

Origin of Chemical Shifts

BCMB/CHEM 8190

Empirical Properties of Chemical Shift

$$\nu_i \text{ (Hz)} = \gamma B_0 (1 - \sigma_i) / 2\pi$$

σ_i , shielding constant dependent on electronic structure, is $\sim 10^{-6}$. Measurements are made relative to a reference peak (TMS). Offsets given in terms of δ in parts per million, ppm, + downfield.

$$\delta_i = (\sigma_{\text{ref}} - \sigma_i) \times 10^6$$

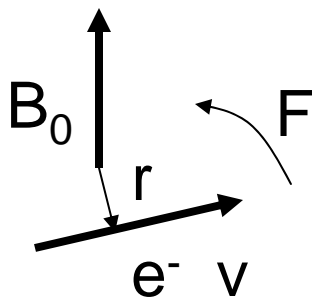
or

$$\delta_i = ((\nu_i - \nu_{\text{ref}}) / \nu_{\text{ref}}) \times 10^6$$

Ranges: ^1H , ^2H , 10 ppm; ^{13}C , ^{15}N , ^{31}P , 300 ppm; ^{19}F , 1000 ppm

Ramsey's Equation for Chemical Shift

- Additional Reference: G.A. Webb, in "Nuclear Magnetic Shielding and Molecular Structure", J.A. Tossel, ed. Nato Adv. Sci. Series (1993) 1-25
- Physical origin: moving charges experience a force perpendicular to the trajectory. Hence electron precess.
- Circulating current gives an opposing field.



$$\vec{F} = - (e/c) \vec{v} \times \vec{B}_0$$

$$\vec{B}' = -(e/c) (\vec{r} \times \vec{v}) / r^3 = -e (\vec{r} \times \vec{p}) / r^3 \text{ (cm)}$$

Quantum Expression for B'

- Have quantum expression of linear momentum:

$$\mathbf{p}_0 = i(\hbar/(2\pi))(\partial/\partial x + \partial/\partial y + \partial/\partial z)$$

- But momentum in magnetic field has a “curl”

$$\vec{p} = \vec{p}_0 + e(\vec{B} \times \vec{r}) / (2c) = \vec{p}_0 + (e/c) \vec{A}$$

A is the vector potential; $\vec{A} = (\vec{B} \times \vec{r})/2$

$$\vec{B}' = -e (\vec{r} \times \vec{p}_0) / r^3 (cm) - e^2 (\vec{r} \times \vec{A}) / (r^3 c^2 m)$$

Quantum mechanically:

$$B' = \langle \psi_0 | -e (\vec{r} \times \mathbf{p}_0) / r^3 (cm) - e^2 (\vec{r} \times \mathbf{A}) / (r^3 c^2 m) | \psi_0 \rangle$$

Diamagnetic Shifts

- Note: only the second term is proportional to B_0 at first order theory; this is the diamagnetic term; Lamb term

$$\vec{B}'_D = \langle \psi_0 | -e^2(\vec{r} \times \vec{B}_0 \times \vec{r}) / (2r^3 c^2 m) | \psi_0 \rangle$$

Only interested in the z component:

$$\vec{k} (x \cdot (\vec{B}_0 \times \vec{r})_y - y \cdot (\vec{B}_0 \times \vec{r})_x) \quad \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \mathbf{x} & \mathbf{y} & \mathbf{z} \\ (\mathbf{Bxr})_x & (\mathbf{Bxr})_y & (\mathbf{Bxr})_z \end{vmatrix}$$

$$B'_D = - (e^2 / (2c^2 m)) \int |\psi_0^*| (x^2 + y^2) / r^3 |\psi_0| d\tau$$

Predictions: depends on electron density near to nucleus
opposes magnetic field (shields)

Examples:

