

On Pentacovalent Phosphorus Intermediates of Enzymatic Phosphoryl Transfer Reactions

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On the basis of ab initio molecular orbital calculations with a large basis set on extended models of the active site (cf.

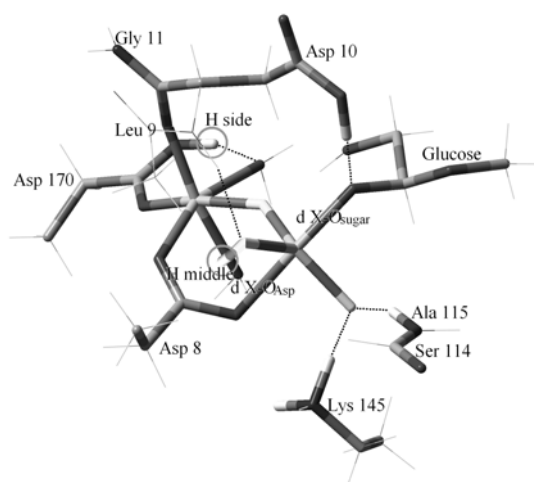


Figure) we question the existence of a symmetric trigonal bipyramidal oxyphosphorane species assumed to be present in the complex of phosphoglucomutase with glucose-6-phosphate substrate. In contrast to this suggestion by Lahiri et al. [1], we located two flat, distorted tetragonal structures on the potential surface, which may represent both the initial and final states of the reaction. Our calculations give also support to another interpretation [2] stating that instead of an oxyphosphorane species a $\text{MgF}_3(-)$ transition-state analogue binds to the active site. Both alternative structures provide electron density patterns similar to that obtained from X-ray diffraction experiments.

[1] S.D. Lahiri, G. Zhang, D. Dunaway-Mariano, and K.N. Allen, *Science* **299**, 2067 (2003).

[2] G.M. Blackburn, N.H. Williams, S.J. Gamblin, S.S. Smerdon, *Science* **301**, 1184c (2003).