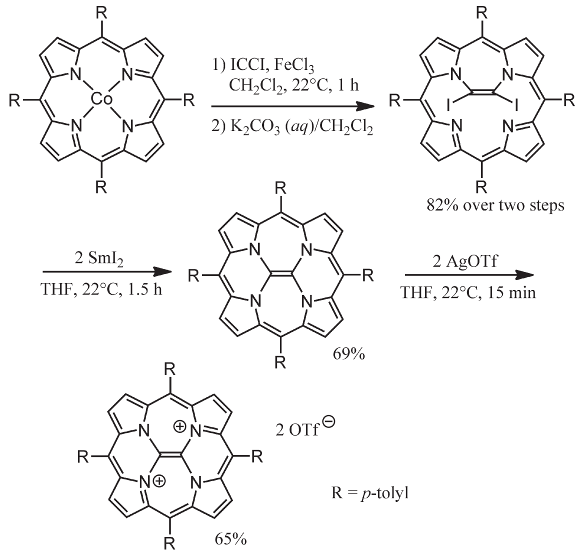
ABSTRACT: The molecule (C=C)TTP (TTP = tetra-*p*-tolylporphyrin) and the triflate salt of its dication, [(C=C)TTP][OTf]$_2$, have been synthesized and characterized. NMR spectroscopy, nucleus-independent chemical shift calculations, and the crystal structure of (C=C)TTP indicate that (C=C)TTP is antiaromatic and (C=C)TTP^{2+} is aromatic.

Porphyrin complexes of nearly every metal in the periodic table have been prepared,[1,2] as have complexes of several main-group metalloid and nonmetallic elements.[3,4] The predefined size of the four-nitrogen coordination sphere of the porphyrin ring system sets a lower limit on the covalent radius of an atom that can form a porphyrin complex in the usual manner, with all four nitrogen atoms bonded to that central atom. Silicon and phosphorus seem to be near this lower limit on the covalent radius, as many silicon[5−9] and phosphorus[10,11] porphyrin complexes are known, but in many cases the porphyrin ring system is ruffled to accommodate these small central atoms.[12] Porphyrin complexes with even smaller atoms (specifically, boron and carbon) bonded to nitrogen have been synthesized; in those compounds, however, an individual boron or carbon is bonded to only one or two nitrogen atoms of the porphyrin, and usually there is more than one boron or carbon atom present. Examples include porphyrins that are methylated one, two, three, or four times at nitrogen (the last two being a cation and dication, respectively).[13−15] Other porphyrins with two nitrogens bridged by CH$_2$CH$_2$,[16] RC=CR′,[17−19] or various one-carbon moieties[20,21] are known. Recently, an N-confused porphyrin with a carbene carbon bridging a porphyrin nitrogen atom and a carbon atom has been synthesized.[22] Known boron-containing porphyrins generally have two boron atoms, each bonded to two nitrogen atoms and often with other heteroatoms (O, Cl, F) present.[23−29]

One reported porphyrin complex contains at its center a simple B−B unit with a boron−boron single bond and each boron bound to two nitrogens.[27] The existence and stability of that compound (in the absence of oxygen and water) suggests an intriguing synthetic target that contains at its center a C=C unit, whose size is similar to that of the B−B unit. Such a molecule would be a completely organic (containing only C, H, and N), conjugated, eight-fused-ring system. Herein we report the synthesis and characterization of (C=C)TTP (TTP = tetra-*p*-tolylporphyrin) and [(C=C)TTP][OTf]$_2$ (OTf = trifluoromethanesulfonate).