He	2 1s e-	$\sigma = 59.93 \times 10^{-6}$
Ne	10 e-	$\sigma = 547 \times 10^{-6}$
H	~2 1s e-	$\sigma = \sim 60 \times 10^{-6}$

range: ~10% > ~6 ppm

Paramagnetic Contribution to Shifts

- This comes from the first term – there was no explicit B_0 dependence – so carry to second order
- B_0 can be in \mathbf{H}'

$$\psi = \psi_0 + \sum_n (\langle \psi_n | \mathbf{H}' | \psi_0 \rangle / (E_n - E_0)) \psi_n = \psi_0 + \psi'$$

$$\mathbf{H}_0 = (1/(2m)) \mathbf{p}_0^2 + V \quad \dots \text{ in absence of field}$$

$$\mathbf{H} = (1/(2m)) (\mathbf{p}_0 + (e/c)\mathbf{A})^2 + V \quad \dots \text{ in presence}$$

$$\mathbf{A} = (\mathbf{B}_0 \times \mathbf{r})/2 \quad \dots \text{ This introduces field dependence}$$

$$\mathbf{H}' = (e/(2mc)) \vec{\mathbf{A}} \cdot \vec{\mathbf{p}}_0$$

Paramagnetic term continued

$$\begin{aligned} \mathbf{A} \cdot \mathbf{p}_0 &= ((\mathbf{B}_0 \times \mathbf{r})/2) \cdot \mathbf{p}_0 \equiv \mathbf{B}_0 \cdot (\mathbf{r} \times \mathbf{p}_0)/2 = \mathbf{B}_0 \cdot (\mathbf{L}h/(2\pi))/2 \\ &= B_0 \mathbf{L}_z h/(2\pi)/2 \end{aligned}$$

$$\mathbf{H}' = B_0 eh/(8\pi mc) \mathbf{L}_z$$

$$\begin{aligned} B'_p &= \langle \psi_0 + \psi' | (e/(cm))(r \times \mathbf{p}_0)/r^3 | \psi_0 + \psi' \rangle \\ &= \langle \psi_0 + \psi' | (e/(cm))(\mathbf{L}_z)/r^3 | \psi_0 + \psi' \rangle \end{aligned}$$

Substituting ψ' and saving only terms linear in B_0 , $B'_p =$

$$\begin{aligned} B_0 (eh/(4\pi mc))^2 \sum_n [&(\langle \psi_0 | \mathbf{L}_z | \psi_n \rangle \langle \psi_n | \mathbf{L}_z / r^3 | \psi_0 \rangle) / (E_n - E_0) + \\ &(\langle \psi_0 | \mathbf{L}_z / r^3 | \psi_n \rangle \langle \psi_n | \mathbf{L}_z | \psi_0 \rangle) / (E_n - E_0)] \end{aligned}$$

Implications for Paramagnetic Term

- σ_P is negative ($B'_P = -\sigma_P$) ... opposite to σ_D
- σ_P is zero unless $L_z |\psi\rangle$ is finite
hence, if only “s” orbitals populated, $L_z |”s”\rangle = 0$
hence, small shift range for 1H
- ^{13}C has “p” orbitals ($L_z |p_1\rangle = 1 p_1$) and finite σ_P
- Electron distribution must also be asymmetric
otherwise, $\sum L_z |p\rangle = 0$
hence, CH_4 shift is small and resonance far upfield

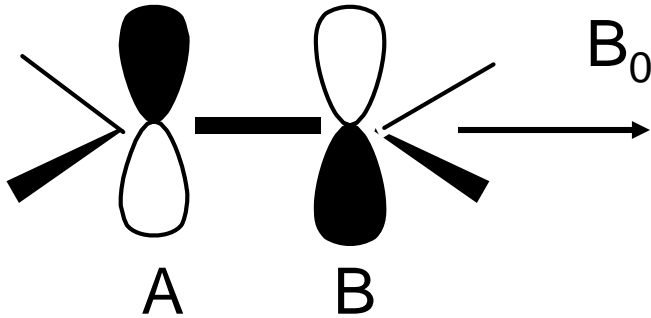
^{13}C Example: Ethane vs Ethylene

- $\text{CH}_3\text{-CH}_3$ 6 ppm, $\text{CH}_2=\text{CH}_2$ 123 ppm, Why?
- σ_D is about the same for both, $\sim 200 \times 10^{-6}$
- $\sigma_P =$

$$-(eh/(4\pi mc))^2 \sum_n [(\langle \psi_0 | \mathbf{L}_z | \psi_n \rangle \langle \psi_n | \mathbf{L}_z / r^3 | \psi_0 \rangle) / (E_n - E_0) + \dots]$$

