Electronic Supplementary Information

for

The hydration of glucose: the local configurations in sugar–water hydrogen bonds

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Table S1: computational details

Table S2: the conformational properties of the staggered hydroxymethyl groups in my *ab initio* molecular dynamics simulations

Fig. S1: three staggered hydroxymethyl rotational conformations

Fig. S2: the dipole moment of water molecules in the first hydration shell

Supplementary Tables

Table S1. Computational details.

Simulation	Initial conformation	Cut-off energy (Ry)	Fictitious mass (au)	Time step (fs)	Time length of microcanonical simulation (ps)
			The β anomer		
1	G^+	70	400	0.0968	8.2
2	G^+	70	400	0.0968	6.0
3	G^+	70	400	0.0968	6.0
4	G^-	80	340	0.0822	10.0
5	G^-	70	400	0.0968	6.0
6	T	70	400	0.0968	6.0
7	T	70	400	0.0968	6.0
			The α anomer		
8	G^+	70	400	0.0968	6.0
9	G^+	70	400	0.0968	6.0
10	G^-	70	400	0.0968	6.0
11	G^-	70	400	0.0968	6.0
12	G^-	80	340	0.0822	10.0
13	T	70	400	0.0968	6.0
14	T	70	400	0.0968	6.0

Table S2. The conformational properties of the staggered hydroxymethyl groups in my *ab initio* molecular dynamics simulations

	O5–C5–C6–O6		C5–C6–O6–H6	
	Average (deg)	Rotamer	Average (deg)	Rotamer
	The β anomer			
1	—	G^{+}/T	—	g^{+}/t/g^{-}
2	62.7	G^{+}	181.5	t
3	75.0	G^{+}	−59.2	g^{-}
4	−68.4	G^{-}	66.8	g^{+}
5	−59.7	G^{-}	−132.6	t
6	129.1	T	183.4	t
7	152.5	T	−81.7	g^{-}
	The α anomer			
8	61.3	G^{+}	−85.0	g^{-}
9	59.5	G^{+}	−138.1	t
10	−58.9	G^{-}	−85.9	g^{-}
11	−66.4	G^{-}	70.7	g^{+}
12	−60.8	G^{-}	75.9	g^{+}
13	166.0	T	137.8	t
14	—	G^{+}/T	—	g^{-}/t

I refer to the rotamers associated with the C5–C6–O6–H6 torsion angle as g+ (≈+60°), g− (≈−60°), and t (≈180°). If there existed two or three distinct rotamers in a simulation, then the average value is not shown because it is almost meaningless; instead, the rotamers that actually appeared in that simulation are simply reported, being separated by the slash. The average value for the O5–C5–C6–O6 angle in **6** (129.1 deg) deviates significantly from its ideal value (180 deg), but the conformation is still viewed as the T rotamer; the deviation of this kind is discussed in my previous work [T. Suzuki, H. Kawashima and T. Sota, *J. Phys. Chem. B*, 2006, **110**, 2405].

Supplementary Figures

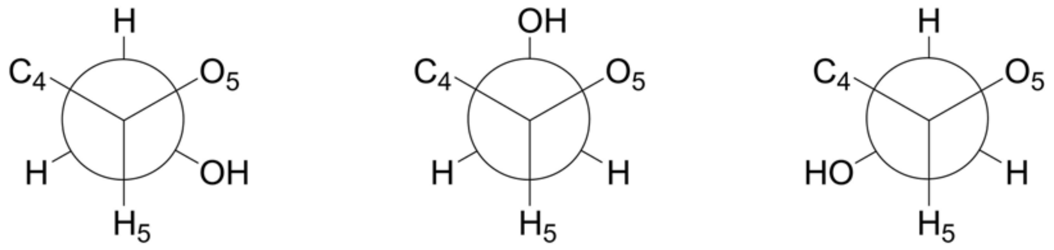

Fig. S1. The three staggered hydroxymethyl rotational conformations. From left to right: G^+, G^-, and T. (These are also referred to as *gt*, *gg*, and *tg* in the literature.)

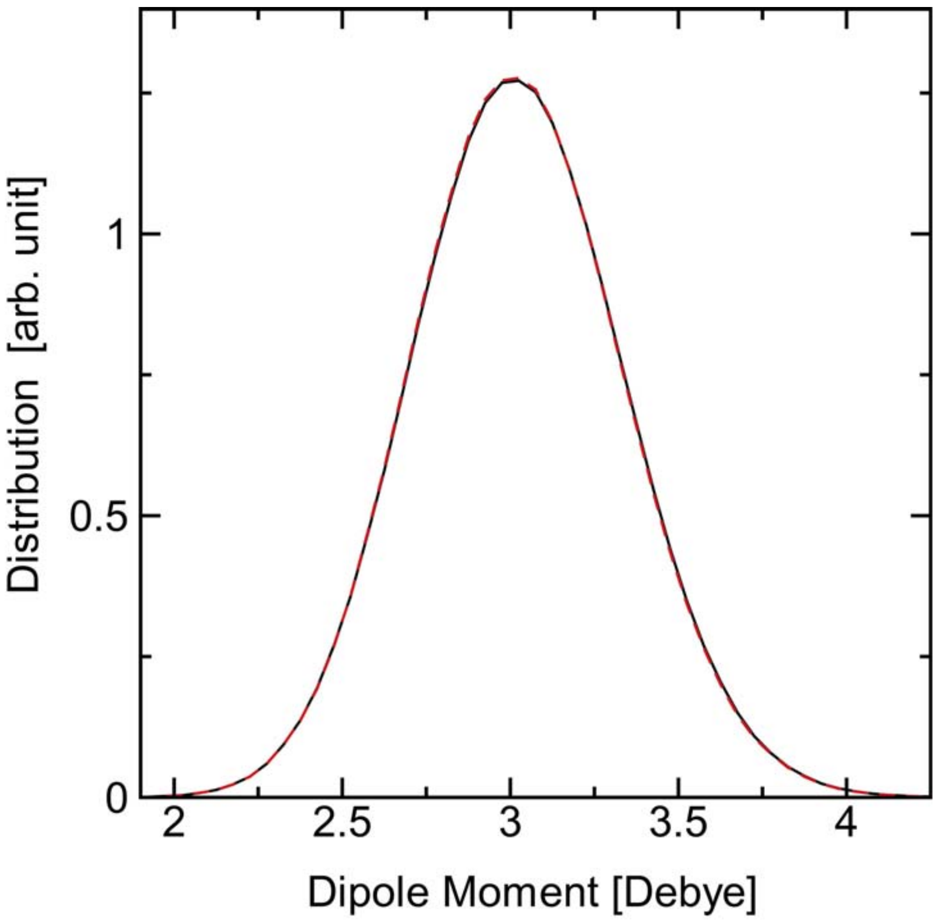

Fig. S2. The dipole moment of water molecules in the liquid: black solid line, the dipole moment of water molecules that formed H-bonds with water molecules (including water molecules forming H-bonds with first-hydration-shell water molecules); red dashed line, the dipole moment of water molecules that formed H-bonds neither with the glucose molecule nor with first-hydration-shell water molecules. The results show that the two distributions are almost identical. For this reason, it is relevant to regard those water molecules which form H-bonds only with water molecules as *bulk* water molecules for my main objective.