A FORMULA FOR THE NMR SHIELDING EFFECT OF A FREELY ROTATING MAGNETICALLY ANISOTROPIC GROUP

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More often than not in calculation of long-range contributions to the NMR shielding either a sufficiently exact equation is not available or more rigorous and elaborate calculations lead to results largely of an estimative nature because of inaccuracies in the available data. In the present paper a simple approximate formula is derived which with literature data yields as good estimates of the shielding effect of a freely rotating magnetically anisotropic group as a more complicated "exact" formula.

The magnetic shielding of a proton in a complex molecule is usually and conveniently regarded as being composed of several contributions. One of the long-range or neighbour atom contributions is that from the magnetic moment induced by the external magnetic field in a group G of electrons within the molecule but remote from a proton A. If the group magnetic molar susceptibility tensor is $\hat{\chi}^G$ then its shielding contribution σ_A^G in the liquid state is[1]:

$$\sigma_A^G = \left\langle \frac{1}{N_0} \left[\frac{\hat{\chi}^G}{R^3} - 3 \frac{\hat{\chi} . \boldsymbol{RR}}{R^5} \right] \right\rangle_{av}, \qquad (1)$$

where the average $\langle \rangle_{av}$ is taken over all molecular orientations. The radius vector $\boldsymbol{R}$ points from the proton A to some point O_G within the group G (usually taken to be the electrical center of gravity of this group). Averaging Eq. (*1*) for an axially (or conically) symmetric group gives the much simpler expression[1]:

$$\sigma_A^G = \frac{\Delta\chi^G}{3R^3 N_0} [1 - 3 \cos^2 \gamma], \qquad (2)$$

where $\Delta\chi^G$ is the anisotropy in the susceptibility ($\Delta\chi = \chi_{\parallel} - \chi_{\perp}$) and γ is the angle between $\boldsymbol{R}$ and the symmetry axis of the group G.

In applying McConnell's Eq. (*2*) to the assesment of the shielding effect of a freely rotating group or bond it is necessary to evaluate the average of σ_A^G over the internal motion in the molecule[1]. Since analytical calculation of the average is difficult authors usually prefered numerical averaging (*e.g.*[2,3]) of Eq. (*2*). ApSimon and coworkers[4], however, were able to derive rigorously from Eq. (*2*) a complicated "exact" formula for the average, containing besides analytical expressions only elliptical integrals of the first (K) and second (E) kind, namely

$$\sigma_A^G = \left[-\frac{K}{2\pi b^2 p^{1/2}} + \frac{(3a^2 - b^2) E}{3\pi p^{1/2} g b^2} - \frac{(a^2 - b^2)^2 . (4wE - gK)}{6\pi b^2 p^{3/2} g^2} \right] \Delta\chi^G . \qquad (3)$$

(The symbols occuring in (*3*) are defined in ref.[4]). Equation (*3*) is exactly equivalent to Eq. (*2*) and can be used to find σ_A^G or $\Delta\chi^G$ when *a*) the approximations implied in Eq. (*1*) and (*2*) are

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justified and *b*) when the geometric factors (*a*, *b*, *R etc.*) are known together with $\Delta\chi^G$ or σ_A^G with sufficient precision.

These requirements are, however, only rarely met. For example the literature values for $\Delta\chi$ for such important bonds as C—H and C—C range[5] from 0 to 3 and from 1·5 to 10 ($\times 10^{-6}$ $cm^3\ mol^{-1}$). In addition to this uncertainty the magnitudes of the geometric factors *a*, *b*, *R*, *etc.* are somewhat arbitrary in that they depend on a rather arbitrary choice for O_G (the site of the dipole in the group *G*). If we bear in mind that quite often it is the order of magnitude of σ_A^G or $\Delta\chi^G$ that is required (in order to determine whether long-range effects are important in a particular case) the need for a simpler approximate formula is evident.