- Examine $\psi_n = \sum_i c_{in} \phi_i$, $\phi_i = 1s_C, 2s_C, 2p_{C0}, 2p_{C+/-1}, 1s_H$
- Only ps count, ΔE small is most important
- Consider first excited state: $\pi^* = (1/\sqrt{2})(p_{iA} - p_{iB})$

Consider Field Parallel to C-C Bond

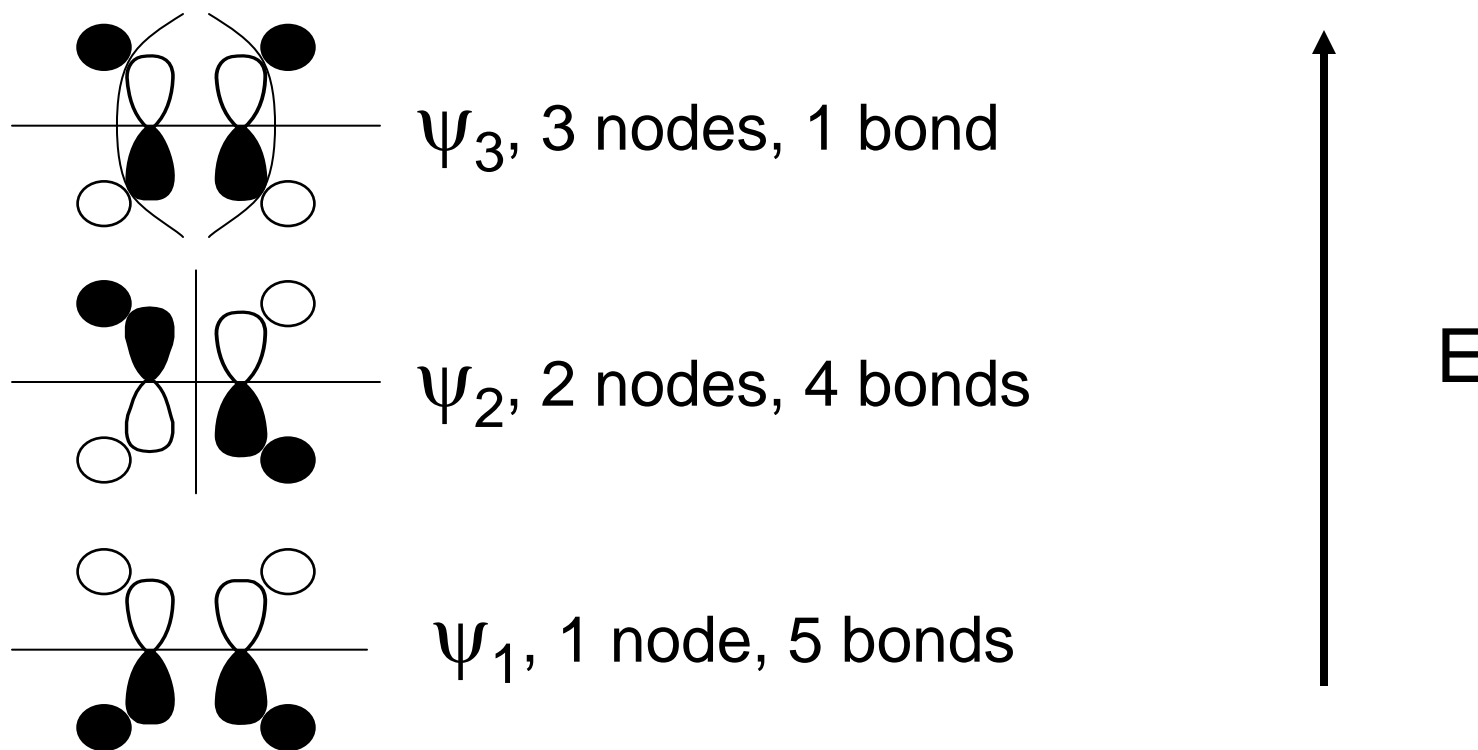


$$\pi^* = (1/\sqrt{2})(p_{xA} - p_{xB})$$

$$\pi^* = (1/\sqrt{2})((p_{1A} + p_{-1A}) - (p_{1B} + p_{-1B}))$$

- $L_z | \pi^* \rangle = (i\hbar\sqrt{2}/\pi)((p_{1A} - p_{-1A}) - (p_{1B} - p_{-1B})) / (2i)$
 $= (i\hbar\sqrt{2}/\pi)(L_z | \pi^* \rangle)$
- $\langle \psi_0 | L_z | \pi^* \rangle$ is finite if p_{yA} , p_{yB} are populated in ψ_0
- ψ_0 must also be asymmetric – look at MOs

Molecular Orbitals for Ethylene

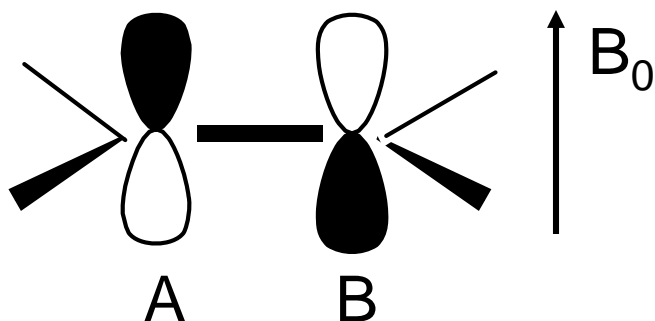


- Fill with electrons: 2×6 for C, 4 for H = 16
- 4 in $1s_C$, 2 in π_0 (\perp to plane), 2 in C-C σ , 4 in C-H σ
- Implies 4 maximum in above

Calculating Paramagnetic Contribution

