Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Anionic Ribose Related Species Explored Through PES Experiments, DFT Calculations, and Through Comparison with Anionic Fructose Species

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More low lying isomers of ribose$^-$, (ribose-H)$^-$, and (ribose-H_2O)$^-$ anions, as well as their corresponding neutrals, are summarized in Figures S4 to S6 as well as Figures S10 to S15 in the Supporting Information. Note that the figure numbers in the S.I. document are related to those of the text figures, as for example Figure S4 ⇔ Figure 4.

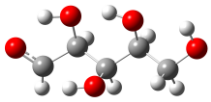
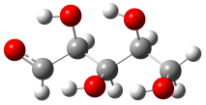
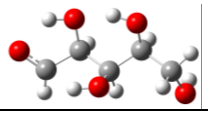
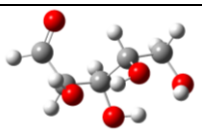
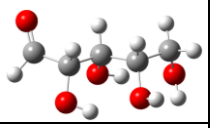
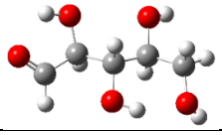
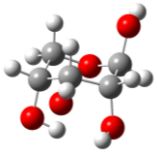
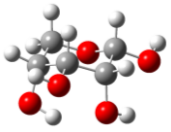
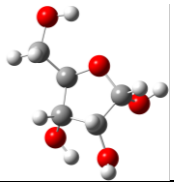
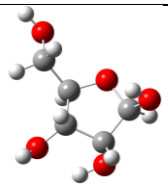
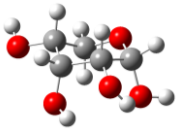
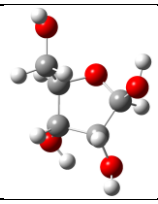
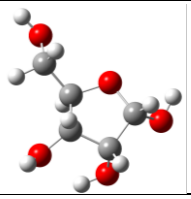
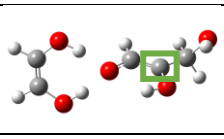
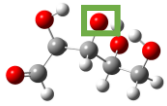
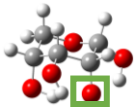
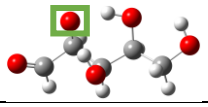
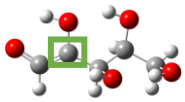
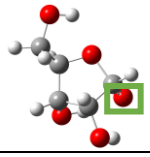
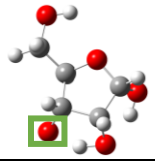
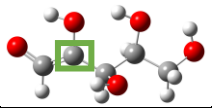
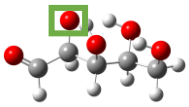
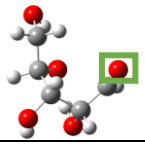
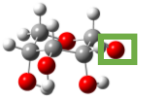
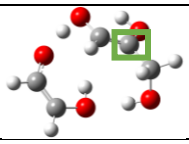
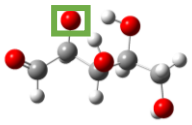
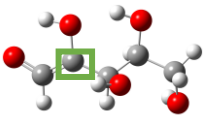
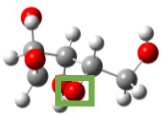
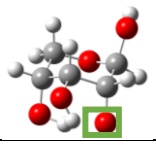
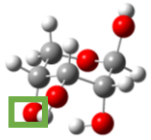
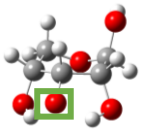
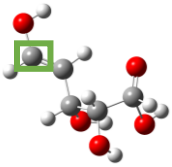
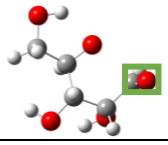
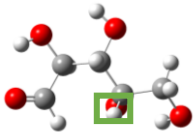
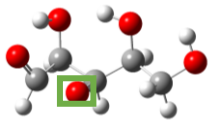
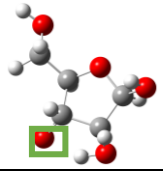
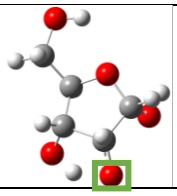
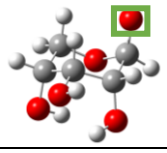
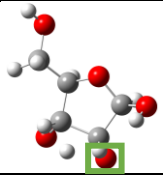
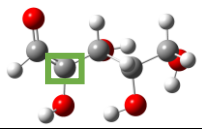
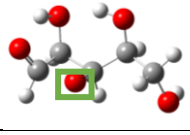
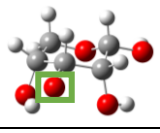
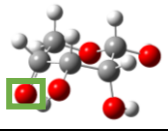
Optimized Anionic structure					
Structural Polymorphism	open chain	open chain	open chain	open chain	open chain
ΔE (eV)	0.00	0.01	0.17	0.25	0.58
VDE (eV)	**1.64**	**1.73**	**1.51**	**1.06**	**0.17**
Optimized Anionic structure					
Structural Polymorphism	open chain	β-pyranose ($^1C_4$-chair)	α-pyranose ($^1C_4$-chair)	α-furanose (C_2 – endo)	β-furanose (C_3 – endo)
ΔE (eV)	0.78	0.80	0.81	0.81	0.87
VDE (eV)	**0.11**	**-0.25**	**-0.17**	**-0.03**	**-0.03**
Optimized Anionic structure					
Structural Polymorphism	α-pyranose ($^4C_1$-chair)	β-pyranose ($^4C_1$-chair)	β-furanose (C_2 – endo)	α-furanose (C_3 – endo)	
