

23. STRUCTURAL ANALYSIS AND CLASSIFICATION

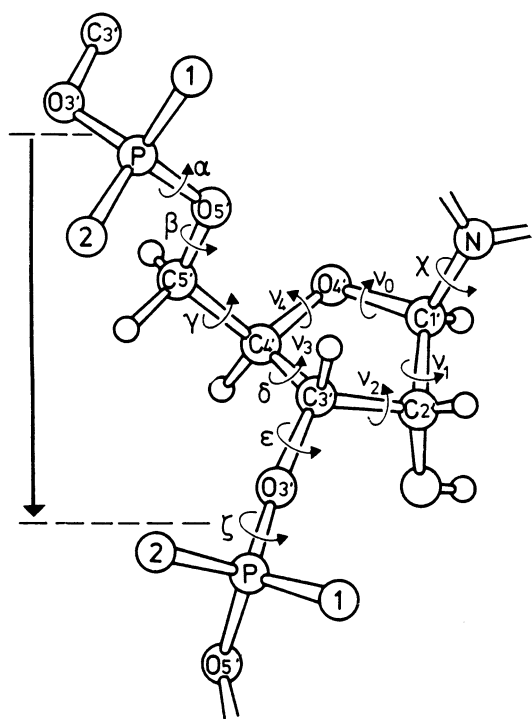


Fig. 23.3.2.2. Sugar-phosphate backbone of RNA and DNA polynucleotides. One nucleotide begins at a phosphorus atom and extends just short of the phosphorus atom of the following nucleotide, with the conventional positive direction being $P \rightarrow O5' - C5' - C4' - C3' - O3' \rightarrow P$, as indicated by the arrows. Main-chain torsion angles are designated α through ζ , and torsion angles about the five bonds of the ribose or deoxyribose ring are ν_0 through ν_4 , as shown. If one imagines atoms $O3' - P - O5'$ as a hump-backed bridge, as one crosses the bridge in a positive chain direction, oxygen atom $O1$ is to the left and $O2$ is to the right. These oxygens, accordingly, are sometimes designated O_L and O_R . The $-OH$ group attached to the $C2'$ atom of the ribose ring in RNA shown here is replaced by $-H$ in the deoxyribose ring of DNA. Atom N to the right is part of the base attached to the sugar ring: $N1$ in pyrimidines and $N9$ in purines. Torsion angle χ is defined by $O4' - C1' - N1 - C2$ in pyrimidines and $O4' - C1' - N9 - C4$ in purines.

groups in the active sites of enzymes.) Hence, with a single-chain DNA, G-A-G-A-G-A-A-C-C-C-C-T-T-C-T-C-T-T-T-C-T-C-T-C-T-T, that folds back upon itself twice to build a triplex, NMR experiments indicate a significant amount of triplex remaining even at pH 8.0 (Sklenár & Feigon, 1990; Feigon, 1996).

23.3.2.4. Helix parameters

An important advantage of single-crystal oligonucleotide structures over fibre-based models is that one can actually observe local sequence-based departures from ideal helix geometry. B-DNA fibre models indicated a mean twist of *ca* 36° per step, or ten base pairs per turn, whereas A-DNA fibre patterns indicated less winding: *ca* 33° per step or 11 base pairs per turn. Twist, rise per base pair along the helix axis, horizontal displacement of base pairs off that axis, and inclination of base pairs away from perpendicularity to the axis are all intuitively obvious parameters. But when single-crystal structures began appearing in great numbers in the mid-1980s, it became imperative that uniform names and definitions be used for these and for less obvious, but increasingly significant, local helix parameters.

An EMBO workshop on DNA curvature and bending, held at Churchill College, Cambridge, in September 1988, led to an agreement on definitions and conventions that was published

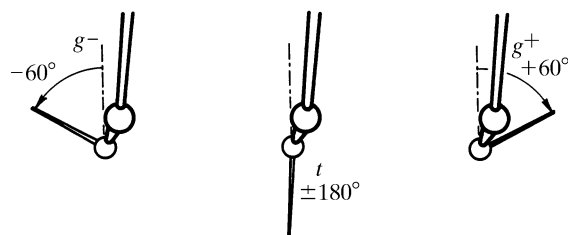


Fig. 23.3.2.3. Definition of torsion angles. A positive angle results from clockwise rotation of the farther bond, holding the nearer bond fixed. Torsion angle $+60^\circ$ is designated as *gauche*⁺ or g^+ , angle 180° is *trans* or t and angle -60° is *gauche*⁻ or g^- .

simultaneously in four journals (Dickerson *et al.*, 1989). Fig. 23.3.2.10 shows the reference frames for two successive base pairs, and Figs. 23.3.2.11 and 23.3.2.12 illustrate local helix parameters involving rotation and translation, respectively. Subsequent experience has shown the most useful parameters to be inclination, propeller, twist and roll among the rotations, and x displacement, rise and slide among the translations. As mentioned at the beginning of this chapter, inclination and x displacement are the two properties that best differentiate A- from B-DNA. The four most widely used computer programs for calculation of local helix parameters are

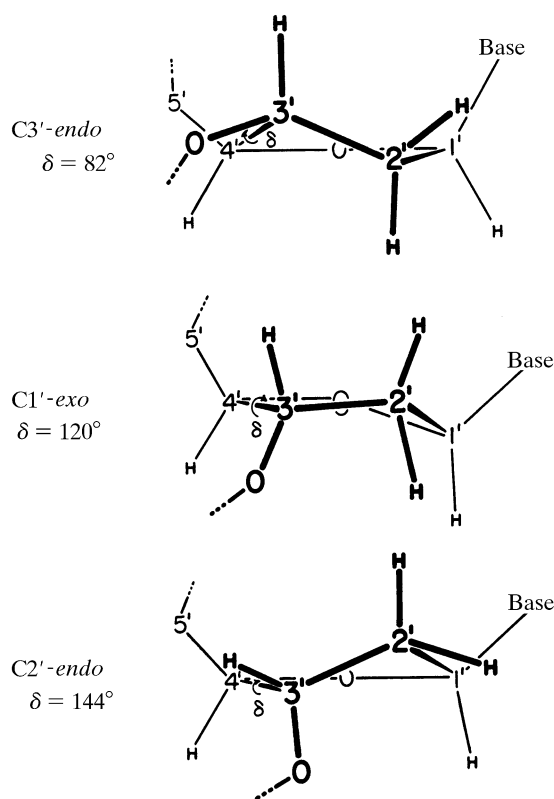


Fig. 23.3.2.4. The three most common furanose ring geometries. The planar form of the five-membered ribose or deoxyribose ring is unstable because of steric hindrance from side groups; one of the five atoms prefers to pucker out-of-plane on one side of the ring or the other. Puckering toward the same side of the ring as the $C5'$ atom is termed *endo*, and puckering toward the opposite 'outside' surface is termed *exo*. The main-chain torsion angle δ is related to sugar ring conformation because of the motion undergone by the $C3' - O3'$ bond during changes in puckering.