The synthetic route is shown in Scheme 1. Cobalt porphyrins [Co(porph)] are known to react with alkynes (RC≡CR′) and an oxidizing agent to yield (RC=CR′)porph(H)$^+$, where the two carbon atoms of the alkene moiety are bonded to two adjacent nitrogen atoms of the porphyrin and one other nitrogen is protonated.[18,19] We found that the reaction of CoTTP with IC≡CI in CH$_2$Cl$_2$ with FeCl$_3$ as an oxidant yielded (IC=CI)TTP(H)$^+$Cl$^-$ after workup with HCl(aq). After chromatographic purification and recrystallization of (IC=CI)TTP(H)$^+$Cl$^-$, deprotonation with K$_2$CO$_3$(aq) to give (IC=CI)TTP was straightforward. Attempts at thermal or photolytic conversion of (IC=CI)TTP to [(C=C)TTP][I]$_2$ were made, but none were successful. Reduction of (IC=CI)TTP with 2 equiv of SmI$_2$ in THF gave (C=C)TTP. Oxidation of (C=C)TTP with 2 equiv of AgOTf in THF yielded [(C=C)TTP][OTf]$_2$.

Scheme 1. Synthesis of (C=C)TTP and [(C=C)TTP][OTf]$_2$



Crystals of (C=C)TTP were grown by slowly cooling a hot heptane/toluene solution. Single-crystal X-ray diffraction revealed the structure shown in Figure 1.[30] There was some disorder in the structure: in ∼11% of the molecules, the central C=C unit is turned 90° relative to the orientation shown in Figure 1. Only those two disordered carbon atoms were refined (isotropically) as separate atoms with partial occupancy, and they are not shown in Figure 1 [see the Supporting Information (SI) for a figure that includes the two carbon atoms with 11% occupancy]. The rest of the molecule in the minor orientation largely overlaps with the major orientation shown, so the structure was refined with 100% occupancy of the remaining major-orientation atoms. The orientations of the displacement ellipsoids of the nitrogen atoms are consistent with the presence of a fraction of the molecules in the second orientation described.

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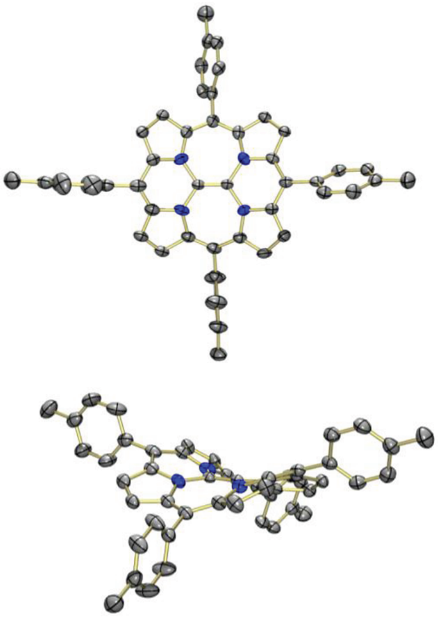

Figure 1. Two views of the structure of (C═C)TTP as determined by single-crystal X-ray diffraction. C atoms are shown in gray and N atoms in blue; H atoms are not shown.

There is a fairly significant ruffling of the porphine core of (C═C)TTP, as shown in the lower image in Figure 1. The mean deviation of the four *meso*-carbons from the N_4 plane is 0.84 Å. A structurally optimized [Gaussian 09,[31] B3LYP/6-31+G(d)] model of (C═C)porphine (in which the *p*-tolyl groups are replaced by H atoms) adopted a similarly ruffled structure, with a 0.86 Å mean deviation of the *meso*-carbons from the N_4 plane. The C═C unit is fairly small for an entity at the center of a porphyrin, even in comparison with the single metal atoms that are usually present in porphyrin complexes, and that small size is the cause of the ruffling in (C═C)TTP.[12]

Figure 2 shows the bond lengths from the crystal structure along with the calculated bond lengths for (C═C)porphine. There are alternating C−C single and double bonds along the 20-atom periphery of the porphine ring system, as indicated in the valence-bond representation of Figure 2. The average differences between the lengths of single and double bonds are 0.050 Å for $C_\beta-C_\beta$, 0.049 Å for $C_\alpha-C_\beta$, and 0.065 Å for $C_{meso}-C_\alpha$. The structure is not in resonance with the equivalent representation in which the outer C−C single and double bonds have been interconverted because the porphine core of (C═C)-TTP is antiaromatic. A similar bond-length alternation has been observed in Si(TPP)$(THF)_2$ (TPP = tetraphenylporphyrin),[9] Ge(TPP)$(pyridine)_2$,[32] and (B−B)TTP.[27] In each of those complexes, the central atom (or pair of atoms for the B−B complex) is formally in the 4+ oxidation state. The remainder of the porphyrin ring system is in the 4− oxidation state and therefore has been reduced by two electrons relative to the usual 2− oxidation state. A standard porphyrin is aromatic and contains an 18-π-electron system, as highlighted in blue for the (C═C)-porphine^{2+} cation in Figure 3. When the porphyrin ring system is reduced by two electrons, one would expect an antiaromatic 20-π-electron system to be formed, and that 20-π-electron circuit in (C═C)porphine is highlighted in blue in Figure 3.