ΔE (eV)	0.89	0.91	0.98	1.04	
VDE (eV)	**-0.18**	**-0.29**	**-0.19**	**-0.10**	

Figure S4 Optimized geometries of the typical low lying anionic isomers of ribose$^-$ based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The structural presentation is the same as those in the main text Figures 4-6. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure					
Structural Polymorphism	open chain (C) - (4C)H	open chain (C) - (3)H	α-pyranose ($^1C_4$-chair) - (2)H	open chain (A) - (2)H	open chain (B) - (2C)H
ΔE (eV)	0.00	0.11	0.22	0.25	0.27
VDE (eV)	**3.16**	**4.47**	**3.75**	**3.91**	**2.74**
Optimized Anionic structure					
Structural Polymorphism	α-furanose (C_2 – endo) - (1)H	α-furanose (C_2 – endo) - (3)H	open chain (A) - (2C)H	open chain (B) - (2)H	β-furanose (C_3 – endo) - (1)H
ΔE (eV)	0.27	0.27	0.28	0.29	0.29
VDE (eV)	**3.79**	**3.83**	**2.64**	**3.93**	**3.96**
Optimized Anionic structure					
Structural Polymorphism	α-pyranose ($^1C_4$-chair) - (1)H	open chain (A) - (4C)H	open chain (C) - (2)H	open chain (C) - (2C)H	open chain (C) - (4)H
ΔE (eV)	0.35	0.42	0.43	0.45	0.48
VDE (eV)	**3.72**	**2.99**	**3.76**	**2.54**	**4.01**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (2)H	β-pyranose ($^1C_4$-chair) - (4)H	β-pyranose ($^1C_4$-chair) - (3)H	α-furanose (C_2 – endo) - (5C)H	β-furanose (C_3 – endo) - (1)H
ΔE (eV)	0.52	0.52	0.56	0.59	0.64
VDE (eV)	**3.31**	**3.32**	**3.67**	**3.50**	**3.67**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) - (4)H	open chain (A) - (3)H	β-furanose (C_3 – endo) - (3)H	α-furanose (C_2 – endo) - (2)H	β-pyranose ($^1C_4$-chair) - (1)H
ΔE (eV)	0.73	0.75	0.78	0.79	0.79
VDE (eV)	**3.42**	**4.17**	**3.28**	**3.28**	**3.20**
Optimized Anionic structure					

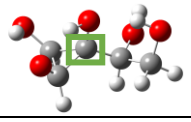
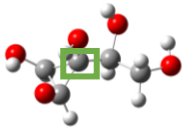
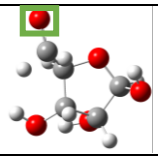
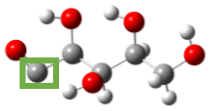
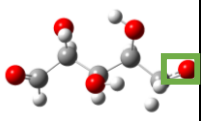
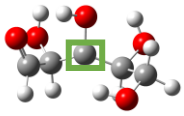
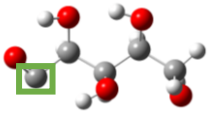
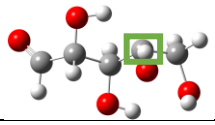
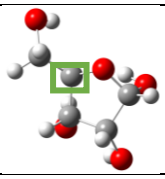
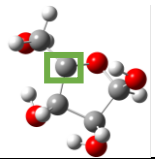
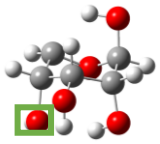
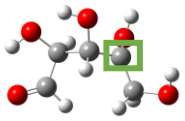
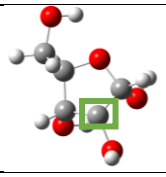
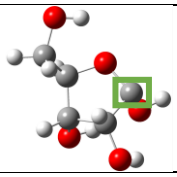
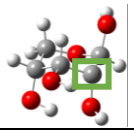
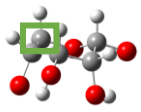
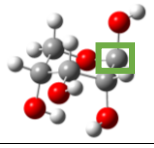
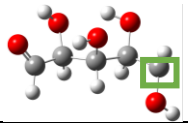
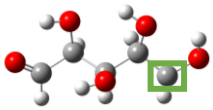
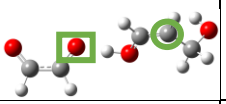
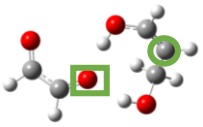
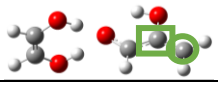
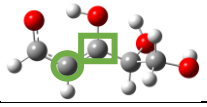
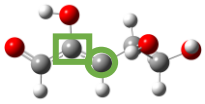
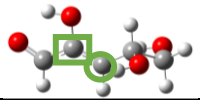
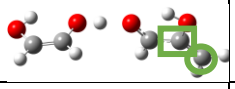
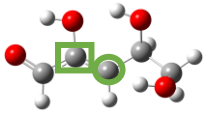
