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Aromatic Ring Current Shifts: Implications for Conformations in Presence of Local and Global Torsional Motions With Respect to a Site in Macromolecules

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The aromatic ring current shifts are useful in certain contexts to infer the proton locations with respect to the aromatic ring present at a specified site within a biological macromolecule. But, there have been ambiguities in applying this method when it was found that the procedure and equations can be applied for using the calculated ring current shift values on the basis of the geometrical specifications. Since in solid crystals only fixed orientations are encountered, the sensitivity of the isotropic ring current shifts can be good enough by taking into consideration the possible range of variations in torsional angles. But, if it has to be applied in solution state the considerations are different due to the fact that there should be an explicit averaging of shift values corresponding to the displacements during torsional motions.

Considering the uncertainties reportedly encountered in such contexts, an effort is being made to find out the possibility of improving the efficacy of the ring current shift applications by calculating the full tensor form of the aromatic ring current shifts instead of using the equations given for the isotropic values of the ring current shifts.

1. One of the striking instance of possible improvement would be due to the fact that, the isotropic shifts are non zero only if the susceptibility tensor is anisotropic (-49×10^{-6}) as in the case of Aromatic Ring. There could be similar contributions also from other groups but with *"much less anisotropy"* whose contributions to isotropic shift values would be negligible. This is the reason always aromatic ring current is considered predominantly to contribute by the "through space" magnetic dipole model.

It may be possible to find that the trace value range is much less than the range of variation of 'xx' component by the full tensor calculation. Thus the sensitivity can be better for fixing the coordinates. When the motions are not fast enough, then the isotropic "averaging" over all orientations may not be applicable. The isotropic shift equation requires that during the motion the proton position remains unchanged in the Aromatic Molecule Fixed coordinate axes system. If the proton is not in any way fixed by chemical bonding relative to the aromatic system but there is a relative motion of the aromatic frame work and the radial vector of the proton with respect to the six-fold symmetry axis of the aromatic ring, then the equations for isotropic average shifts are no longer relevant but by the full tensor equation can be subjected to appropriate coordinate transformations and the full shielding tensor can be calculated for the displacements under a torsional motion and after from the set of the full tensors calculated appropriate averaging can be effected..

A simplified "model" calculation would be presented for the case (i) when the radial proton vector is fixed with respect to the six fold symmetry axis (local motion) and for the case (ii) when the radial vector oscillates (global motion) with respect to the six fold symmetry axes to examin for the advantages of the calculation of Full Tensor over the only isotropic ring current shift values. *http://www.geocities.com/sankarampadi/ForIbs2006.html*