- Only ψ_1 , ψ_2 , contribute
- ψ_1 , is symmetric, implies $\langle \psi_1 | \mathbf{L}_z | \pi^* \rangle$ is zero
- ψ_1 , is asymmetric and counts
- $\sigma_P = -(eh/(2\pi mc))^2 \langle (1/r^3) \rangle_{2p} c_2^2 \cong -200 \times 10^{-6}$
- $\sigma_{c-c} = \sigma_D + \sigma_P = (200-200) \times 10^{-6} = 0 \times 10^{-6}$

What about Field Perpendicular to Plane?



$$\pi^* = (1/\sqrt{2})(p_{zA} - p_{zB})$$

$$\pi^* = (1/\sqrt{2})(p_{0A} - p_{0B})$$

- $L_z | p_0 \rangle = 0$; therefore, $\sigma_P = 0$
- $\sigma_{\perp} = \sigma_D + \sigma_P = (200 + 0) \times 10^{-6}$
- Similar for in plane, perpendicular to ps
- σ (predict) = $\begin{bmatrix} 0 & & \\ & 0 & \\ & & 200 \end{bmatrix}$ (observe) $\begin{bmatrix} -20 & & \\ & 120 & \\ & & 200 \end{bmatrix}$
- Isotopic shift = $1/3 \text{ Tr } \sigma = 70\text{-}100$ ppm below Me
- Waugh, Griffin, Wolff, JCP, **67** 2387 (1977) – solids NMR