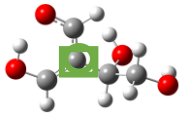
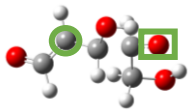
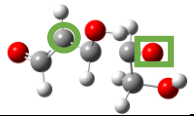
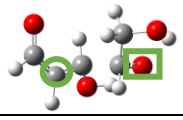
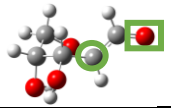
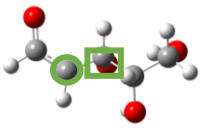
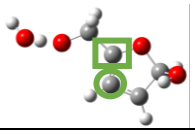
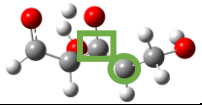
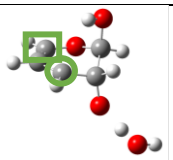
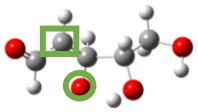
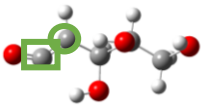
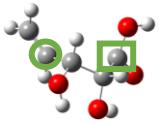
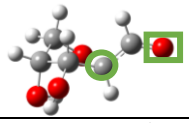
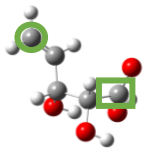
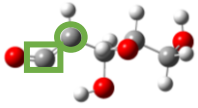
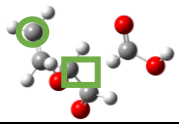
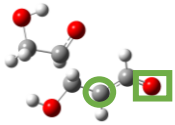
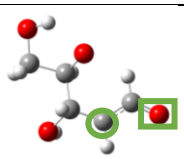
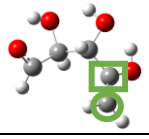
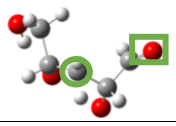
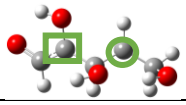
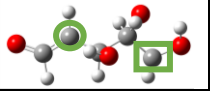
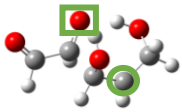
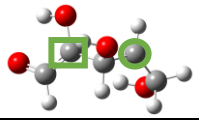
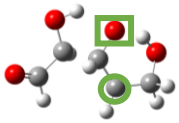
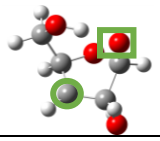
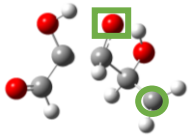
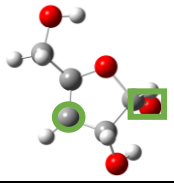
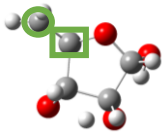
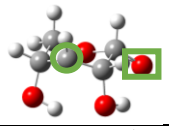
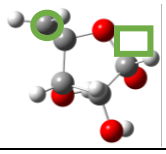
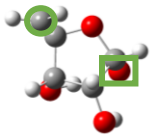
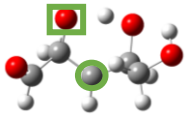
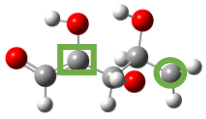
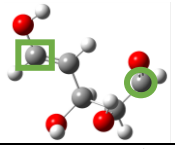
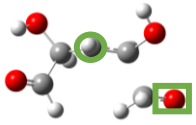
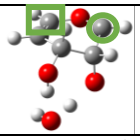
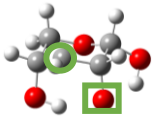
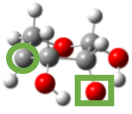
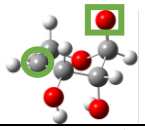
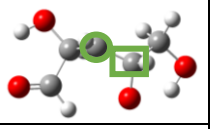
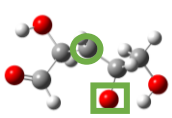
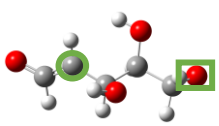
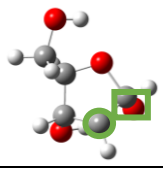
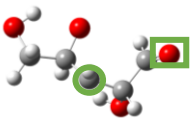
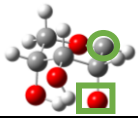
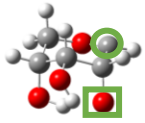
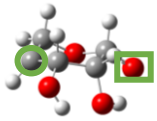
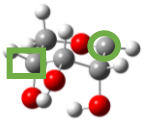
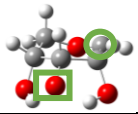
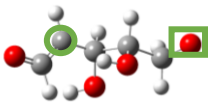
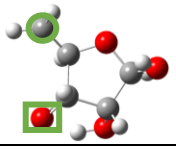
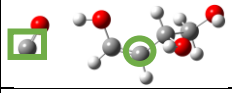
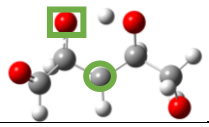
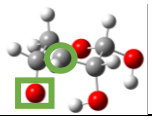
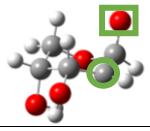
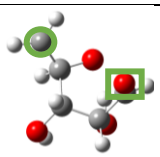
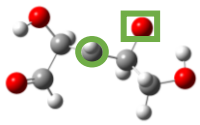
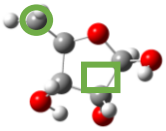
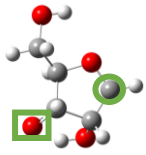
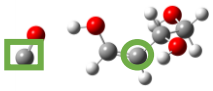
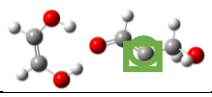
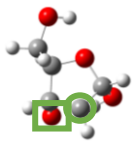
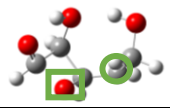
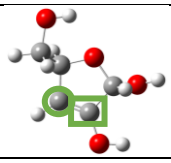
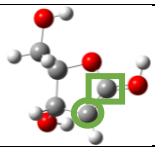
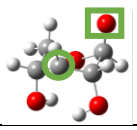
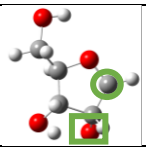
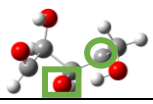
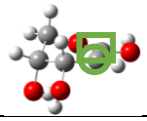
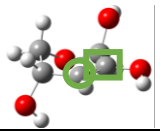
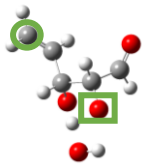
