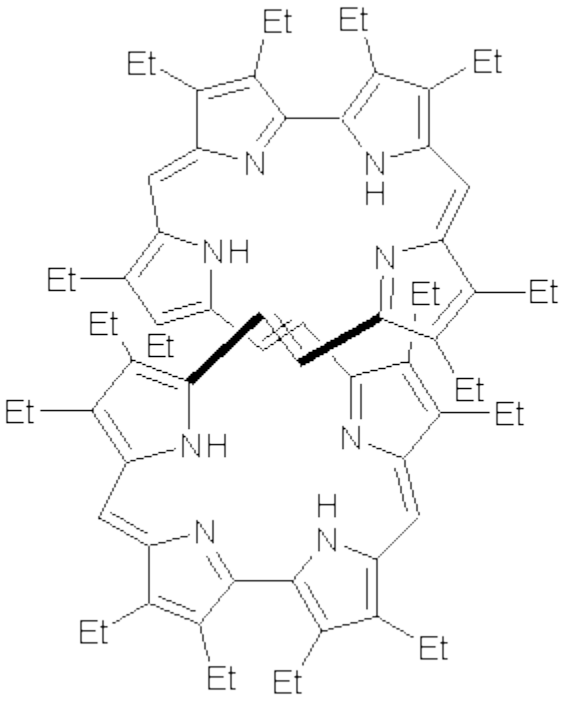
FANTASTIC OPTICAL ACTIVITY OF AN OCTAPHYRIN

The octaphyrin **1** has been prepared and its crystal structure and electronic circular dichroism (ECD) spectra reported.[1] The x-ray structure identified the compound as having the *M,M* helical structure. The optical rotation however could not be determined.



1

Rzepa now reports the computed ECD spectrum and optical activity of **1** and some related compounds.[2]

These computed spectra were obtained using TD0DFT with the B3LYP/6-31G(d) method with the CPCM treatment of the dichloromethane solvent. (The structure of **1** and other computed properties are available from the enhanced web table that Rzepa has deposited with the article. Once again this material seems to be available only to subscribers! My repeated discussions with ACS Pubs people that these "web objects" should be treated as data and not as copyrighted materials have fallen on deaf ears.) The computed ECD spectrum matches nicely with the experimental one, except that the *signs at 570 and 620 nm are opposite*. Rzepa suggests that either the compound is really of *P,P* configuration or the authors of experimental work have erroneously switched their assignments.

The computed value of $[\alpha]_D$ of **1** is about -4000 °, with the negative sign in agreement with the sign for $[\alpha]_D$ of *M*-hexahelicene. However, what is truly fantastic is the magnitude of the optical activity of the dication of **1** produced by loss of 2 electrons. This dication should be aromatic and it is predicted to have $[\alpha]_{1000}$ = -31597°!

Source: http://comporgchem.com/blog/?p=349