^{13}C Chemical Shift Calculations on Peptides

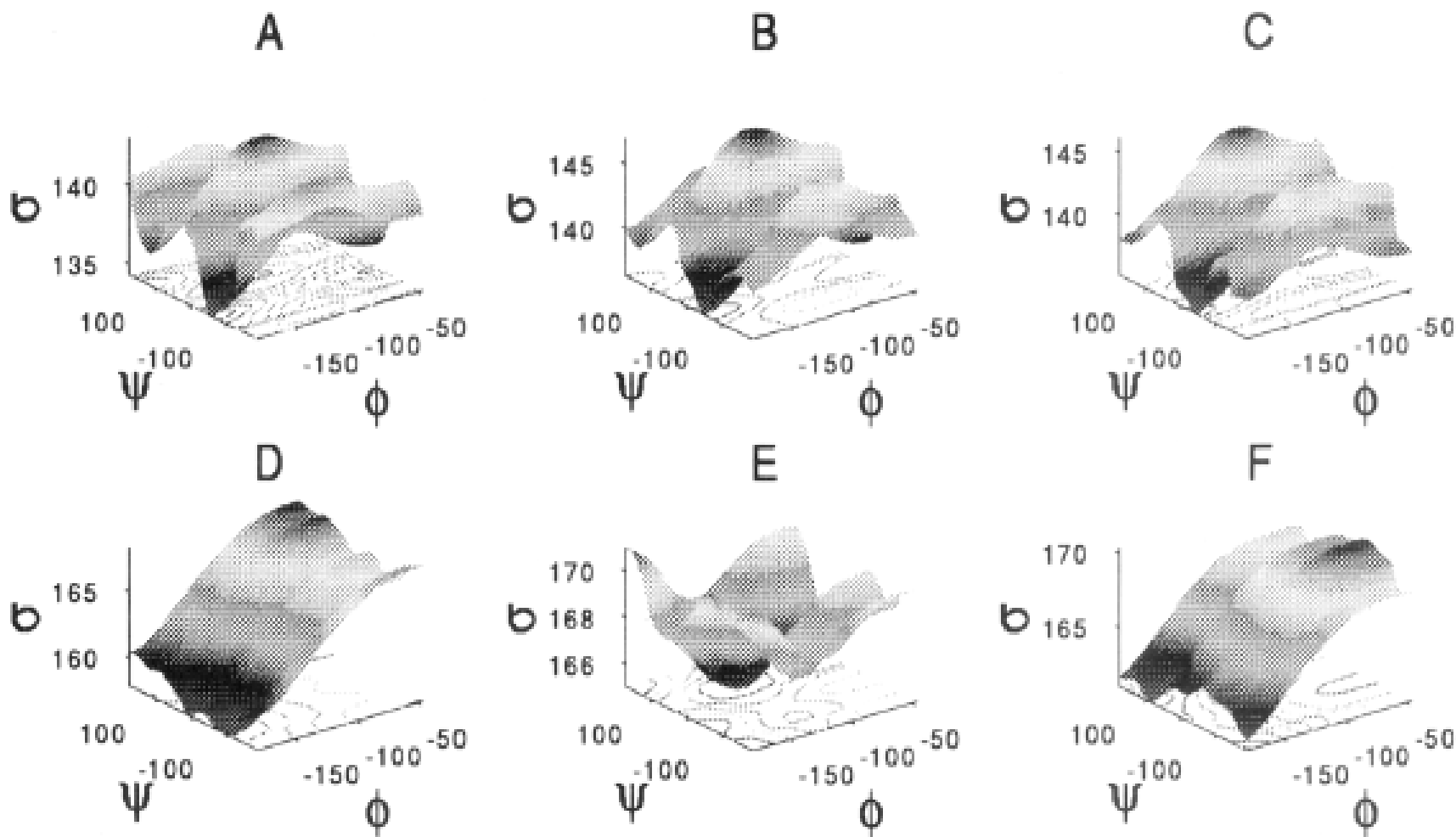
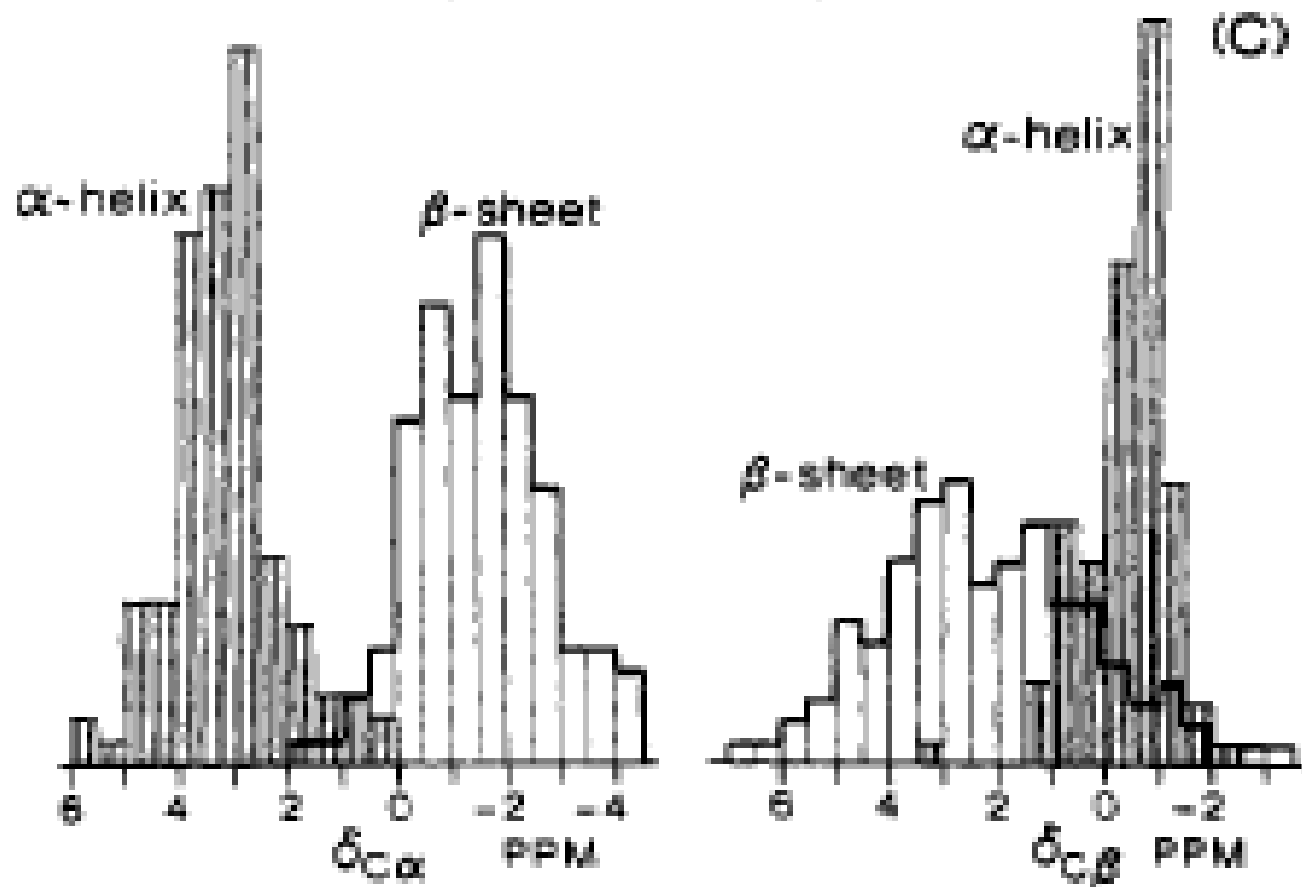