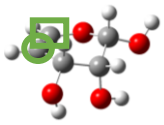
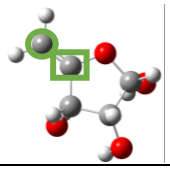
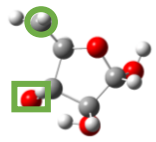
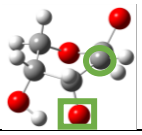
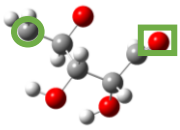
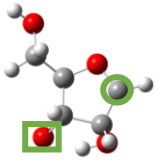
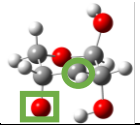
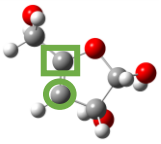
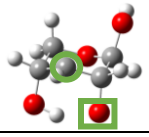
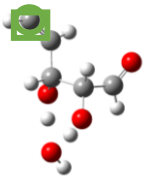
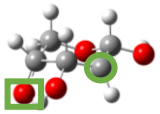
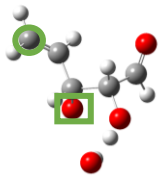
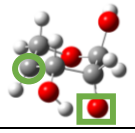
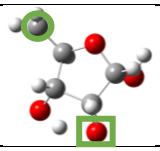
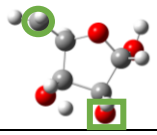
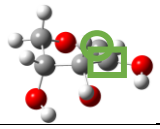
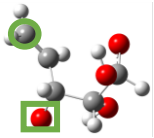
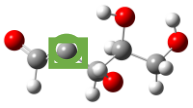
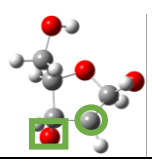
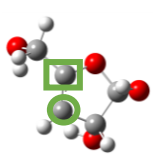
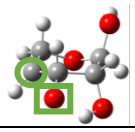
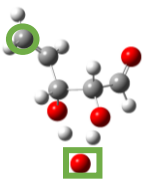
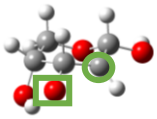
Structural Polymorphism	β-furanose (C_3 – endo) - (2)H	open chain (D) - (2C)H	open chain (C) - (3)H	α-pyranose ($^1C_4$-chair) - (3)H	α-pyranose ($^1C_4$-chair) - (4)H
ΔE (eV)	0.80	0.86	0.94	1.14	1.17
VDE (eV)	**3.40**	**2.25**	**4.06**	**2.83**	**2.81**
Optimized Anionic structure					
Structural Polymorphism	open chain (B) - (C3)H	open chain (A) - (C3)H	β-furanose (C_3 – endo) - (5)H	open chain (A) - (1C)H	open chain (A) - (5)H
ΔE (eV)	1.26	1.30	1.36	1.43	1.52
VDE (eV)	**3.41**	**3.53**	**2.71**	**2.47**	**2.58**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) - (3C)H	open chain (C) - (1C)H	open chain (D) - (4C)H	α-furanose (C_2 – endo) - (4C)H	β-furanose (C_3 – endo) - (4C)H
ΔE (eV)	1.56	1.60	1.73	1.77	1.78
VDE (eV)	**2.40**	**2.35**	**2.60**	**2.27**	**2.16**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (5C)H	open chain (B) - (4C)H	α-furanose (C_2 – endo) - (2C)H	α-furanose (C_2 – endo) - (1C)H	β-pyranose ($^1C_4$-chair) - (2C)H
ΔE (eV)	1.83	2.05	2.21	2.21	2.23
VDE (eV)	**2.29**	**1.74**	**1.75**	**2.24**	**2.01**
Optimized Anionic structure					
Structural Polymorphism	α-pyranose ($^1C_4$-chair) - (5C)H	β-pyranose ($^1C_4$-chair) - (1C)H	open chain (C) - (C5)H	open chain (A) - (C5)H	
ΔE (eV)	2.24	2.67	2.94	3.04	
VDE (eV)	**1.93**	**1.54**	1.06	0.64	

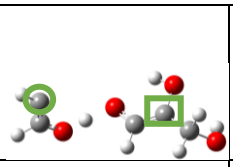
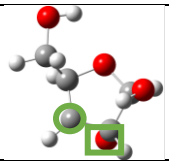
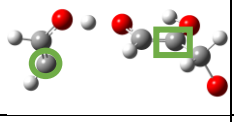
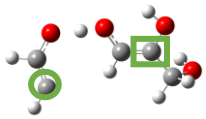
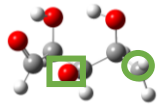
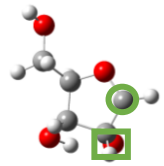
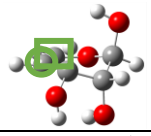
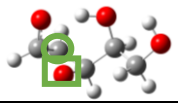
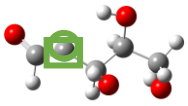
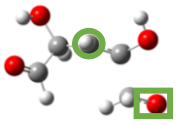
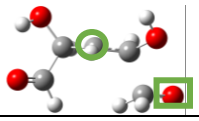
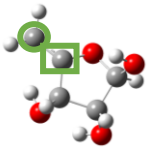
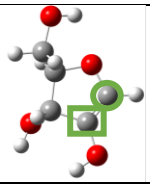
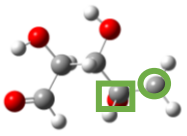
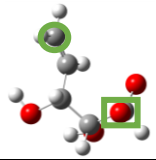
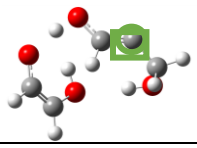