Cyclic voltammetry of (C═C)TTP in THF with 0.10 M $[NBu_4][PF_6]$ as the supporting electrolyte showed four reversible one-electron waves at −0.26, −0.59, −1.91, and −2.17 V vs ferrocene$^{+/0}$ ($Fc^{+/0}$). The waves at −0.59 and −0.26 V are presumably due to oxidation of (C═C)TTP to its cation and dication, respectively, while the waves at −1.91 and −2.17 V are due to the reduction to the anion and dianion. Most metalloporphyrin complexes containing a redox-inactive metal (such as Zn or Mg) similarly undergo two reversible oxidations and two reversible reductions, with the redox occurring on the organic ring system of the porphyrin. However, oxidation of those metalloporphyrins to their radical cations occurs at about +0.4 V vs $Fc^{+/0}$,[33] while (C═C)TTP is oxidized at a potential about 1.0 V more negative. The easy oxidation of (C═C)TTP is unsurprising because the removal of two electrons converts it from an antiaromatic 20-π-electron system to an aromatic 18-π-electron system. In addition, the $N_2C{=}CN_2$ core of (C═C)TTP is the same as that of tetrakis(dimethylamino)ethene and other organic reducing agents.[34,35]

The dication (C═C)TTP^{2+} was synthesized and isolated as its triflate salt by oxidizing (C═C)TTP with 2 equiv of AgOTf. We were not able to grow crystals of $[(C{=}C)TTP][OTf]_2$ suitable for single-crystal X-ray diffraction, but density functional theory (DFT) calculations at the B3LYP/6-31G* or higher level have proven to give reliable predictions of the structures of (C═C)-TTP (see Figure 2) and other porphyrin complexes.[9,32,36,37] The calculated [Gaussian 09,[31] B3LYP/6-31+G(d)] structure of (C═C)porphine^{2+} is as ruffled as that of (C═C)TTP, with the *meso*-carbons displaced from the N_4 plane by an average of 0.84 Å, which indicates that the ruffling of (C═C)TTP is not primarily due to its antiaromaticity but is instead due to the small size of the C═C unit. The calculated bond lengths for (C═C)porphine^{2+} are shown in Figure 4. As expected for an

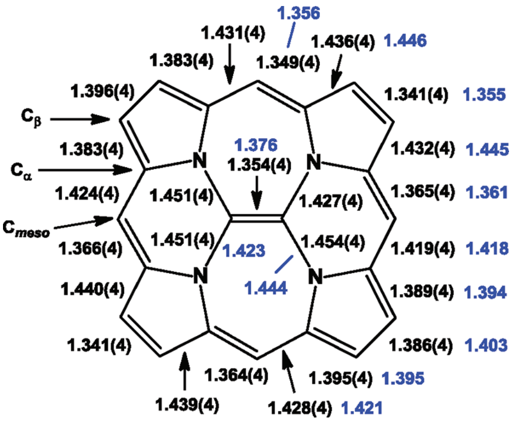

Figure 2. Valence-bond representation of the bonding in the porphine core of (C═C)TTP, with bond distances from the crystal structure shown in black and B3LYP/6-31+G(d)-calculated bond distances shown in blue.

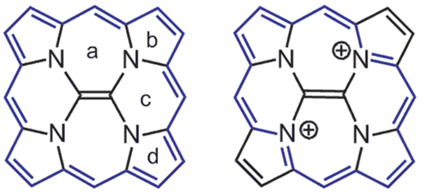

Figure 3. (left) Structure of (C═C)porphine, with its 20-π-electron circuit highlighted in blue. The letters a, b, c, and d indicate where NICS calculations were conducted. (right) One resonance structure of (C═C)porphine^{2+}, with its 18-π-electron circuit highlighted in blue.

