Abstract

Subject: *Determination of structure and dynamics of biomolecules by theoretical calculations of NMR spectroscopic parameters*

Author: Ladislav Benda, ladislav.benda@gmail.com

Department/Institute: Institute of Organic Chemistry and Biochemistry, AS CR

Supervisor: Dr. Vladimír Sychrovský, Institute of Organic Chemistry and Biochemistry, AS CR, vladimir.sychrovsky@uochb.cas.cz

Abstract: This doctoral work was focused on theoretical modeling of nuclear magnetic resonance (NMR) parameters in peptides and nucleic acids. Dependences of NMR parameters on molecular structure and solvation were primarily modeled. Great emphasis was put on the comparison of the calculated data with the NMR experiment. The molecular models studied included the L-alanyl-L-alanine di-peptide (AA) and the phosphate group of nucleic acid backbone. Conformations of all three charged forms of AA in solution were determined and the respective pH-induced changes of experimental NMR chemical shifts and nuclear spin–spin coupling constants were explained. Dependences of NMR cross-correlated relaxation rates on the AA backbone geometry were calibrated. The ^{31}P NMR parameters in nucleic acid phosphate were systematically calculated in dependence on the backbone conformation and the phosphate solvation pattern. Qualitative rules for the structural interpretation of two-bond nuclear spin–spin couplings $^2J_{\mathrm{PC}}$ were proposed. Changes in the ^{31}P NMR parameters induced by the coordination of the Mg^{2+} cation to the nucleic acid phosphate were calculated. Specific low-frequency bands observed in the Raman spectra of aqueous Mg^{2+} salt solutions were successfully simulated.

Keywords: quantum-chemistry calculations, NMR parameters, peptides, nucleic acids, metal ions