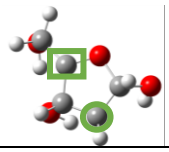
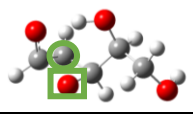
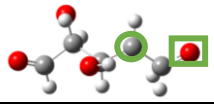
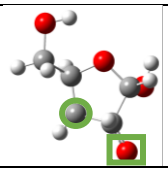
Figure S5 Optimized geometries of the typical low lying anionic isomers of (ribose-H)$^-$ based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates loss of hydrogen at the indicated position. The green labels indicate loss of hydrogen from carbon atom. The structural presentation is the same as those in the main text Figures 4-6. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure					
Structural Polymorphism	open chain (C) - (2)H - (4)OH	open chain (A) – [(2)H + (4)OH]	open chain (C) - (4C)H - (5)OH	open chain (A) - (3C)H - (2)OH	open chain (A) - (2C)H - (3)OH
ΔE (eV)	0.00	0.04	0.32	0.41	0.41
VDE (eV)	**3.13**	**3.09**	**2.16**	**1.05**	**1.50**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) - (2C)H - (3)OH	open chain (A) - (4C)H - (5)OH	open chain (B) - (2C)H - (3)OH	open chain (A) - (3C)H - (3)OH	open chain (A) – [(4)H + (2)OH]
ΔE (eV)	0.43	0.44	0.57	0.59	0.85
VDE (eV)	**1.58**	**1.97**	**1.50**	**1.01**	**3.85**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) - (2)OH - (4)H	open chain (A) - (4)H - (2)OH	open chain (A) - (2)OH - (1)H	open chain (C) - (3)H - (2)OH	β-furanose (C_3 – endo) - (4C)H - (2/3)OH
ΔE (eV)	0.94	0.94	0.94	1.02	1.03
VDE (eV)	**3.86**	**4.08**	**3.90**	**4.00**	**2.84**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) - (3C)H - (4)OH	β-pyranose ($^1C_4$-chair) - (5C)H - (3/4)OH	open chain (A) – [(3)H + (2)OH]	open chain (A) - (1C)H - (2)OH	β-pyranose ($^1C_4$-chair) - (1C)H - (4)OH
ΔE (eV)	1.04	1.08	1.09	1.11	1.18
VDE (eV)	**1.60**	**2.64**	**4.20**	**2.39**	**0.58**
Optimized Anionic structure					
Structural Polymorphism	α-pyranose ($^1C_4$-chair) - (1)H - (2)OH	α -furanose (C_2 – endo) - (1C)H - (5)OH	open chain (C) - (1C)H - (2)OH	β-furanose (C_3 – endo) - (5)OH - (2)H	β-furanose (C_3 – endo) - (1)H - (2)OH
ΔE (eV)	1.27	1.27	1.29	1.29	1.34
VDE (eV)	**3.30**	**1.07**	**2.28**	**0.75**	**3.79**
Optimized Anionic structure					

Structural Polymorphism	β-furanose (C_3 – endo) - (1)H - (2)OH	open chain (B) - (4C)H - (5)OH	β-furanose (C_3 – endo) - (1)H - (3)OH	open chain (A) - (2C)H - (4)OH	open chain (A) - (5C)H - (2)OH
ΔE (eV)	1.35	1.36	1.39	1.46	1.48
VDE (eV)	**4.06**	**1.10**	**3.41**	**2.88**	**3.66**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) – [(2)H + (4)OH]	open chain (C) - (2C)H - (4)OH	open chain (C) - (3)H - (4)OH	β-furanose (C_3 – endo) - (1)H - (3)OH	open chain (C) - (3)H - (5)OH
ΔE (eV)	1.50	1.50	1.51	1.54	1.57
VDE (eV)	**3.30**	**2.64**	**3.27**	**3.65**	**3.82**
Optimized Anionic structure					
Structural Polymorphism	α -furanose (C_2 – endo) - (1)H - (3)OH	α -furanose (C_2 – endo) - (1)H - (4C)OH	α-pyranose ($^1C_4$-chair) - (1)H - (3)OH	α-furanose (C_2 – endo) - (1)H - (5)OH	α-furanose (C_2 – endo) – [(1)H + (5)OH]
ΔE (eV)	1.59	1.60	1.61	1.63	1.63