In order to obtain a simpler formula the following model was adopted. The model is well within the assumptions made by McConnell[1] in deriving Eq. (*1*). The approximations, usually referred to as the point-dipole approximation, permit the group *G* to be approximated by a point dipole if it is small relative to *R*. If this group dipole rotates ar an angle ϑ about an axis *z* and if the rotation is fast enough for proton A (sufficiently remote from the group *G*) to see only the average effect of the group then it can be approximated by an effective stationary group *G'* which is conically symmetric about the axis *z*. The shielding effect of such a group *G'* will be described by Eq. (*2*) in which $\Delta\chi^G$ is replaced by $\Delta\chi^{G'}$ and the angle γ is now the angle between *z*-axis and the vector **R**.

The remaining problem to be solved is the relation between the two anisotropies. The relation can be obtained by a tensor transformation and averaging over the rotations of the group *G* First, we transform the tensor $\hat{\chi}^G$ according to Eq. (*4*) from its principal axis coordinate system into the Cartesian coordinate system *x*, *y*, *z* where *z* coincides with the axis of rotation of *G*

$$\hat{\tilde{\chi}}^G = \mathbf{M}\hat{\chi}^G\mathbf{M}^{-1} \tag{4}$$

$$\text{where } \mathbf{M} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\vartheta & \sin\vartheta \\ 0 & -\sin\vartheta & \cos\vartheta \end{bmatrix}.$$

Then we let the tensor rotate with a constant angular velocity ω (free rotation) about the axis *z*, we obtain

$$\hat{\tilde{\chi}}^G = \mathbf{T}\hat{\chi}^G\mathbf{T}^{-1} \tag{5}$$

$$\text{where } \mathbf{T} = \begin{bmatrix} \cos\omega t & \sin\omega t & 0 \\ -\sin\omega t & \cos\omega t & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

The magnetic susceptibility $\hat{\chi}^{G'}$ of the new effective group *G'* is obtained as an average over all the angles

$$\hat{\chi}^{G'} = \frac{1}{2\pi}\int_0^{2\pi} \hat{\tilde{\chi}}^G\, d(\omega t).$$

The calculated tensor $\hat{\chi}^{G'}$ is diagonal axially symmetric and,

$$\chi_\perp^{G'} = \chi^{G'}(1,1) = \chi^{G'}(2,2) = \tfrac{1}{2}[\chi_\perp^G(1 + \cos^2\vartheta) + \chi_\parallel^G \sin^2\vartheta]$$
$$\chi_\parallel^{G'} = \chi^G(3,3) = \chi_\parallel^G \cos^2\vartheta + \chi_\perp^G \sin^2\vartheta \tag{6}$$

so that the anisotropy is

$$\Delta\chi^{G'} = \Delta\chi^{G}(1 - \tfrac{3}{2}\sin^2\vartheta)\,, \qquad (7)$$

which gives the formula for the shielding effect

$$\sigma_A^G = \frac{\Delta\sigma^G}{3R^3N_0}(1 - 3\cos^2\gamma)(1 - \tfrac{3}{2}\sin^2\vartheta)\,. \qquad (8)$$

The assumptions and approximations involved are apparent from the description of the model used. It should be emphasized that they are essentially those of the point-dipole approximation, so within the applicability of this approximation the formula (*8*) is as exact as the formula (*2*). Numerical calculations for CH_3 group showed that Eq. (*8*) gives results of the same sign and order of magnitude Eq. (*3*) for a wide range of values of R (3—10 Å) and γ (0—90°). The difference between the two expressions varied according to the values of R and γ but in the average it amounted to some 25% of the calculated values.

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STABILITY CONSTANTS OF CHLORIDE AND BROMIDE COMPLEXES OF BIVALENT COBALT AND NICKEL IN EUTECTIC MELT OF LITHIUM, SODIUM AND POTASSIUM NITRATES

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Study of composition and stability of complexes in molten salts is of importance for estimating the properties of molten salts, which represent the widest scope of inorganic solvents. Moreover, it is important also from the practical point of view, *e.g.* for the applica-