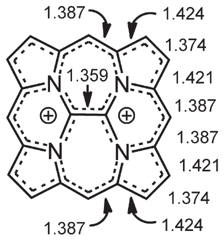

Figure 4. B3LYP/6-31+G(d)-calculated structure of (C═C)porphine^{2+}. Selected bond lengths are indicated.

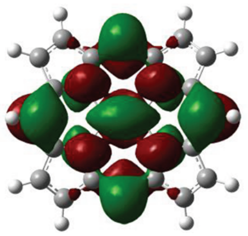

Figure 5. Calculated HOMO of (C═C)porphine^{2+}.

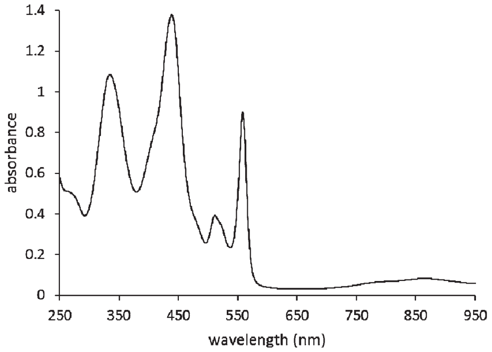

Figure 6. UV−vis−NIR absorption spectrum of [(C═C)TTP][OTf]$_2$ in CH$_2$Cl$_2$, showing λ_{max} values of 335, 439, 512, 559, and 864 nm.

aromatic porphyrin, there is no alternation of C−C single and double bonds of the type observed in (C═C)TTP. The point group of (C═C)porphine is C_2, while that of (C═C)porphine^{2+} is C_{2v}.

A comparison of the NMR spectra of (C═C)TTP and [(C═C)TTP][OTf]$_2$ provides further evidence for the antiaromaticity of (C═C)TTP and aromaticity of (C═C)TTP^{2+}. A strong magnetic field induces a diatropic ring current in an aromatic compound, leading to the familiar downfield shift of the resonances for nuclei outside the ring and upfield shift for nuclei inside the ring. In an antiaromatic compound, a paratropic ring current is induced, and the effects on the chemical shifts are in the opposite direction.[38] The effects are clearly evident in the ^{1}H NMR resonances of the β-pyrrole protons of [(C═C)TTP][OTf]$_2$ and (C═C)TTP. In a typical (diamagnetic and aromatic) porphyrin complex, the β-pyrrole protons resonate at ~9.0 ppm. In [(C═C)TTP][OTf]$_2$, they are slightly downfield at 9.44 and 9.47 ppm, perhaps as a result of the positive charge on the molecule. In contrast, the β-pyrrole protons of (C═C)TTP resonate far upfield at 2.38 and 2.67 ppm, indicating a paratropic ring current in its porphine core. All of the ^{13}C resonances of both compounds were assigned through a combination of multidimensional experiments (see the SI for full assignments). Of most interest are the two central carbon atoms. In (C═C)TTP their chemical shift is 135.43 ppm, and in [(C═C)TTP][OTf]$_2$ they resonate at 102.57 ppm. The positive charge on (C═C)-TTP^{2+} should shift the central ^{13}C resonance to lower field (higher chemical shift), but it is instead 33 ppm upfield of the resonance for neutral (C═C)TTP. A diatropic ring current in (C═C)TTP^{2+} and a paratropic ring current in (C═C)TTP would explain the chemical shifts.