Figure 7. Calculated $^{13}\text{C}^\alpha$ and $^{13}\text{C}^\beta$ shieldings in formylvaline amide as a function of ϕ and ψ (at various χ^1 values): (A) C^α , $\chi^1 = 180^\circ$; (B) C^α , $\chi^1 = 60^\circ$; (C) C^α , $\chi^1 = -60^\circ$; (D) C^β , $\chi^1 = 180^\circ$; (E) C^β , $\chi^1 = 60^\circ$; (F) C^β , $\chi^1 = -60^\circ$.

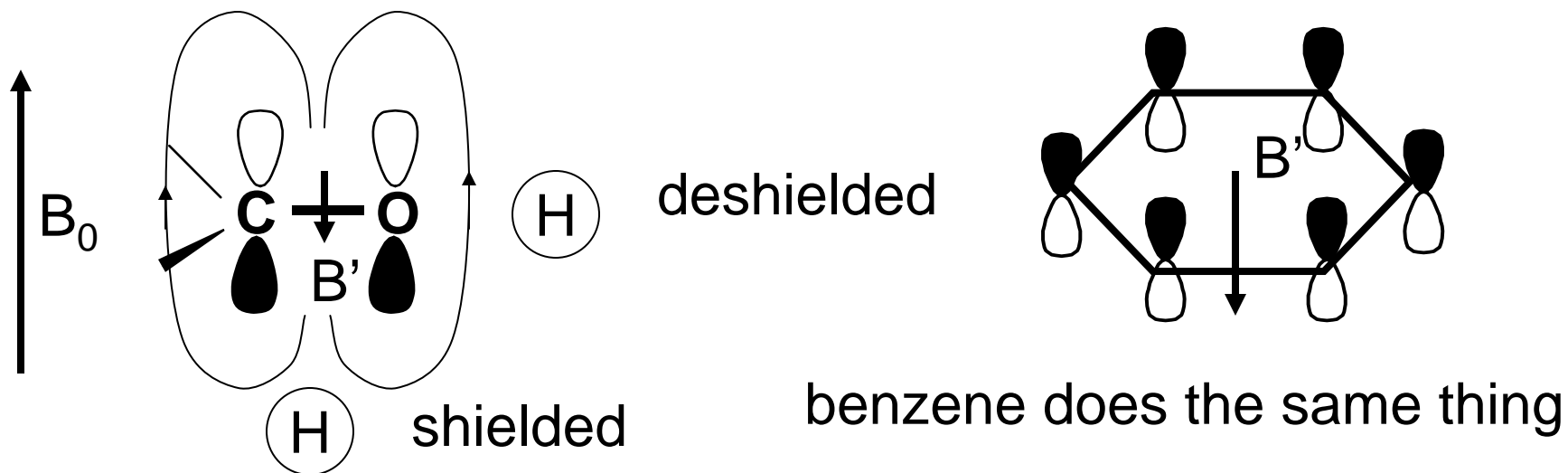
α helix, -57, -47; β sheet, -139, 135; Oldfield and Dios, JACS, **116**, 5307 (1994)

^{13}C shifts and Peptide Geometry



- Shifts relative to random coil with same amino acid
- Spera and Bax, JACS, **113**, 5490 (1991)
- See also: Case, <http://www.scripps.edu/mb/case> (Shifts)
- See also: Wishart, <http://redpoll.pharmacy.ualberta.ca/shiftz>

Remote Group Effects



- $\sigma'_{\text{remote}} = \Delta\chi/r^3 (1-3\cos^2\theta)$
- Benzene protons are 2 ppm further downfield
- Johnson and Bovey, JCP, **29**, 1012 (1962)

