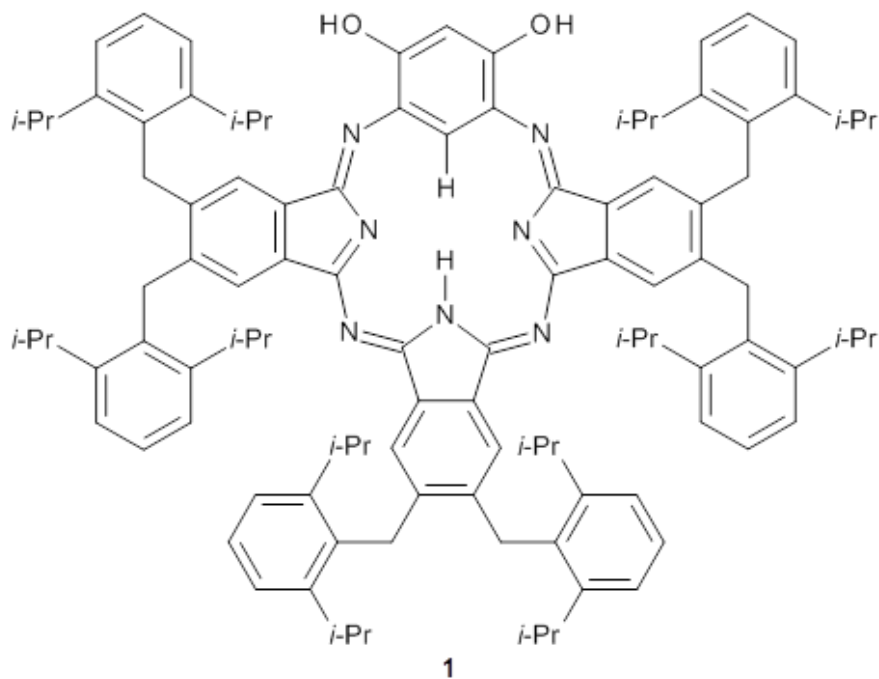
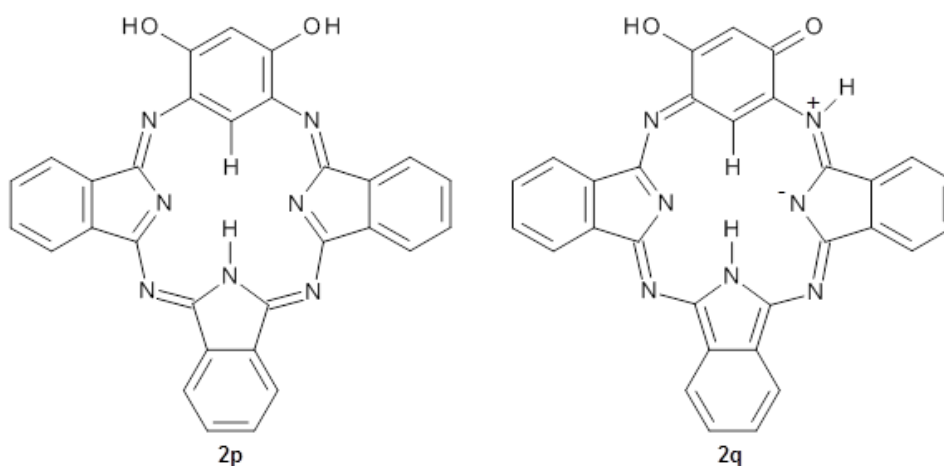


8 π -ELECTRON TAUTOMERIC BENZIPHTHALOCYANINE: A FUNCTIONAL NEAR-INFRARED DYE WITH TUNABLE AROMATICITY

Muranaka and Uchiyama have prepared an 18 π -electron system that exhibits variable aromaticity in its tautomeric forms.¹ The synthesized benziphthalocyanine **1** shows upfield resonances in the ¹H NMR for the internal hydrogens: 1.89 ppm for the C-H proton and 4.67 ppm for the N-H proton. This indicates some weak diatropicity.



