How to name atoms in phosphates, polyphosphates, their derivatives and mimics, and transition state analogues for enzyme-catalysed phosphoryl transfer reactions (IUPAC Recommendations 2016) (June 2018)

[Prepared by Gerry Moss]

The Protein Databank (PDB) includes many examples of phosphoryl transferase enzymes (EC 2.7) that contain phosphates or polyphosphates and their derivatives or mimics. A new IUPAC Recommendation published in Pure and Applied Chemistry* recommends how to identify and uniquely identify each atom of the phosphate or polyphosphate.

For monoesters the phosphorus atoms are identified as P^{A}, P^{B}, P^{G}, P^{D}, etc., starting from the ester end. For diesters the new recommendations explain how to determine which ester should be used to number the phosphorus atoms. When both a nucleic acid and a non-nucleic acid groups are present, the former takes precedence. If both are nucleic acid groups, then alphabetic order (A > C > G > T > U) is used.

With phosphate multi-esters, the phosphorus atoms are identified by the position at which they are attached. For example, in fructose 1,6-bisphosphate the two phosphorus atoms are named P^{1} and P^{6}. In polyphosphates the phosphorus atoms are named P^{A1}, P^{B1}, P^{G1}, etc.

The oxygen atom directly bonded to the sugar moiety is numbered using the number of the carbon it is attached to. For example, in ATP it is $O^{5'}$. The other three oxygen atoms of P^{A} are named O^{1A}, O^{2A} and O^{3A}, where O^{3A} bonds to P^{B}, O^{1A} is *pro*-*R*, and O^{2A} is *pro*-*S*.

When a terminal phosphoryl oxygen is replaced by sulfur, fluorine or nitrogen, the remaining two oxygen atoms are prochiral and are identified accordingly. For example, for ATP with a sulfur substitution, the sulfur atom is named S^{1G} and the two oxygens are O^{2G} (*pro*-*R*) and O^{3G} (*pro*-*S*).

Where the oxygen is hydrogen bonded to an adjacent amino acid (with bond length 3 Å), the primary sequence number of the amino acid is used to determine the oxygen numbering, as in O^{1A}, O^{2A}, O^{3A}, etc.

Other topics discussed in this recommendation include substitution by other atoms, trigonal bipyramidal phosphate transition state analogues, and metal coordination.

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