Shielding from a Benzene Ring

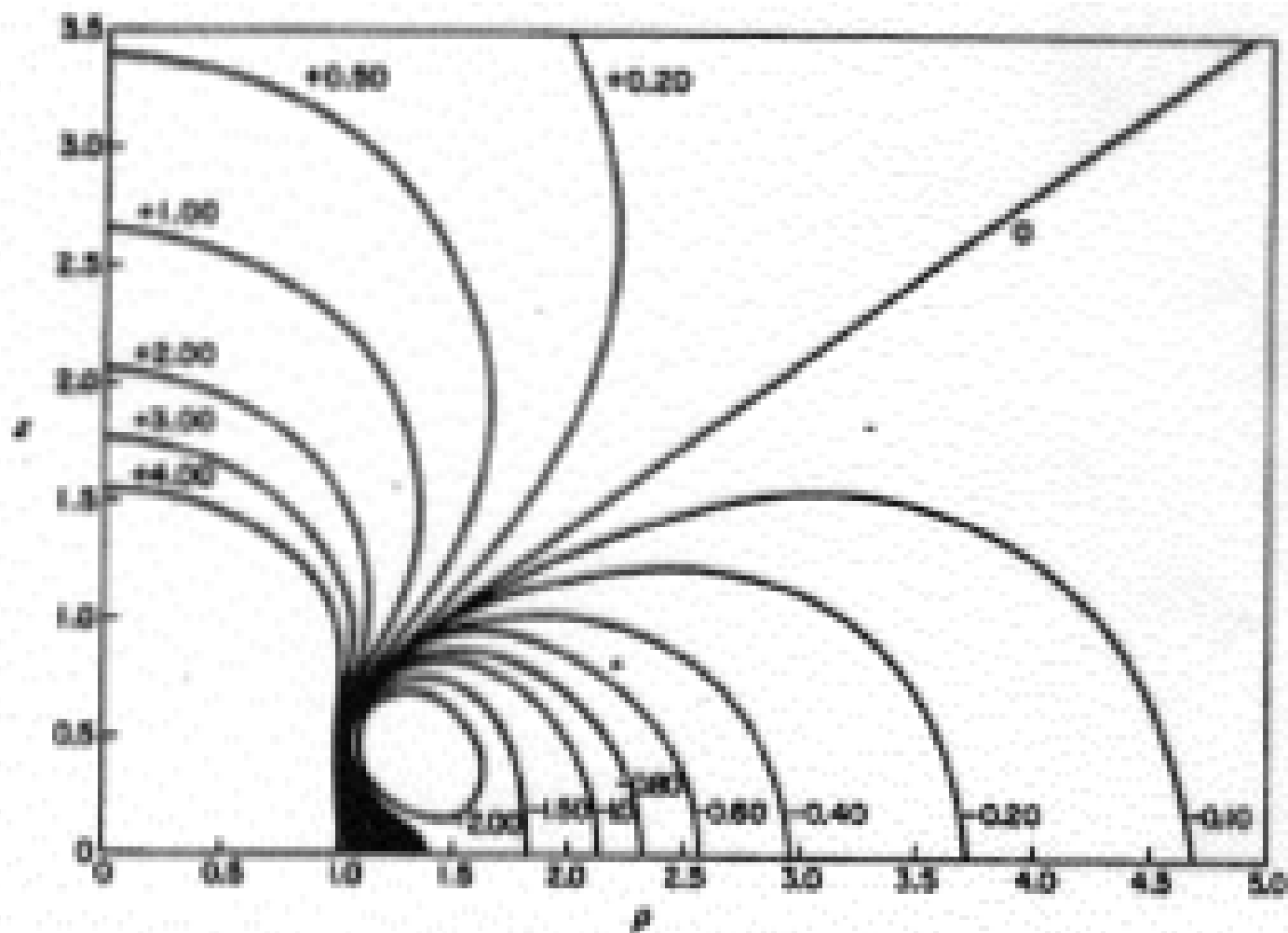


Fig. 4.13 Effect on the chemical shifts of a nucleus at various positions due to the ring current in benzene. The plot represents one quadrant of a plane passing normally through the center of the ring, which lies horizontally. A positive sign denotes an upfield contribution to the chemical shift; ρ and z are in units of the benzene C—C distance, 1.39 Å (Johnson and Bovey²⁰).