

## PROVISIONAL

# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

and

## INTERNATIONAL UNION OF BIOCHEMISTRY JOINT COMMISSION ON BIOCHEMICAL NOMENCLATURE\*

# SYMBOLS FOR SPECIFYING THE CONFORMATION OF POLYSACCHARIDE CHAINS

Comments on these recommendations are welcome and should be sent within 8 months from August 1983 to the present Secretary of the Commission

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Comments from the viewpoint of languages other than English are especially encouraged. These may have special significance regarding the publication in various countries of translations of the nomenclature eventually approved by IUPAC.

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## IUPAC-IUB Joint Commission on Biochemical Nomenclature (JCBN)

## Symbols for Specifying the Conformation of Polysaccharide Chains

## Recommendations 1981

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These recommendations are made to allow polysaccharide conformation to be specified; the nomenclature of carbohydrates is published elsewhere [1], as are symbols for specifying ring forms of monosaccharides [3] and recommendations for the symbolic representation of oligosaccharides [4]. They are in conformity with recommendations also being published on polynucleotide conformation [5] and with earlier recommendations [6] on polypeptide conformation.

## 1. GENERAL PRINCIPLES OF NOTATION

## 1.1. Direction of Numbering

Polysaccharides are macromolecules formed from many sugar units connected by glycosidic linkages.

The chain is numbered from the reducing glucose residue to the non-reducing glycosyl group. Thus  $i$  refers to a partic-

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ular saccharide unit in the polymer chain,  $(i-1)$  to the adjacent unit in the direction *away* from the non-reducing end and  $(i+1)$  in the direction of the non-reducing end. This direction of numbering is chosen so that gain or loss of a residue at the non-reducing end by transfer of a glycosyl group does not change the numbering of every unit in the chain. Some polysaccharides lack reducing end groups and are initiated by formation of a glycosidic linkage, e.g. to O1 (section 1.3) of another sugar, to an alditol or to an alcohol. For these polysaccharides the residue forming this glycosidic linkage is regarded as the first member of the chain.

## 1.2. Monomeric Unit

The monomeric unit is the monosaccharide. With complicated polysaccharides the primary structure should be given as described in 'Abbreviated terminology of oligosaccharide chains' [4]. The oxygen of the glycosidic bond is part of the residue glycosylated. Since its position is of importance in specifying the unit, the torsion angle at the glycosidic bond is included in the characteristics of the sugar residue (section 2.2). The limits of an individual unit are shown in Fig. 4.

## 1.3. Atomic Numbering

The atom numbering of two monosaccharide units (a hexopyranose and a hexofuranose) is shown in Fig. 1. The notation used here conforms with that being proposed for specifying polynucleotide conformation. Atoms are thus designated C3, O2, H4, etc. The hydrogen atoms of a methylene group may be distinguished by an additional number, e.g. H61 and H62 where the lower number is selected for the *pro-S* atom [7]. When it is necessary to indicate the particular saccharide unit its number may be added in parenthesis, e.g. O3( $i$ ), C4( $i+1$ ), H61( $i-1$ ).

## 1.4. Interatomic Distances

In tabulating interatomic distances, non-bonded atoms are represented with a single dot between them, e.g. O2.C3, and covalent bonds are represented by hyphens between atoms, e.g. C1-C2. Hydrogen bonds are denoted by dotted lines whether or not the hydrogen is shown, e.g. O6...O5 or O6-H...O5. The atom donating the hydrogen is written first if specification is possible.

The interatomic distance may be symbolized as  $b(C1, C2)$ ; the symbol  $l$  is avoided because it can be confused with the numeral 1 and because  $l$  is used for vibration amplitude in electron diffraction (section 1.4 of reference 5).

Table 1. Examples of torsion angles in sugar rings

	Aldofuranoses	Aldopyranoses	Ulofuranoses (e.g. D-fructofuranose)
$\nu_0$	C4–O4–C1–C2	C5–O5–C1–C2	C5–O5–C2–C3
$\nu_1$	O4–C1–C2–C3	O5–C1–C2–C3	—
$\nu_2$	C1–C2–C3–C4	C1–C2–C3–C4	O5–C2–C3–C4
$\nu_3$	C2–C3–C4–O4	C2–C3–C4–C5	C2–C3–C4–C5
$\nu_4$	C3–C4–O4–C1	C3–C4–C5–O5	C3–C4–C5–O5
$\nu_5$	—	C4–C5–O5–C1	C4–C5–O5–C2

