

Secondary shift = $\delta_{\text{expt}} - \delta_{\text{coil}}$

Helical residues generally have positive $\delta_{C\alpha}$ and negative $\delta_{C\beta}$ while strand residues generally have negative $\delta_{C\alpha}$ and positive $\delta_{C\beta}$.

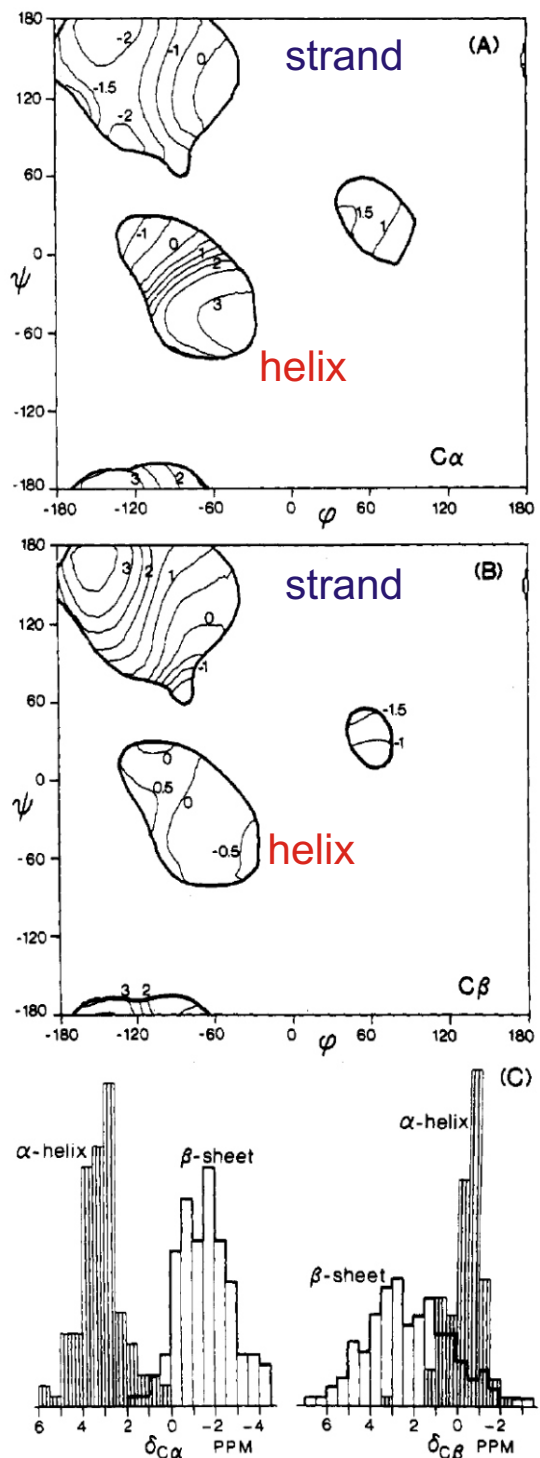


Figure 1. Contour plots of the average secondary shift, $\Delta(\phi, \psi)$, of (A) $C\alpha$ and (B) $C\beta$ resonances and (C) histograms of secondary shift distribution in α -helix and β -sheet. The $\Delta(\phi, \psi)$ surface is calculated by convolution of each of the $\delta(\phi_k, \psi_k)$ values with a Gaussian function, prior to addition and normalization: where the summations extend over all

$$\Delta(\phi, \psi) = \frac{\sum \delta(\phi_k, \psi_k) \exp(-((\phi - \phi_k)^2 + (\psi - \psi_k)^2)/450)}{\sum \exp(-((\phi - \phi_k)^2 + (\psi - \psi_k)^2)/450)}$$

residues k . Contours are only shown in regions of the ϕ, ψ plot where the residue density function, $\sum_k \exp(-((\phi - \phi_k)^2 + (\psi - \psi_k)^2)/450)$, is larger than 3.1, where the summation extends over all residues k . The data used for constructing Figure 1 are given in the supplementary material. $C\alpha$ and $C\beta$ random coil chemical shifts used for calculating the $\Delta(\phi, \psi)$ surfaces are as follows: Ala, 52.3, 19.0; Arg, 56.1, 30.3; Asn, 52.8, 37.9; Asp, 54.0, 40.8 (nonprotonated); Cys (reduced) 56.9, 28.9; Gln, 56.1, 28.4; Glu, 56.4, 29.7 (nonprotonated); Gly, 45.1; Ile, 61.3, 38.0; Leu, 55.1, 42.3; Lys, 56.5, 32.5; Met, 55.3, 32.6; Phe, 58.0, 39.0; Pro, 63.1, 31.7; Ser, 58.2, 63.2; Thr, 62.1, 69.2; Trp, 57.7, 30.3; Tyr, 58.1, 38.8; Val, 62.3, 32.1. Values are relative to internal TSP, where the 0 ppm ^{13}C frequency is obtained indirectly by multiplying the spectrometer frequency that corresponds to 0 ppm in the ^1H spectrum by 0.251 449 50.