

AIM and NBO analyses on hydrogen bonds formation in sugar-based surfactants (α/β -D-mannose and *n*-octyl- α/β -D-mannopyranoside): a density functional theory study

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Density functional theory calculations on α/β -D-mannose (α/β -D-Man) and the corresponding glycosides of *n*-octyl- α/β -D-mannopyranoside (C_8O - α/β -D-Man) were carried out for geometrical optimisation and stability predictions at the B3LYP/6-31G level of theory. These compounds are related anomericly, since they differ by only the orientation of the hydroxyl group at the C1 position. The aim of this study is to investigate the effect of the hydroxyl group's orientations (axial vs. equatorial) at the C1 position on the intra-molecular interactions and the conformational stability of these isomers. The structural parameters of X-H...Y intra-molecular hydrogen bonds were analysed, while the nature of these bonds was considered using the atoms-in-molecules (AIM) approach. Natural bond orbital (NBO) analysis was used to determine bond orders and the effective non-bonding interactions. We have also reported thermodynamic properties and the electronic properties, such as the highest occupied molecular orbital, lowest unoccupied molecular orbital, ionisation energy, electron affinity, electronic chemical potential, chemical hardness, softness and electrophilicity index in the gas phase for all compounds. These results showed that while α -anomers possess only one intra-molecular hydrogen bond, β -anomers possess two intra-molecular hydrogen bonds, which further confirms the anomalous stability of the latter in the self-assembly phenomena.

Keywords: mannose; hydrogen bonding; density functional theory; atoms in molecules theory; natural bond orbital analysis

Introduction

Like glucose, mannose is classified as a simple sugar from the aldohexose series of the carbohydrate family.[1] Mannose are generally found in a number of fruits (including cranberries),[2] and dextro mannose (D-mannose) is thought to keep bacteria from remaining on the walls of the urinary tract, which is why it is used to prevent and treat urinary tract infections.[3] Mannose and glucose are different from each other since they are epimers at the C2 position but, surprisingly, many of their physical behaviours are different.[4] In addition, there are two possible stereoisomers at the C1 position, two possible orientations (axial/equatorial) of the hydroxyl group, thus resulting in two anomers, namely, α -D-mannose and β -D-mannose. Mannose is chiral in the ring form, but achiral in the linear form. Physically, α -D-mannose is a sweet-tasting sugar, while β -D-mannose, on the other hand, tastes bitter. A pure solution of α -D-mannose, however, loses its sweetness over time. When monosaccharides are dissolved in water, they undergo reversible ring-opening reactions, so the ring forms exist in equilibrium with the linear forms. The C1 is then free to rotate (mutarotation), and β -D-mannose can then form

when it changes back into the ring form. When equilibrium is reached, there is more of the β -isomer than the α -isomer, because in the β -isomer, the hydroxyl on the C1 is in a more stable (equatorial) position.[5] The physical and chemical properties of these monosaccharides depend upon the molecular shape and the extent of hydrogen bonding interactions. By attaching a lipid to sugar moiety, it results in a glycolipid molecule, whose solubility and other physical properties are substantially changed. A glycolipid molecule possesses a water-loving polar head group linked to a water-hating hydrophobic alkyl tail. This dichotomy within the glycolipid molecule is an enabling feature, which drives the molecules to form many interesting self-assembly structures, hence resulting in liquid-crystalline properties, both via thermal and solvent effects. The ability of these materials to form a diverse range of self-assembly structures thermotropically as well as lyotropically paves the way to many potential applications in nano-and biotechnology.[6,7] Compared to many conventional ionic surfactants, glycolipids are biodegradable, non-toxic and may be derived from many common and cheap natural resources.[8] Glycolipids are commonly found in nature, especially in cell

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