

AROMATIC RING CURRENT SHIFTS IN BIOLOGICAL MACROMOLECULES : GENERATING WEIGHT FACTORS FOR THE INSTANTANEOUS SHIFT VALUES FOR AN EFFECTIVE MOTIONAL AVERAGING

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By using the Full Tensor Form of the equation for the aromatic ring current shifts in the NMR spectra of Biological Macromolecules, it has been possible to show (1) that there are definite advantages of calculating the full shielding tensor for such cases of molecules in motion, rather than merely using the equations for the isotropic shift values. However, in the model calculation presented (2) equal weights were given for the shift values sampled at the several instantaneous dispositions during the motion while arriving at a average value. Based on the experiences till now on this type of approach, it is possible now to further investigate for the possible improvements that may result if one uses weight factors generated by specifying the characteristics of the motion and the nature of the shift dependences along the motional paths.

Conventionally, an oscillatory motion (torsion) is satisfactorily taken into account on the basis of the characteristics of Simple Harmonic Motion. In such a case it is also known that depending on the frequency of oscillation and the swing amplitudes, the resident time for the molecule at the equilibrium (mean) position is small compared to the times at the maxima for the amplitude. Hence the shift values at the extremes would be effective more than the shift values corresponding to the mean positions. Hence the weight factor must be more for the values corresponding to the extremes of oscillations than to that at the mean position. Such criteria if it gets built in to the averaging procedure, then the results could have better confidence indices. An approach of this type would be illustrated and to what ever extent possible a comparison with the approaches as in Reference (3) would be presented.

REFERENCES :

1. <http://www.geocities.com/sankrampadi/Forlbs2006.html> Poster Sheet 11: A specific hypothetical case of how the Tensor Form can be useful when the isotropic values cannot be indicative of the motional state of the system. And further results as captions for graphical plots in the subsequent sheets. This sheet contains the main conclusions which resulted from the Calculations made at this instance of IBS2006
2. <http://www.geocities.com/sankarampadi/Forlbs2006.html> Poster Sheets 10 & 11
3. "Fluctuations and Averaging of Proton Chemical Shifts in the Bovine Pancreatic Trypsin Inhibitor", Jeffrey C. Hoch, Christopher M. Dobson, and Martin Karplus *Biochemistry* 21, 1118-1125 (1982)