# The Anisotropies of the C–C, C–H, and C=C Bonds

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THE shielding effect of a distant bond (possessing axial symmetry) upon a resonating nucleus may be calculated from the McConnell equation[1] (Term I). We have modified this equation to include a correction, Term II (as below), for the situations where the resonating nucleus is near to the bond

$$\sigma = \overset{\text{Term I}}{\left[\frac{\Delta\chi}{3R^3}(1 - 3\cos^2\theta)\right]} + \overset{\text{Term II}}{\frac{S^2}{R^5}\left[-\frac{(\chi_L + 2\chi_T)}{2} + 5\,(\chi_L\cos^2\theta + \chi_T\sin^2\theta) - \frac{35}{6}\,(\chi_L\cos^4\theta + \chi_T\sin^4\theta)\right]} \quad (1)$$

(*i.e.*, ~3 Å or less.) In (1) $S$ is half the length of the induced dipole: for the C–C and C–H bonds we use $S = 0{\cdot}6$ Å and $S = 0{\cdot}25$ Å respectively.

In calculating the shift of a distant nucleus, produced by the introduction of a substituent into a molecule, both the substituted and unsubstituted molecules must be considered since the resultant shift

$$\Delta\sigma = {}_1^n\Sigma\sigma_{\text{substituted}} - {}_1^n\Sigma\sigma_{\text{unsubstituted}}$$

where ${}_1^n\Sigma$ is the sum of the screening effects of all $n$ bonds in the molecules. It follows that the net chemical shift is caused only by those bonds which differ in the substituted and unsubstituted molecules. *Hence the chemical shift for any proton in proceeding from an unsubstituted to a substituted molecule is the algebraic sum of the screening constants for all the bonds displaced together with all the bonds introduced.*

We have deduced values for the C–H and C–C anisotropies by applying this concept and Equation (1) to cyclohexane where the chemical shift difference ($\Delta\sigma_{\text{a-e}}$) between the axial and equatorial protons has been accurately measured and for which the relationship (2) has been derived.[2] For

$$0{\cdot}114\Delta\chi^{\text{C-C}} - 0{\cdot}094\,\Delta\chi^{\text{C-H}} = 0{\cdot}46 \times 10^{-6} \quad (2)$$

any pair of geminal protons several of the screening bonds responsible for the differential *axial—equatorial* shift are less than 3 Å distant. An initial estimate of the correction factor [Term II in (1)] was made using the susceptibilites of Davies.[3] From our measurements and calculations $\Sigma\Delta\sigma_{\text{a-e}}$ (Term II) = 0·093 p.p.m.

Since $\Sigma\Delta\sigma_{\text{a-e}}$ (Term I) + $\Sigma\Delta\sigma_{\text{a-e}}$ (Term II) = $0{\cdot}46 \times 10^{-6}$

$$\Sigma\Delta\sigma_{\text{a-e}}\ (\text{Term I}) = 0{\cdot}367 \times 10^{-6}$$

Hence Equation (2) becomes

$$0{\cdot}114\Delta\chi^{\text{C-C}} - 0{\cdot}094\Delta\chi^{\text{C-H}} = 0{\cdot}367 \times 10^{-6} \quad (3)$$

From magnetic-birefringence measurements upon ethane it has been deduced[4] that

$$\Delta\chi^{\text{C-C}} - 2\Delta\chi^{\text{C-H}} = -\,4{\cdot}8 \times 10^{-6} \quad (4)$$

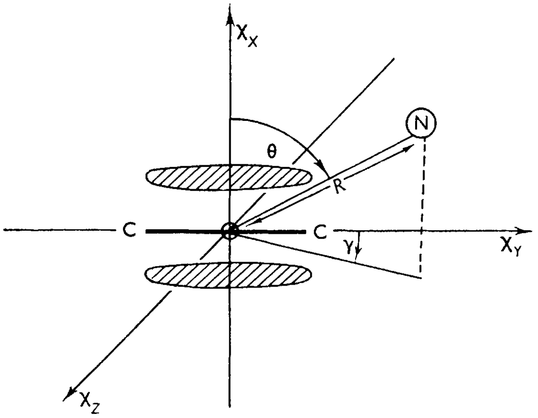
Thus, solving (3) and (4) simultaneously $\Delta\chi^{\text{C-C}} = +\,8{\cdot}86 \times 10^{-6} = +\,14{\cdot}77 \times 10^{-30}$ and $\Delta\chi^{\text{C-H}} = +\,6{\cdot}84 \times 10^{-6} = +\,11{\cdot}40 \times 10^{-30}$. Using the relationships[5]

