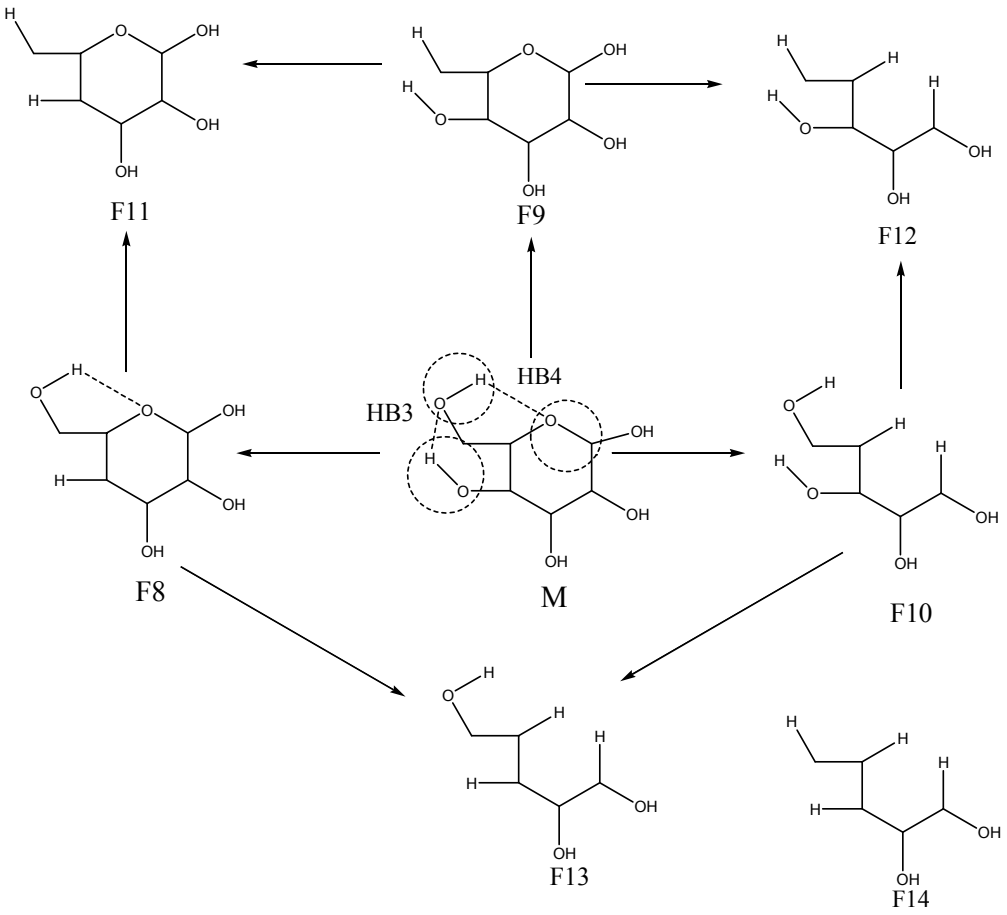
Supplementary Material

Supplementary Table 1: Intramolecular O-H…O hydrogen bond angles (in degree) in various sugar molecules optimized at MP2/6-311++G(2d,2p) level. See text and Fig. 2 for details.

Molecules	OH1···OH2	OH2···OH3	OH3···OH4	OH4···OH6	OH6···O5	OH1···OH3	OH2···O5	OH2···OH4
α-D-glucose	111.4	105.7	107.9	135.8	-	-	-	-
β-D- glucose	101.4	104.6	106.5	-	106.7	-	-	-
α-D-mannose	-	113.4	109.3	136.4	-	-	110.1	-
β-D-mannose	111.0	112.4	109.0	135.8	-	-	-	-
α-D-allose	103.6	98.3	107.7	103.1	104.4	141.6	-	-
β-D-allose	105.8	107.4	114.1	-	106.8	-	-	-
α-D-galactose	113.9	109.3	112.5	145.1	104.4	-	-	-
β-D-galactose	111.4	107.4	113.4	146.8	105.0	-	-	-
α-D-altrose	-	-	114.5	139.4	-	144.5	112.5	-
β-D-altrose	112.1	-	108.2	100.7	106.4	-	-	-
α-D-talose	-	108.7	94.9	144.1	103.9	-	-	140.8
β-D-talose	116.0	106.0	96.9	144.7	103.1	-	-	141.8
α-D-gulose	115.9	96.6	-	146.3	104.8	142.4	-	-
β-D-gulose	105.0	110.1	-	145.7	106.3	-	-	-
α-D-idose	-	-	-	145.4	104.2	141.4	-	144.1
β-D-idose	115.7	-	-	146.5	104.3	-	-	143.6



Supplementary Figure 1: Schematic fragmentation schemes for a prototype sugar molecule (shown as M) for estimating hydrogen bond energies of HB3 and HB4, the latter involving ring O-atom. See text for details of fragmentation and H-bond energy estimates.