

# NMR SHIFTS OF AROMATIC AND ANTIAROMATIC COMPOUNDS USING BLW

The chemical shift of the benzene proton is about 7.3ppm, significantly downfield from the range of olefinic protons (5.6-5.8ppm). This is rationalized as the standard induced diatropic ring current, found in aromatic species. But what should we make of the chemical shift of the protons in cyclobutadiene at 5.8 ppm? Shouldn't this be much further upfield?

Schleyer and Mo have applied the block localized wavefunction (BLW) technique to aromatic and antiaromatic chemical shifts.<sup>1</sup> In BLW, self-consistent localized orbitals are produced to describe a particular resonance structure. So, for benzene, BLW describes in effect 1,3,5-cyclohexatriene, lacking any resonance energy. When chemical shifts are computed with the BLW description, the proton chemical shift is 6.6 ppm, and is even more upfield if the geometry is optimized (in  $D_{3h}$  symmetry) with the BLW method ( $\delta=6.2$ ppm).

Furthermore the  $\text{NICS}(0)_{\pi_{zz}}$  (the tensor component corresponding to the perpendicular direction evaluated in the ring center using just the  $\pi$  orbitals) is -36.3 for benzene and 0.0 for the  $D_{3h}$  BLW variant, strongly indicating the role of cyclic delocalization in affecting chemical shifts.

Now for cyclobutadiene, the proton chemical shift of 5.7 ppm becomes 7.4 in the BLW case.  $\text{NICS}(0)_{\pi_{zz}}$  for cyclobutadiene is +46.9 and +1.6 in the BLW case. The problem is that typical alkenes are poor references for cyclobutadiene – when resonance is turned off, the chemical shift does move downfield – indicating the expected *upfield* shift for cyclobutadiene. Schleyer and Mo suggest that 3,4-dimethylenecyclobutene is a more suitable reference; its ring protons have chemical shifts of 7.65ppm.

They also describe computations of benzocyclobutadiene and tricyclobutenabenzene and offer straightforward rationalizations of their aromatic vs. antiaromatic behavior.

Source: <http://comporgchem.com/blog/?p=853>