Conformational studies of gas-phase ribose and 2-deoxyribose by density functional, second order PT and multi-level method calculations: the pyranoses, furanoses, and open-chain structures.

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Streszczenie

We present an extensive computational study of a complex conformational isomerism of two gas phase pentoses of biological and potential astrobiological importance, d-ribose and 2-deoxy-d-ribose. Both cyclic (α- and β-pyranoses, α- and β-furanoses) and open-chain isomers have been probed using second order Møller–Plesset perturbation theory (MP2), M06-2X density functional, and multi-level G4 methods. This study revealed a multitude of existing minima structures. Numerous furanose conformers found are described with the Altona and Sundaralingam pseudorotation parameters. In agreement with the recent gas-phase microwave (MW) investigation of Cocinero et al., the calculated free ribose isomers of lowest energy are the two β-pyranoses with the $^{1}C_{4}$ and $^{4}C_{1}$ ring chair conformations. Both β-pyranoses lie within 0.9 kJ/mol in terms of Δ*G*(298 K) (G4), thus challenge the computational methods used to predict the ribose global minimum. The calculated most favoured ribofuranose is the α-anomer having the twist $^{2}T_{1}$ ring conformation, put 10.4 kJ/mol higher in Δ*G* than the global minimum. By contrast with d-ribose, the lowest energy 2-deoxy-d-ribose is the α-pyranose, with the most stable 2-deoxy-d-furanose (the α-anomer) being only 6.2 kJ/mol higher in free energy. For both pentoses, the most favoured open-chain isomers are significantly higher in energy than the low-lying cyclic forms. A good overall agreement is observed between the M06-2X and MP2 results in terms of both the existing low-energy minima structures and intramolecular H-bonding geometrical parameters. The natural orbital analysis confirms the occuring of the *endo*- and *exo*-anomeric effects and maximization of intramolecular H-bonding in the lowest-lying pyranoses and furanoses of both sugars.