Notes on CSA Tensor Parameters

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Methods

Calculation of CSA

In studies on the structure of phage fd (Marvin et al., 2006), we used the program FX-PLOR (Wang & Stubbs, 1993) to refine models against the X-ray fibre diffraction data and stereochemical constraints, followed by the program CNS-SS02 (Bertram et al., 2000; 2003) to refine the X-ray model further against the solid-state NMR data of Zeri et al. (2003). Simultaneous refinement is clearly preferable to such sequential refinement, and since the refinement against fibre diffraction data and the refinement against solid-state NMR data are now both implemented in the program Xplor-NIH (Schwieters et al., 2003; 2006), we use Xplor-NIH for simultaneous refinement in our current studies.

A few considerations are important to ensure that the refinement against CSA data is the same for Xplor-NIH as for CNS-SS02. First, in CNS-SS02 the plane of the peptide is defined by the atoms N, C, CA. According to convention, the torsion angle $\omega$ about the C-N bond is defined in terms of CA-N-C-CA (IUPAC, 1970). To be consistent with the IUPAC definition of $\omega$, one should use the C, N, CA atoms to define the x-y plane of the CSA molecular frame. This is important because the $\omega$ torsion angle is known to be not precisely 180.0°, although it is within a few degrees of 180°, as found by theoretical studies (Nambudripad et al., 1981), by analysis of experimental data (MacArthur & Thornton, 1996), and by more recent studies by Priestle (2002) and Esposito et al. (2005) among others. Therefore the plane defined by atoms N, C, HN (as used by some authors and in earlier versions of Xplor-NIH) will not be identical to the plane defined by atoms N, C, CA. We edited csaPotTools.py in Xplor-NIH version 2.20 to a new file, csaPotToolsCA3.py, which includes a new name, NCA, mimicking N, but with atom names C, N, and CA, mimicking C, N, and HN. We used this to calculate CSA, with the bond order N, C, CA; the angle $\beta = 103.3^\circ$ for non-glycine residues; and $D_a = 10.862$. The scale factor $D_a$ can be calculated in Xplor-NIH with the python routine calcDaRh.

Further potential confusion arises from the existence of different notations for defining the chemical shift tensor. There are two main sets of notations for the principal components of the chemical shift tensors.


These notations are:

$\sigma_{xx}$, $\sigma_{yy}$, $\sigma_{zz}$ : the Haeberlen convention (Haeberlen, 1976)

or $\sigma_{11}$, $\sigma_{22}$, $\sigma_{33}$ : the IUPAC or "standard" convention (Mason, 1993)

The isotropic chemical shift, $\sigma_{iso}$, is

$\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$

The $\sigma_{xx}$, $\sigma_{yy}$, $\sigma_{zz}$ notation is defined by:

$|\sigma_{zz} - \sigma_{iso}| \geq |\sigma_{xx} - \sigma_{iso}| \geq |\sigma_{yy} - \sigma_{iso}|$

The $\sigma_{11}$, $\sigma_{22}$, $\sigma_{33}$ notation is defined for $^{15}$N by:

$\sigma_{11} < \sigma_{22} < \sigma_{33}$

The relationship between the two notations is:

$\sigma_{xx} = \sigma_{iso} - \sigma_{11}$
\[ \sigma_{yy} = \sigma_{\text{iso}} - \sigma_{22} \]
\[ \sigma_{zz} = \sigma_{\text{iso}} - \sigma_{33} \]

and thus,
\[ \sigma_{xx} + \sigma_{yy} + \sigma_{zz} = 0 \]

Straus et al. (2003), Bertram et al. (2000; 2003) (in CNS-SS02), and the Opella group (Zeri et al., 2003; Thiriot et al., 2005) use the \( \sigma_{11}, \sigma_{22}, \sigma_{33} \) notation, with \( \sigma_{11} \) directed from N along the N-C bond, and \( \theta \) measuring the angle from the NH bond to \( \sigma_{33} \). The value of \( \beta \) corresponds to 120 - \( \theta \).

The values are (Straus et al., 2003):

For non-glycine residues:
\[ \sigma_{11}=56.3 \text{ ppm, } \sigma_{22}=79.0 \text{ ppm, } \sigma_{33}=224.0 \text{ ppm, } \theta = 16.7^\circ \]
\[ \sigma_{\text{iso}} = 119.77 \]

For glycine residues:
\[ \sigma_{11}=45.6 \text{ ppm, } \sigma_{22}=66.3 \text{ ppm, } \sigma_{33}=211.6 \text{ ppm, } \theta = 21.6^\circ \]
\[ \sigma_{\text{iso}}=107.83 \]

Cornilescu & Bax (2000) and Schwieters et al. (2006) (in Xplor-NIH) use the \( \sigma_{xx}, \sigma_{yy}, \sigma_{zz} \) notation, so for non-Gly
\[ \sigma_{xx}= 63.5 \quad \sigma_{yy}=40.8 \quad \sigma_{zz}= -104.2, \quad \beta = 103.3^\circ \]

and for Gly
\[ \sigma_{xx}= 62.2 \quad \sigma_{yy}=41.5 \quad \sigma_{zz}= -103.8, \quad \beta = 98.4^\circ \]

The latest version of Xplor-NIH uses the order
\[ 63.5, -104.2, 40.8, \quad \beta = 103.3^\circ \]

for non-Gly, that is \( \sigma_{xx}, \sigma_{zz}, \sigma_{yy} \), and the analogous order for Gly. This is due to the choice of bond order in csaPotToolsCA3.py.

**Differences between CSA tensor values**

It is found experimentally that the tensor values for Gly residues are significantly different from the values for other residues, as shown above.

Also, Thiriot et al. (2005) found that the experimentally measured values of \( \sigma_{33} \) for 6 residues in Pf1\(^{1}\) phage (namely residues 13, 18, 28, 32, 39, 42) are higher than the usual maximum \( \sigma_{33} = 224.0 \text{ ppm} \), although slightly high values have been found in some other systems (Hall & Fushman, 2006). This might be a function of the low temperature at which these values are measured (Cordier et al., 2002). Note that residue 28 of Pf1\(^{1}\) (Thiriot et al., 2005) is Gly, but since it has a high measured \( \sigma_{33} \) (234.0 ppm), we group it with the anomalous non-Gly residues in the CSA calculations. We use for these 6 anomalous residues
\[ \sigma_{11}=56.3 \text{ ppm, } \sigma_{22}=79.0 \text{ ppm, } \sigma_{33}=234.0 \text{ ppm} \]
\( \sigma_{\text{iso}} = 123.1 \)

so in Xplor-NIH we use

66.8, -110.9, 44.1, \( \beta = 103.3^\circ \)

References


Cordier et al. (2002) JMB, 715:739


Haeberlen (1976) Advances in Magnetic Resonance, Suppl. 1, ed. J.S. Waugh

Hall & Fushman (2006) JACS 128: 7855


