

Rotational Spectrum and Conformational Preferences of the 6-Carbon Cetose Sugar of Fructose

E. J. Cocinero^a, A. Lesarri^b, P. Écija^a, A. Cimas^c, B. G. Davis^d, F. J. Basterretxea^a, J. A. Fernández^a, F. Castaño^a,

^a Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Ap. 644, 48080 Bilbao (Spain),

^b Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid (Spain), *E-mail: lesarri@qf.uva.es*

^c Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement, Université d'Évry val d'Essonne, 91025, Evry (France)

^d Chemistry Department, Oxford University, OX1 3TA (UK)

Last year we reported the rotational spectrum of the pentose sugar ribose [1]. The molecule exhibits a large conformational variety, with six conformers confined within a small energy window of ca. 4.6 kJ mol⁻¹. In all cases a six-membered pyranose form was found, with β -anomers slightly more stable and a distribution of both ¹C₄ and ⁴C₁ rings.

In order to check how the conformational equilibrium is affected by the introduction of an additional carbon atom and a cetose group we now report the rotational spectrum of fructose [2]. Similarly to the previous study the sample was vaporized using a ps Nd-YAG laser and probed in a supersonic expansion with a Balle-Flygare-type Fourier-transform microwave spectrometer.

The rotational spectrum revealed that fructose is essentially locked around a most stable pyranose conformation with a ²C₅ ring configuration (equivalent to ¹C₄ in aldoses). The structure of the molecule was derived from the rotational constants of the parent and seven additional ¹³C and D isotopologues, some of them measured in natural abundance. The enhanced stability of the observed conformation is attributed to a cooperative network of five O-H...O intramolecular hydrogen bonds. Exo and endo anomeric effects are consistent with the observed structure. A comparison with ribose and deoxyribose will also be presented.

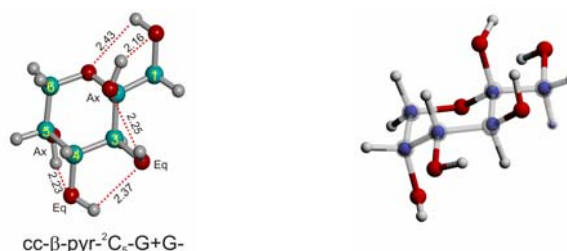


Figure 1. Intramolecular hydrogen bonds (red dots, angström) in the most stable conformation of fructose (cc- β -pyr-²C₅-G+G-, left) and comparison between the experimental carbon skeleton (inner blue spheres) and the best matching ab initio structure (right).

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

[2] E. J. Cocinero, A. Lesarri, P. Écija, A. Cimas, B. G. Davis, F. J. Basterretxea, J. A. Fernández, F. Castaño, *J. Am. Chem. Soc.*, **2013**, *135*, 2845.