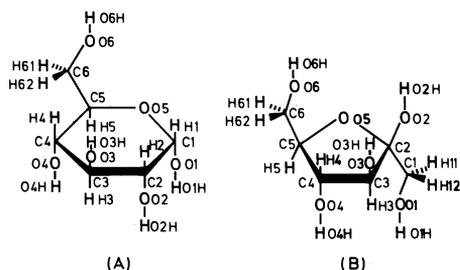


Fig. 1. Notation for atomic numbering of (A) a hexapyranose and (B) a hexafuranose unit

### 1.5. Bond Angles

The bond angle included between three atoms A–B–C is written 'tau' as  $\tau(A, B, C)$ . If there is no ambiguity, because the central atom is bivalent, this may be abbreviated to  $\tau(B)$ . The angle at the ring-oxygen atom of an aldopyranose may thus be written as  $\tau(C1, O5, C5)$  or  $\tau(O5)$ .

### 1.6. Ring Shape

The ring shape of a sugar residue can be defined either by the endocyclic torsion angles (1.6.1) or in terms of the notation for conformations of five and six-membered monosaccharide rings (1.6.2)

#### 1.6.1. Endocyclic Torsion Angles

In order to provide a complete description of the sugar ring conformation, it is necessary to specify the endocyclic torsion angles about at least some of the ring bonds, in addition to the bond lengths and bond angles. These ring torsion angles, denoted by the symbol  $\nu(\text{nu})$ , can be described by adding a number indicating the bond as listed in Table 1 (see also Fig. 2). The torsion angle of the atoms A–B–C–D is the angle between A–B and C–D in a projection of the four atoms on to a plane normal to B–C. It is considered positive when the bond to the front, viewed along the central bond, must be rotated clockwise to eclipse the bond to the rear. For further details, see section 1.6 of the recommendations on polypeptide conformation [6] or the recommendations on stereochemistry [7].

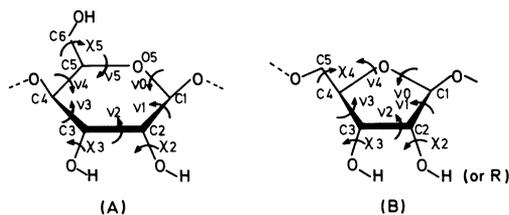
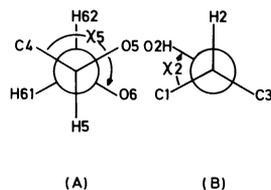
The reference atoms for these torsion angles are always ring atoms. The index of  $\nu$  refers to the first atom of the torsional bond, e.g. the ring oxygen for  $\nu_0$ , and C2 for  $\nu_2$ . Hence  $\nu_1$  has no meaning for 2-uloses.

#### 1.6.2. General Notation of Residue Conformation

In many studies a complete description of the sugar ring in terms of torsion angles is not feasible and may perhaps be unnecessary. An easier description is possible by means of the conventional notation of 5 and 6-membered rings [3]. In this notation the approximate conformation of the ring is indicated with a *italic*, capital letter, which designates the ring shape, and numerals, which distinguish between the variant forms of each shape, e.g.  ${}^4C_1$ .

### 1.7. Conformation of Side Groups

A ring substituent of a pyranosidic sugar unit, e.g. a hydroxyl group, may be designated as being axial or equatorial in a given conformation.

Fig. 2. Notation for torsion angles for (A) a hexapyranose and (B) a pentafuranose unit. The torsion angle ' $\nu$ ' are defined in Table 1. The exocyclic torsion angles ' $\chi$ ' are defined in section 1.7Fig. 3. Newman projections [7] showing the exocyclic torsion angle  $\chi$ . (A) View along the C5–C6 bond from C5 to C6, showing  $\chi_5$ ; (B) view along the C2–O2 bond from C2 to O2, showing  $\chi_2$ 

For the precise specification of the orientation of a polyatomic ring substituent, it is necessary to specify the torsion angle about the exocyclic bond. The reference atom in the ring is the carbon atom with the number one lower than that of the substituted carbon, unless substitution is on the anomeric carbon, when the ring oxygen is the reference atom. The reference atom in an exocyclic  $-\text{CH}_2\text{X}$  group is X.

