FLUORINATION AND DEOXYGENATION AS CHEMICAL TOOLS TO STUDY THE CONFORMATIONAL PREFERENCES OF HEXOPYRANOSES: A JOURNEY FROM GAS PHASE TO SOLUTION

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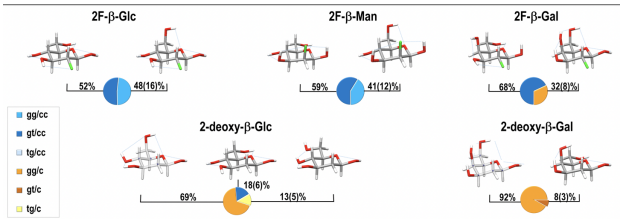

The 3D-arrangement of carbohydrates and, particularly, the orientation of their hydroxymethyl groups are structural features crucial for their biological activities. In this work, we investigate the influence of water on the conformational preferences of model hexopyranoses by performing a comprehensive analysis in the gas phase via microwave spectroscopy[a,b] of different fluorinated and deoxygenated carbohydrate analogues and comparing the results with those obtained in solution using a combination of NMR data and molecular dynamics simulations. The gg conformation is stabilized in the gas phase by intra molecular HBs that lock this conformation when oriented clockwise. However, and contrary to previously reported data, the conformation of the hydroxymethyl group in D-gluco and D-mannopyranose series follows a similar tendency in the gas phase and in solution, indicating the importance of stereo electronic and minimizing the importance of competing water molecules against stabilizing intra molecular HBs.

[a]C. Calabrese, I. Uriarte, A. Insausti, M. Vallejo-Lopez, F. J. Basterretxea, S. A. Cochrane, B. G. Davis, F. Corzana and E. J. Cocinero *ACS Cent. Sci.*, **6**, 293-303, 2020.

[b]E. J. Cocinero, A. Lesarri, P. Ecija, F. J. Basterretxea, J.-U. Grabow, J. A. Fernandez, F. Castaño *Angew. Chem. Int. Ed.*, **51**, 3119, 2012.