MONOSACCHARIDE PES

The conformational space of monosaccharides is amazingly complex. If we consider just the pyranose form, the ring can in principal exist as a chair, a half-chair, skew (or twist boat) and boat form, for a total of 38 puckering configurations. Layer on top of this the axial and equatorial positions of the hydroxyl and methylhydroxyl groups, and then the rotamers of these substituents, and one is faced with a dauntingly vast space. It is just this space that Beckham and co-workers[1] take on for α- and β-glucose, β-xylose, β-mannose and β-acetylglucosamine.

For each sugar, and for each of the 38 puckering configurations, full rotamer scans for each of the substituents led to 27,702 conformations of each of the four monosaccharides, and 36,936 conformations of β-acetylglucosamine. This totals to over 123,000 geometry optimizations that were carried out at M06-2x/6-31G(d). Then taking the structures within 5 kcal mol^{-1} of the lowest energy structure for each pucker, they reoptimized at M06-2X/6-31+G(d,p).

Pruning once again those structures that were above 5 kcal mol^{-1} of the minimum, they performed CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(2df,p) computations. What a tour de force!

The results of these conformational space surveys are not terribly exciting. The substituents do make a difference in dictating the most and least favorable structures and the activation barriers for interconversion of ring forms.

These PESs will be quite useful in understanding carbohydrate conformations and the role these may play in their chemistry. But the point of bringing this paper to your attention is the tremendously complex, detailed PES that is uncovered, representing the scale of what can be done with modern computers and modern algorithms.

Source: http://comporgchem.com/blog/?p=2999