$\frac{1}{3}(\chi_L + 2\chi_T) = -\,6{\cdot}2 \times 10^{-30}$ cm.$^3$ molecule$^{-1}$ for the C–C bond

and $\frac{1}{3}(\chi_L + 2\chi_T) = -\,6{\cdot}41 \times 10^{-30}$ cm.$^3$ molecule$^{-1}$ for the C–H bond,

magnetic susceptibilities corresponding to these anisotropies were then calculated for the C–C and C–H bonds. These susceptibilities were then used to compute the correction Term II. Successive iterations to constant values gave (5).

$$\begin{aligned} \Delta\chi^{\text{C-C}} &= +\,13{\cdot}98 \times 10^{-30}; & \Delta\chi^{\text{C-H}} &= +\,11{\cdot}00 \times 10^{-30} \\ \chi_L{}^{\text{C-C}} &= +\,3{\cdot}15 \times 10^{-30}; & \chi_L{}^{\text{C-H}} &= +\,0{\cdot}92 \times 10^{-30} \\ \chi_T{}^{\text{C-C}} &= -\,10{\cdot}83 \times 10^{-30}; & \chi_T{}^{\text{C-H}} &= -\,10{\cdot}08 \times 10^{-30} \end{aligned} \quad (5)$$



All values are in cm.$^3$ molecule$^{-1}$. The C–H anisotropy is thus not zero[6,7] or negligible[8] but is of a value similar to that suggested ($+11{\cdot}33 \times 10^{-30}$ cm$^3$. molecule$^{-1}$) by Pople.[7] For $\Delta\chi^{\text{C-C}}$ our value compares satisfactorily with Pople's estimate[9] of $+18{\cdot}33 \times 10^{-30}$ cm.$^3$ molecule$^{-1}$ and that of $+16{\cdot}7 \times 10^{-30}$ cm.$^3$ molecule$^{-1}$ based[10] on $^{13}$C–H coupling constants.

This treatment has been extended to the C=C bond, which does not possess cylindrical or conical symmetry. Hence *three* susceptibilities (*i.e.*, *two* anisotropies) are necessary to describe the anisotropy in the magnetic susceptibility. It is mathematically convenient to redefine the angles involved as in the Figure. The relevant equation for non-axially symmetrical groups is then (7).

$$\sigma = \frac{1}{3R^3}\left[\Delta\chi_1(1 - 3\cos^2\theta) + \Delta\chi_2(1 - 3\sin^2\theta \,.\, \sin^2\gamma)\right] \tag{7}$$

where $\Delta\chi_1 = \chi_Y - \chi_X$, $\Delta\chi_2 = \chi_Z - \chi_X$; the $X$-axis coincides with the bond axis and the $Y$-axis is the direction orthogonal to the nodal plane of the $\pi$-orbitals.

Using the data for twenty-one steroidal examples twenty-one equations were set up and solved by the method of least squares. Value (5) for $\Delta\chi^{C-C}$ and $\Delta\chi^{C-H}$ gave (8).

$$\Delta\chi_1^{C=C} = -\ 12{\cdot}75 \times 10^{-30} \text{ and } \Delta\chi_2^{C=C} = -\ 14{\cdot}27 \times 10^{-30} \text{ cm}^3\text{. molecule}^{-1} \tag{8}$$

The susceptibilities corresponding to (8) are: $\chi_X = +\ 3{\cdot}68 \times 10^{-30}$, $\chi_Y = -9{\cdot}07 \times 10^{-30}$, and $\chi_Z = -10{\cdot}59 \times 10^{-30}$ cm³. molecule⁻¹. The anisotropies (5) and (8) were used to calculate the chemical shifts of the C-18 and C-19 methyl groups of thirteen representative steroidal examples with double bonds in various positions. In a plot of calculated/observed results the line of best fit is approximately that of the theoretical line: with only two exceptions all calculated values of the methyl resonances are within ± 3 c./sec. of the observed values.

Calculations were carried out on the Atlas computer of the University of London.

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