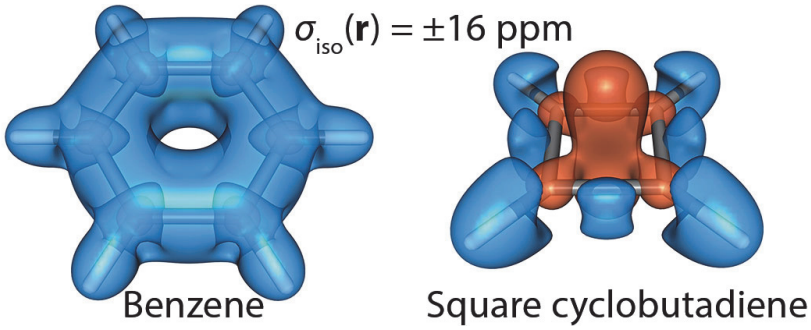
Magnetic Shielding as a Source of Information about Aromaticity, Antiaromaticity and Chemical Bonding

Peter B. Karadakov, Kate E. Horner

Department of Chemistry, University of York, UK

E-mail: peter.karadakov@york.ac.uk

It has been demonstrated [1, 2] that that the inclusion of nondynamic electron correlation effects through an appropriate complete-active-space self-consistent field CASSCF or multi-configuration SCF (MCSCF) wavefunction is essential for a balanced analysis of the magnetic properties of cyclic conjugated hydrocarbons, including nucleus-independent shieldings (NICS), and of their ground and excited state aromaticity and antiaromaticity. In fact, detailed analyses of the changes in the isotropic shielding $\sigma_{iso}(\mathbf{r})$ within the space surrounding a molecule, calculated using CASSCF wavefunctions, rather than of discrete NICS values such as NICS(0) and NICS(1), provide significant additional insights into the differences between aromatic, and antiaromatic molecules [3].



We show that the $\sigma_{iso}(\mathbf{r})$ isosurface and contour plots are significantly more feature-rich than analogous plots depicting the total electronic density which are usually employed to analyze chemical bonding and can be used to perform meaningful comparisons of strong and weak bonds. One important advantage of the $\sigma_{iso}(\mathbf{r})$ plots is that the isotropic shielding at any point in space close to a molecule 'senses' the behaviour of the electrons in all directions originating from that point, whereas the value of the total electronic density at a point carries no information about the density distribution in its surroundings, except that inferred by the fact that it is a smooth function.

[1] Karadakov, P.B., *J. Phys. Chem. A*, 112:7303–7309, 2008.
[2] Karadakov, P.B., *J Phys Chem A*, 112:12707–12713, 2008.
[3] Karadakov, P.B., Horner K.E., *J Phys Chem A*, 117:518–523, 2013.