VDE (eV)	**3.62**	**3.21**	**2.78**	**3.86**	**3.86**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) – [(2)H + (3)OH]	open chain (C) - (2C)H - (5)OH	α-pyranose ($^1C_4$-chair) - (5C)H - (1)OH	open chain (A) – [(2)H + (5)OH]	open chain (A) - (3)OH - (5)H
ΔE (eV)	1.63	1.63	1.64	1.66	1.67
VDE (eV)	**3.23**	**3.06**	**0.76**	**3.82**	**3.55**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (5C)H - (1/4)OH	α-pyranose ($^1C_4$-chair) - (2)H - (3)OH	α-pyranose ($^1C_4$-chair) - (2)H - (4)OH	β-pyranose ($^1C_4$-chair) - (1)H - (4)OH	open chain (A) – [(4)H + (3)OH]
ΔE (eV)	1.68	1.70	1.71	1.71	1.72
VDE (eV)	**2.69**	**3.35**	**3.26**	**3.47**	**3.25**
Optimized Anionic structure					

Structural Polymorphism	open chain (A) - (4)H - (3)OH	open chain (A) - (2)OH - (5)H	open chain (A) - (5)H - (2)OH	α-furanose (C_2 – endo) - (1)H - (2)OH	β-furanose (C_3 – endo) - (1)H - (3)OH
ΔE (eV)	1.72	1.73	1.74	1.75	1.76
VDE (eV)	**3.13**	**4.34**	**4.11**	**3.28**	**3.23**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (2)H - (1)OH	α-pyranose ($^1C_4$-chair) - (2)H - (1)OH	α-pyranose ($^1C_4$-chair) - (1)H - (4)OH	α-pyranose ($^1C_4$-chair) - (4)H - (1)OH	α-pyranose ($^1C_4$-chair) - (3)H - (1)OH
ΔE (eV)	1.79	1.80	1.80	1.80	1.82
VDE (eV)	**2.67**	**2.67**	**3.71**	**3.12**	**3.20**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) – [(5)H + (2)OH]	β-furanose (C_3 – endo) - (4)H - (5)OH	open chain (A) - (1C)H - (3)OH	open chain (C) - (2)H - (3)OH	α-pyranose ($^1C_4$-chair) - (4)H - (3)OH
ΔE (eV)	1.82	1.82	1.82	1.83	1.83
VDE (eV)	**4.29**	**2.96**	**0.28**	**3.20**	**3.07**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (1)H - (2)OH	β-furanose (C_3 – endo) - (1)H - (5)OH	open chain (A) - (3)OH - (4)H	β-furanose (C_3 – endo) - (2)H - (5)OH	α-furanose (C_2 – endo) - (3)H - (1)OH
ΔE (eV)	1.83	1.84	1.85	1.86	1.86
VDE (eV)	**2.96**	**3.40**	**3.03**	**3.54**	**2.81**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) - (1C)H - (3)OH	open chain (C) - (4C)H - (4)OH	α-furanose (C_2 – endo) - (3)H - (2)OH	open chain (A) - (3)H - (4)OH	α-furanose (C_2 – endo) - (2C)H - (3)OH
ΔE (eV)	1.88	1.89	1.90	1.94	1.94
VDE (eV)	**0.39**	**3.82**	**3.11**	**3.61**	**-0.11**
Optimized Anionic structure					
Structural Polymorphism	α-furanose (C_2 – endo) - (1C)H - (2)OH	β-pyranose ($^1C_4$-chair) - (1)H - (3)OH	α-furanose (C_2 – endo) - (2)H - (1)OH	open chain (C) - (3)H - (4)OH	β-pyranose ($^1C_4$-chair) - (1C)H - (2)OH
ΔE (eV)	1.95	1.95	1.95	1.96	1.96

VDE (eV)	**-0.25**	**3.02**	**2.72**	**3.44**	**-0.32**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (2C)H - (3)OH	α-furanose (C_2 – endo) - (5)OH - (2)H with (1)OH transferring	α-pyranose ($^1C_4$-chair) - (5C)H - (4)OH	α-furanose (C_2 – endo) - (4C)H - (5)OH	α-furanose (C_2 – endo) – [(3)H + (5)OH]
ΔE (eV)	1.97	1.99	1.99	2.00	2.01
