

THEORETICAL INSIGHTS INTO THE STRUCTURE AND NMR SPIN-SPIN COUPLING CONSTANTS IN BIOLOGICALLY ACTIVE SACCHARIDES

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High-resolution NMR spectroscopy, combined with theoretical analysis is one of the most important tools for the determination of the 3D structure and dynamics of carbohydrate molecules in solution. The 3D structural NMR analysis relies heavily on indirect spin-spin coupling constants and NOEs. However, the correct interpretation of these spectroscopic parameters also depends also on the theoretical analysis of the carbohydrate molecular structures. Density Functional Theory (DFT) method is currently the method of choice for the determination of molecular structures and the calculation of NMR parameters.

This paper presents several examples of theoretical analyses and calculations of spin-spin coupling constants on important biological carbohydrates – including dermatan sulphate, chondroitin sulphate, keratan sulphate and heparin. These saccharides are highly charged molecules and their structures are strongly influenced by complex electronic properties. Determining the correct molecular structures in aqueous solutions is therefore a challenge for computational methods. The same is true for the spin-spin coupling constants – the data presented show that direct calculations of the three-bond coupling constants ($^3J_{\text{H-H}}$ or $^3J_{\text{C-H}}$) by DFT often give better data than the application of the parametrized relationships between the $^3J_{\text{X-H}}$ magnitudes and the torsion angles. It is shown that geometry optimization using DFT with hybrid functionals and the 6–311++G(2d,2p) basis set, together with proper evaluation of the solvent effect, can yield sufficiently accurate structural and NMR data for biologically active saccharides.

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