Nucleus-independent chemical shift (NICS) calculations provide a computational measure of ring currents.[39] NICS values are commonly calculated at or near a ring center, but NICS(1) measurements (in which the calculation is done 1 Å "above" a ring centroid) are a better reflection of the magnitude of a paratropic or diatropic ring current.[40] We performed NICS(1) calculations [B3LYP/6-31+G(d)] for both (C═C)porphine and (C═C)porphine^{2+} at the ring centroids denoted a, b, c, and d in Figure 3. Because the two sides of the ring (above and below) are inequivalent, calculations were performed both 1 Å above and 1 Å below the ring system for each position, and the results were averaged. For (C═C)porphine, the NICS(1) values at a, b, c, and d were 38.5, 19.2, 25.1, and 15.6, respectively, and those for (C═C)porphine^{2+} were −13.6, −13.8, −16.2, and −13.7, respectively. Those results are consistent with a paratropic ring current and antiaromaticity in (C═C)porphine and a diatropic ring current and aromaticity in (C═C)porphine^{2+}.

The standard model of porphyrins as aromatic 18-π-electron systems explains the aromaticity of (C═C)TTP^{2+} and the antiaromaticity of (C═C)TTP if the π-electron circuits highlighted in blue in Figure 3 are considered. That 18-π-electron model for aromatic porphyrins is also consistent with the antiaromatic 20-π-electron circuit present in doubly reduced porphyrins such as Si(TPP)(THF)$_2$[9,27,32] and the antiaromatic 16-π-electron circuit present in doubly oxidized porphyrins.[37,41] However, Hückel's (4n + 2)-π-electron rule for aromaticity was formulated for monocyclic systems,[42] and some caution may be warranted when applying it to polycyclic systems such as porphyrins.[43] Also, the π electrons from the N atoms are left uncounted in the blue circuits of Figure 3, although they would add either four or eight π electrons and leave the predicted aromaticity or antiaromaticity unchanged. In the (C═C)-containing porphyrins there are two additional π electrons that, if counted, would reverse the predicted aromaticity/antiaromaticity of the porphyrin. For that reason, at the start of this project it was not obvious which oxidation state of (C═C)TTP would be aromatic, and in fact, the calculated HOMO of (C═C)porphine^{2+} (Figure 5) looks much like the HOMO of Zn(porphine)[44] with an additional component on the central C═C π bond. Nevertheless, the standard rubric of aromaticity in porphyrins due to an 18-π-electron system seems to apply to (C═C)TTP^{2+}.

While (C═C)TTP^{2+} contains the nominal 18-π-electron circuit of an aromatic porphyrin, its overall electronic structure is fairly different from that of a metalloporphyrin such as ZnTTP (see the SI for more images of MOs and for MO energy-level diagrams). The UV−vis−NIR absorption spectrum of [(C═C)TTP]-[OTf]$_2$ is shown in Figure 6. It differs markedly from the spectra of standard porphyrins, which have an intense Soret absorption at ~420 nm and smaller Q bands between 500 and 650 nm.[45] The major changes in the spectrum are not due to the positive charge on (C═C)TTP^{2+}, since doubly protonated porphyrins such as H$_4$TPP^{2+} have a Soret band that is red-shifted by ~20 nm relative to H$_2$TPP and Q bands with some changes in intensity.[46] Nor is the ruffling of (C═C)TTP^{2+} the cause of the unusual spectrum, as ruffling simply causes some red-shifting of both the Soret and Q bands of metalloporphyrins and free-base porphyrins.[47] The spectrum of $[(C{=}C)TTP][OTf]_2$ does bear some resemblance to that of $(ClB{-}BCl)TTP$,[27] which implies that it is the interaction of these two-atom central units with the π system of the porphyrin that leads to the multiple high-absorptivity peaks in their spectra.

In conclusion, a metalloporphyrin complex has been transformed into a new fused polycyclic organic molecule containing only carbon, hydrogen, and nitrogen. The compound $(C{=}C)TTP$ can be isolated as either an antiaromatic neutral molecule or an aromatic dication. The relatively small perturbation of replacing the typical single metal atom or two hydrogen atoms at the center of a porphyrin with a C=C unit results in a significant change in the molecule's electronic structure.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthetic, spectroscopic, and crystallographic details; selected NMR spectra; a CIF for $(C{=}C)TTP$ and an image of its structure with disordered carbon atoms; MO diagrams and images for $(C{=}C)TTP$ and $(C{=}C)TTP^{2+}$; and complete ref 31. This material is available free of charge via the Internet at http://pubs.acs.org.

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