

Assessing aromaticity using the Aromatic Ring Current Shielding method

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The Aromatic Ring Current Shieldings (ARCS) approach is a new method to determine the strength of the induced ring current which is related to the molecular aromaticity. In the ARCS method, the strength of the induced aromatic ring current and the size of the current ring are obtained from nuclear magnetic shieldings calculated in discrete points along a line perpendicular to the molecular plane starting at the center of the molecule. The induced ring currents have been used to determine the relative degree of aromaticity for molecules such as benzene, Al_4Li^- , Al_4Cu^- , hexadehydro[12]annulene, dodecadehydro[18]annulene and free-base porphyrin.

The calculations on free-base porphyrin show that it sustains a large diatropic ring current. We found that the pyrrole rings with an inner hydrogen has its own ring current which is about as large as the ring current for the pyrrole molecule. For the pyrrolic ring without an inner hydrogen its internal ring current is between half and one fourth of the pyrrole value. The ARCS and NMR shieldings for Al_4Li^- and Al_4Cu^- were calculated at the Hartree-Fock (HF) level, the second-order Møller-Plesset (MP2) level, the coupled-cluster singles and doubles (CCSD) level, and at the coupled-cluster singles and doubles level augmented by a perturbative correction for triple excitations (CCSD(T)). The NMR shieldings show that electron correlation is of great importance for these systems, but the ring current is almost independent of the correlation effects. The ARCS calculations show that these species can sustain large diatropic ring currents, and hence should be considered aromatic. The ARCS calculations on hexadehydro[12]annulenes and dodecadehydro[18]annulenes show that the unsubstituted dehydro[12]annulene sustains a paratropic ring current in an external magnetic field, and it can therefore be considered anti-aromatic, while the ring current for the unsubstituted dehydro[18]annulene is diatropic.

1. Jusélius J. and Sundholm D., *Ab initio* determination of the induced ring current in aromatic molecules, *Phys. Chem. Chem. Phys.*, **1**:3429-3435 (1999)
2. Jusélius J. and Sundholm D., The aromatic pathways of porphins, chlorins and bacteriochlorins, *Phys. Chem. Chem. Phys.*, **2**:2145-2151 (2000)
3. Jusélius J. and Sundholm D., The aromatic character of magnesium porphyrins, *J. Org. Chem.*, **65**:5233-5237 (2000)
4. Jusélius J. and Sundholm D., The aromaticity and antiaromaticity of dehydroannulenes, *Phys. Chem. Chem. Phys.*, (in press)