

MONOSACCHARIDES BENCHMARK

A comprehensive evaluation of how different computational methods perform in predicting the energies of monosaccharides comes to some very interesting conclusions. Sameera and Pantazis¹ have examined the eight different aldohexoses (allose, alltrose, glucose, mannose, gulose, idose, galactose and talose), specifically looking at different rotomers of the hydroxymethyl group, α - vs. β -anomers, pyranose vs. furanose isomers, ring conformations (1C_4 vs skew boat forms), and ring vs. open chain isomers. In total, 58 different structures were examined. The benchmark computations are CCSD(T)/CBS single point energies using the SCS-MP2/def2-TZVPP optimized geometries. The RMS deviation from these benchmark energies for some of the many different methods examined are listed in Table 1.

Table 1. Average RMS errors (kJ mol^{-1}) of the 58 different monosaccharide structures for different computational methods.

method	average RMS error
LPNO-CEPA	0.71
MP2	1.27
SCS-MP2	1.55

<i>m</i> PW2PLYP-D	2.02
M06-2x	2.03
PBE0	3.62
TPSS	4.78
B3LYP-D	4.79
B3LYP	5.06
HF	6.69
B97D	7.66

Perhaps the most interesting take-home message is that CEPA, MP2, the double hybrid methods and M06-2x all do a very good job at evaluating the energies of the carbohydrates. Given the significant computational advantage of M06-2x over these other methods, this seems to be the functional of choice! The poorer performance of the DFT methods over the *ab initio* methods is primarily in the relative energies of the open-chain isomers, where errors can be on the order of 10-20 kJ mol⁻¹ with most of the functionals; even the best overall methods (M06-2x and the double hybrids) have errors in the relative energies of the open-chain isomers of 7 kJ mol⁻¹. This might be an area of further functional development to probe better treatment of the open-chain aldehydes vs. the ring hemiacetals.

Source: <http://comporgchem.com/blog/?p=2436>