An All-Organic Porphyrin and its Properties

Significance: Reaction of cobalt porphyrin 1 with diiodoacetylene in the presence of FeCl₃ followed by treatment with K₂CO₃ affords compound 2, which is reduced with SmI₂ to form porphyrin 3. Characterization of this neutral C=C porphyrin reveals alternating single and double C–C bonds, owing to the antiaromatic properties of the compound. Further, cyclic voltammetry measurements indicate an easy oxidation of 3 to its dicationic, 18π-electron aromatic form. Chemical oxidation of 3 in the presence of AgOTf affords ionic species 4. NMR measurements and DFT calculations confirm the aromatic character of 4, that does not possess alternating single and double C–C bonds.

Comment: Although the typical aromatic character of porphyrins is preserved in compound 4, its electronic structure significantly differs from that of classical metalloporphyrins. In particular, the UV/Vis absorbance spectrum of 4 features several intense bands where the single Soret band is usually observed for porphyrins. Such properties make this new type of porphyrins of potential interest for light-harvesting systems.

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