VDE (eV)	**-0.24**	**4.44**	**-0.19**	**-0.03**	**2.97**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (3)H - (2)OH	β-furanose (C_3 – endo) - (1)H - (5)OH	β-furanose (C_3 – endo) - (3)H - (1)OH	β-pyranose ($^1C_4$-chair) - (4)H - (3)OH	α-furanose (C_2 – endo) - (4C)H - (3)OH
ΔE (eV)	2.02	2.03	2.04	2.05	2.05
VDE (eV)	**3.03**	**3.32**	**2.69**	**2.85**	**-0.24**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (2)H - (3)OH	α-furanose (C_2 – endo) - (5C)H - (5)OH with (1)OH transferring	α-pyranose ($^1C_4$-chair) - (4)H - (2)OH	α-furanose (C_2 – endo) - (5)OH - (3)H with (1)OH transferring	β-pyranose ($^1C_4$-chair) - (2)H - (4)OH
ΔE (eV)	2.05	2.06	2.06	2.07	2.07
VDE (eV)	**2.84**	**4.62**	**2.84**	**4.55**	**2.81**
Optimized Anionic structure					
Structural Polymorphism	α-furanose (C_2 – endo) - (2)H - (5)OH	α-furanose (C_2 – endo) – [(2)H + (5)OH	β-pyranose ($^1C_4$-chair) - (2C)H - (1)OH	β-furanose (C_3 – endo) - (5)OH - (3)H	open chain (A) - (2C)H - (2)OH
ΔE (eV)	2.08	2.08	2.09	2.09	2.09
VDE (eV)	**3.45**	**3.45**	**-0.03**	**4.28**	**3.54**
Optimized Anionic structure					

Structural Polymorphism	β-furanose (C_3 – endo) - (3)H - (2)OH	β-furanose (C_3 – endo) - (4C)H - (3)OH	β-pyranose ($^1C_4$-chair) - (3)H - (4)OH	α-furanose (C_2 – endo) - (5)OH - (1)H with (1)O transferring	α-pyranose ($^1C_4$-chair) - (3)H - (2)OH
ΔE (eV)	2.10	2.13	2.13	2.13	2.13
VDE (eV)	**2.97**	**0.52**	**3.02**	**5.82**	**3.07**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) - (4C)H - (2)OH	β-furanose (C_3 – endo) - (2)H - (3)OH	open chain (C) - (4C)H - (2)OH	open chain (A) - (4C)H - (2)OH	open chain (A) - (3)H - (5)OH
ΔE (eV)	2.14	2.14	2.14	2.14	2.15
VDE (eV)	**3.94**	**2.83**	**3.94**	**2.69**	**3.84**
Optimized Anionic structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (2)H - (1)OH	β-pyranose ($^1C_4$-chair) - (5C)H - (4)OH	open chain (A) - (3)H - (2)OH	open chain (C) - (2C)H - (2)OH	open chain (A) – [(5)H + (3)OH]
ΔE (eV)	2.15	2.19	2.23	2.25	2.27
VDE (eV)	**2.37**	**-0.37**	**3.61**	**3.41**	**2.64**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) - (5)H - (3)OH	β-furanose (C_3 – endo) - (4C)H - (5)OH	α-furanose (C_2 – endo) - (2C)H - (1)OH	open chain (A) – [(4)H + (5)OH]	β-furanose (C_3 – endo) - (5)OH - (1)H
ΔE (eV)	2.27	2.27	2.29	2.30	2.37
VDE (eV)	**2.54**	**0.41**	**-0.004**	**2.87**	**3.53**
Optimized Anionic structure					
Structural Polymorphism	open chain (A) - (4C)H - (4)OH	α-furanose (C_2 – endo) - (4C)H - (2)OH	open chain (C) - (3)H - (2)OH	open chain (A) - (5)H - (4)OH	α-furanose (C_2 – endo) - (3)H - (4)OH
ΔE (eV)	2.38	2.40	2.43	2.46	2.54
VDE (eV)	**3.86**	**2.35**	**3.44**	**2.82**	**2.68**

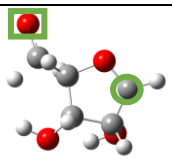
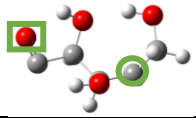
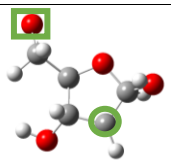
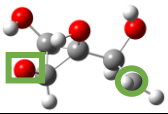
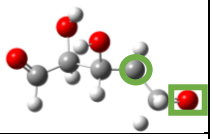
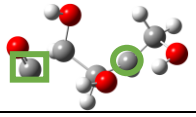
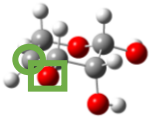
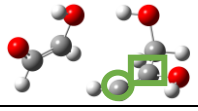