The exocyclic torsion angle is denoted by  $\chi(\text{chi})$ , followed by the atoms to which it refers, e.g.  $\chi(C1-C2-O2-H)$ , or, if no ambiguity arises, simply by  $\chi_2$  (Fig. 2 and 3).

## 2. ORIENTATION OF THE GLYCOSIDIC LINKAGE

### 2.1. Designation of Bonds

The glycosidic bonds are part of the backbone of the polysaccharide. The glycosidic linkage is most easily described using the symbols for the monomeric units and the locants together with the anomeric descriptor, e.g. in cellobiose:  $\text{Glc}(i)(\beta 1-4)\text{Glc}(i-1)$ . If a more detailed description is necessary, this can be given in the form  $\text{C1}(i)-\text{O4}(i-1)-\text{C4}(i-1)$ . The limits of the  $i$ th residue are shown in Fig. 4.

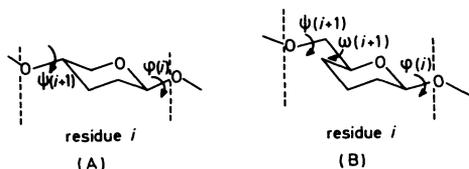


Fig. 4. Notation for the torsion angles specifying the orientation of glycosidic bonds for a pyranose unit (A) varying a ring hydroxyl that is glycosylated and (B) in which the glycosylated hydroxyl group is on an exocyclic carbon. The limits of the  $i$ th residue are indicated by the vertical dash lines. The residue number attached to  $\phi$ ,  $\psi$  and  $\omega$  is conventionally that of the glycosylating residue

Table 2. The torsion angle  $\phi$  defining part of the glycosidic bond

Unit	Torsion angle
Aldopyranose	O5( $i$ )–C1( $i$ )–OX( $i-1$ )–CX( $i-1$ )
Aldofuranose	O4( $i$ )–C1( $i$ )–OX( $i-1$ )–CX( $i-1$ )
Ulopyranose	O6( $i$ )–C2( $i$ )–OX( $i-1$ )–CX( $i-1$ )
Ulofuranose	O5( $i$ )–C2( $i$ )–OX( $i-1$ )–CX( $i-1$ )

## 2.2. Torsion Angles

Two torsion angles,  $\phi$  (phi) and  $\psi$  (psi), are required to describe the glycosidic bond from the  $i$ th unit to a carbon atom located in the ring of the ( $i-1$ )th unit. The angle  $\phi$  about the bond from the anomeric carbon to the oxygen that joins the two residues (Fig. 4) is specified using the ring oxygen as a reference atom (Table 2).

The torsion angle  $\psi$  about the bond from the glycosylated oxygen of the ( $i-1$ )th residue to a carbon of this residue (Fig. 4) uses the carbon atom one lower in numbering as a reference atom. Since this angle relates to the mode of attachment of the  $i$ th residue, it may be designated  $\psi(i)$ .

When the glycosidic bond does not involve a carbon atom located in the ring, but rather on a side chain, the angle,  $\omega$  (omega), around the next C–C bond is also of importance. For a 1→6 linked aldohexopyranose, this angle is the exocyclic angle  $\chi_5$  of the ( $i-1$ )th residue. Nevertheless it may be designated as  $\omega(i)$  (Fig. 4B) since it refers to attachment of the  $i$ th residue. The torsion angle is that of the atoms OX–CX–CX–1–CX–2, where X is the number of the carbon atom whose hydroxyl group if glycosylated.

## 3. HELIX CHARACTERISTICS

In the description of helices or helical segments the following symbols may be used:

$n$  = number of repeating units per turn

$h$  = unit height (translation per repeating unit along the helix axis)

$t = 360^\circ/n$  = unit twist (angle of rotation per repeating unit about the helix axis)

$p$  = pitch height of helix =  $n \cdot h$ .

Note. The repeating unit in a homopolysaccharide is a sugar residue. Heteropolysaccharides may possess repeating units of two or more residues, e.g.  $[-6\text{Glc}(\beta 1-4)\text{GalA}(\beta 1-)]_n$  [4].

A polysaccharide may be described accurately in terms of the polar atomic co-ordinates  $r_i$ ,  $\phi_i$ ,  $z_i$ , where for each atom  $i$ ,  $r_i$  is the radial distance from the helix axis, and  $\phi_i$  and  $z_i$  are the angular and height differences respectively, relative to a reference point. The reference point should be a symmetry element, or, if no symmetry element between polysaccharide chains is present, the C1 atom of a monosaccharide.

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