To address this interesting magnetic property, they reported B3LYP/6-31+G(d) computations on the model system **2** in its phenol **2p** and quinoidal **2q** tautomeric forms.



The optimized structures are shown in Figure 1. The phenol form **2p** has NICS(0) and NICS(1) values of -6.77 and -6.04 ppm, respectively, indicating only modest aromaticity. However, the NICS values for the quinoidal form **2q** are much more negative, -11.43 (NICS(0)) and -10.10 (NICS(1)) ppm, indicating a more significant aromatic character. The calculated chemical shift of the internal C-H is most telling: for **2q** it is -4.55 ppm but for **2p** it is 0.97 ppm, in good agreement with experiment. Thus, **1** has an 18π -electron modestly aromatic periphery, with the phenol form dominant. There is no evidence of a 20π -electron periphery.

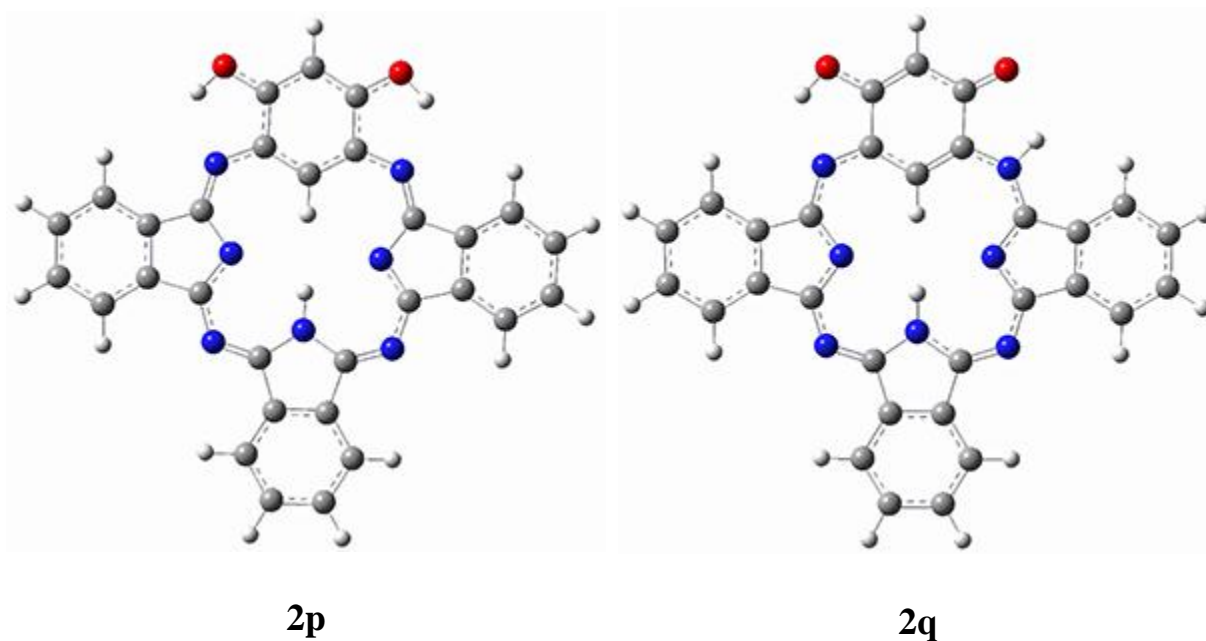


Figure 1. B3LYP/6-31+G(d) optimized geometries of **2p** and **2q**.

(Note that the supporting materials have a missing carbon in **2q** and I have made a guess at its proper location – so this is not quite the optimized structure! Once again, a statement about the quality of SI!)

Source: <http://www.compchemhighlights.org/2014/09/8-electron-tautomeric.html>