

Investigating the Feasibility of Calculating Intramolecular Shielding Tensors Using a Magnetic Dipole Model

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The neighbour-group susceptibility anisotropy contribution to the shielding of a proton in molecules is well known.¹ This magnetic dipole model for the calculation of intermolecular contributions to the shielding tensor has proved to some extent, capable of restoring the intramolecular symmetry features to the experimentally observed proton shielding tensors in single crystals of organic molecules.² As a natural extension to the discussions reported³ earlier, the possibilities of calculating the shielding tensor of protons in molecules (intramolecular), from the available group or atom susceptibility tensor values, on the basis of the magnetic dipole model is reported here. For such a calculation it is only necessary to break up the molecules into such small fragments of groups or atoms so that each group or atom can have a susceptibility tensor with a dipole origin within the respective group or atom and the size of the groups are small compared to the respective distances of dipole origin to the proton so that the point-dipole approximation is reasonably valid and the fragmented groups susceptibility tensor when added, with proper consideration to the geometry of the total molecule and the constituent fragments, reproduce the total molecular susceptibility tensor measured experimentally. If the magnetic dipole model equation can be used to calculate shielding tensors from known susceptibility tensor values, then, in favourable cases the susceptibility tensors may be calculated for known shielding tensor values. Such a back and forth calculation of shielding tensor and susceptibility tensor values can pave the way to provide revealing measures to improve the respective abinitio theoretical procedures.

The above considerations are illustrated by calculating the full shielding-tensor of protons in benzene molecule.

The Z-axis of the molecular axes system points to the direction above the plane of the paper (perpendicular to the molecular plane) The Y-axis is along the C₁--H₁ bond pointing towards the proton from the centre of the molecule which is the origin of the coordinate system. X-axis is perpendicular to Z and Y direction and these form a right handed orthogonal system.

Consistent groups and their respective Susceptibility tensors

The benzene molecule's (total) experimental susceptibility tensor is diagonal in the above described molecular X,Y,Z axes system with three component values $\chi_{xx} = -35 \times 10^{-6}$ CGS units $\chi_{yy} = -35 \times 10^{-6}$ and $\chi_{zz} = -95 \times 10^{-6}$ CGS units.

From the available theoretical studies⁵ of the susceptibility anisotropy of aromatic systems the benzene molecule can be conveniently broken up into the following constituent groups for the various types of susceptibility contributions:-

(i) C-C bond σ contributions : 2.05×10^{-6} CGS units (χ_{\parallel}^{C-C}) along the C-C bond, 3.05×10^{-6} CGS units (χ_{\perp}^{C-C}) \perp to the C-C bond in the molecular plane, 3.05×10^{-6} CGS units \perp to the molecular plane and (χ_{\perp}^{C-C}) \perp to the C-C bond. Origin of the magnetic dipole due to the susceptibility of C-C bond is placed at the center of the C-C bond. There are 6 symmetry related C-C bonds in the benzene molecule. (ii) C-H bond σ contributions : $\chi_{\parallel}^{C-H} = 3.41 \times 10^{-6}$ CGS units, $\chi_{\perp}^{C-H} = 4.21 \times 10^{-6}$ CGS units - origin at the center of the C-H bond. There are 6 such C-H bonds. (iii) Carbon atomic diamagnetic isotropic susceptibility for each of the 6 carbon atoms is 9.35×10^{-6} CGS units. (iv) The localized Π contributions at each of the 6 carbon atoms (origin on the carbon atoms itself) have the principal axes system coinciding with the principal axes system for the C-H contributions with χ along C-H direction = 10.8×10^{-6} , $\chi \perp$ to C-H bond in the plane 7.9×10^{-6} and along the perpendicular to the plane -6.5×10^{-6} CGS units. (v) The delocalized Π electrons susceptibility contribution has non-zero only along the molecular perpendicular direction $\chi_{zz} = -33 \times 10^{-6}$ located at the centre of molecule. When each of these individual group contributions is transformed into the common molecular X,Y,Z system and the values are summed up the resulting molecular susceptibility tensor component values are comparable to experimental values. $\chi_{xx} = -34 \times 10^{-6}$, $\chi_{yy} = -34 \times 10^{-6}$, $\chi_{zz} = -89.0 \times 10^{-6}$.

Conclusion

At each proton in the benzene molecule 24 groups contributions to σ tensor can be calculated (for example for proton 1, the C_1-H_1 contributions are not calculated since the dipole approximation will not be valid) and diagonalized which results in principal axes system coinciding with the local C-H bond symmetry and component values respectively the same for each proton. σ along C-H = 1.89×10^{-6} σ (in plane \perp to C-H = -2.8×10^{-6} , $\sigma \perp$ to molecular plane = -12.9×10^{-6} . A rationalization of such calculated values with the reported experimental values indicating future necessary efforts would be dealt with. Due to a possible ambiguity in the numerical diagonalization program, the above assignment of shielding tensor components to the principal direction is being ascertained.

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