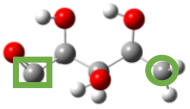
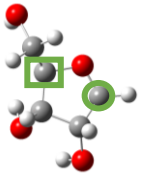
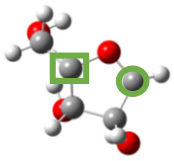
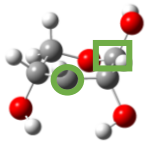
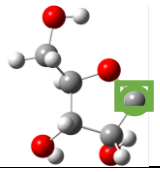
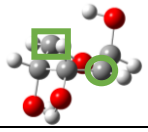
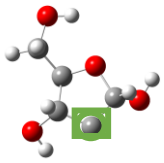
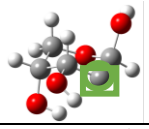
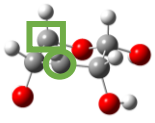
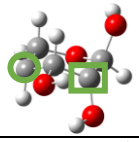
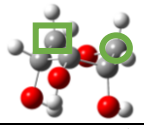
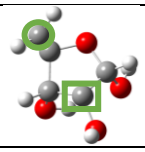
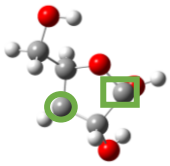
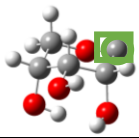
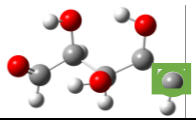
Optimized Anionic structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (5)H - (1)OH	open chain (A) - (1C)H - (4)OH	β-furanose (C_3 – endo) - (5)H - (2)OH	open chain (A) - (3C)H - (5)OH	open chain (A) – [(5)H + (4)OH]
ΔE (eV)	2.58	2.59	2.61	2.67	2.67
VDE (eV)	**2.98**	**2.83**	**3.50**	**3.72**	**2.65**
Optimized Anionic structure					
Structural Polymorphism	open chain (C) - (1C)H - (4)OH	α-pyranose ($^1C_4$-chair) - (3)H - (4)OH	open chain (A) - (4C)H - (3)OH	open chain (A) - (1C)H - (5)OH	α-furanose (C_2 – endo) - (4C)H - (1)OH
ΔE (eV)	2.69	2.73	2.77	2.80	2.94
VDE (eV)	**2.69**	**2.67**	**3.40**	**3.25**	**1.91**
Optimized Anionic structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (4C)H - (1)OH	β-pyranose ($^1C_4$-chair) - (1C)H - (3)OH	α-furanose (C_2 – endo) - (1C)H - (1)OH	β-pyranose ($^1C_4$-chair) - (5C)H - (2)OH	α-furanose (C_2 – endo) - (2C)H - (2)OH
ΔE (eV)	3.02	3.04	3.12	3.13	3.17
VDE (eV)	**1.62**	**2.06**	**1.42**	**3.11**	**2.18**
Optimized Anionic structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (2C)H - (2)OH	α-pyranose ($^1C_4$-chair) - (5C)H - (3)OH	β-pyranose ($^1C_4$-chair) - (2C)H - (4)OH	α-pyranose ($^1C_4$-chair) - (5C)H - (1)OH	α-furanose (C_2 – endo) - (2C)H - (5)OH
ΔE (eV)	3.20	3.26	3.32	3.42	3.44
VDE (eV)	**2.24**	**1.92**	1.62	2.05	**2.01**
Optimized Anionic structure					
Structural Polymorphism	α-furanose (C_2 – endo) - (1C)H - (3)OH	β-pyranose ($^1C_4$-chair) - (1C)H - (1)OH	open chain (C) - (5C)H - (5)OH		
ΔE (eV)	3.52	3.81	4.09		
VDE (eV)	**2.70**	**1.46**	**1.61**		

Figure S6 Optimized geometries of the typical low lying anionic isomers of (ribose-H_2O)$^-$ based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates loss of hydrogen and the green circle indicates loss of an OH group. The structural presentation is the same as those in the main text Figures 4-6. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

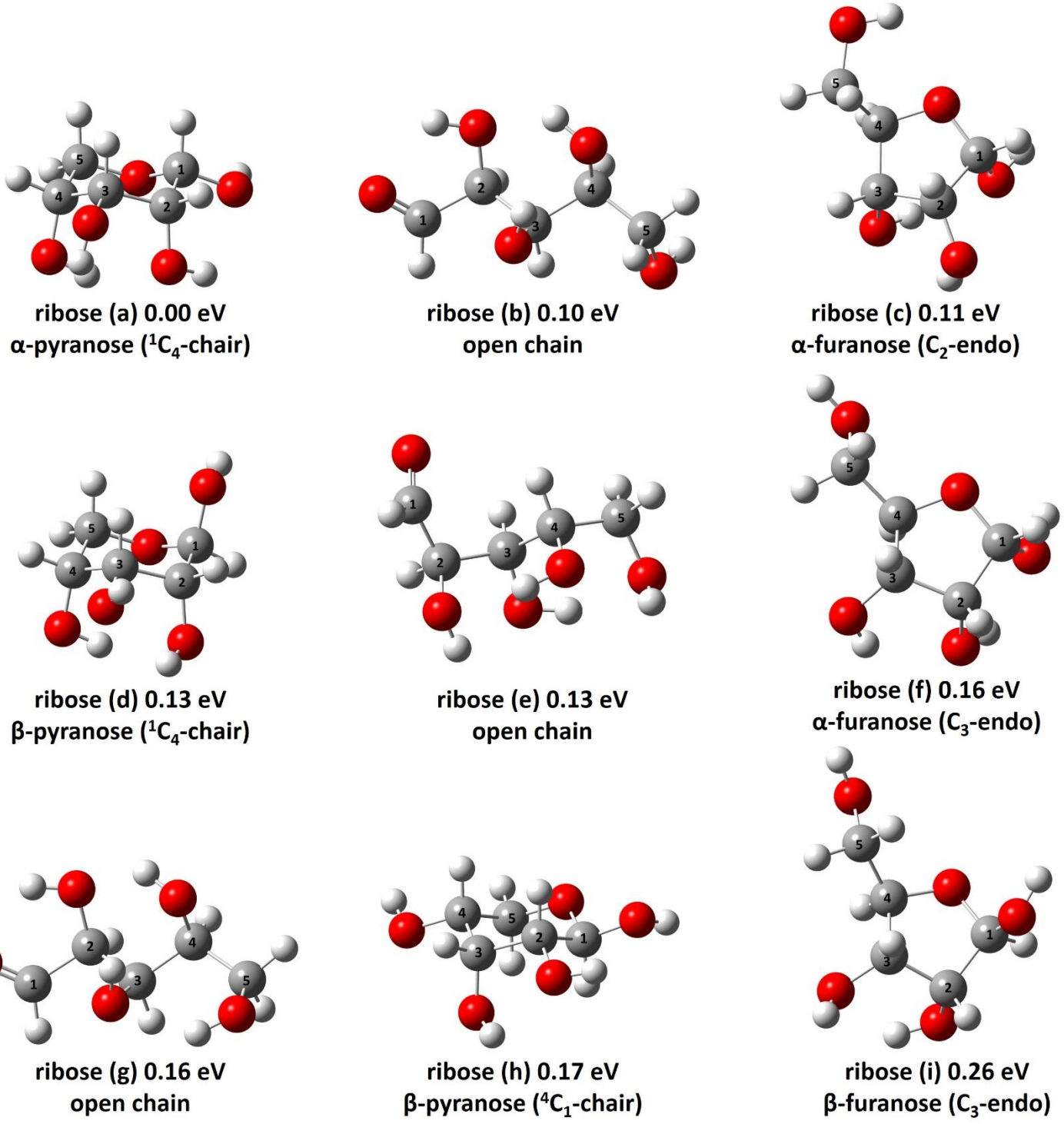


Figure S10 Optimized geometries of the typical low lying neutral isomers of ribose based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The C atom numberings are given. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction. C atom numbering for open chain structures corresponds to that in the cyclic structures, for instance (1)C ⇔ (1)C.

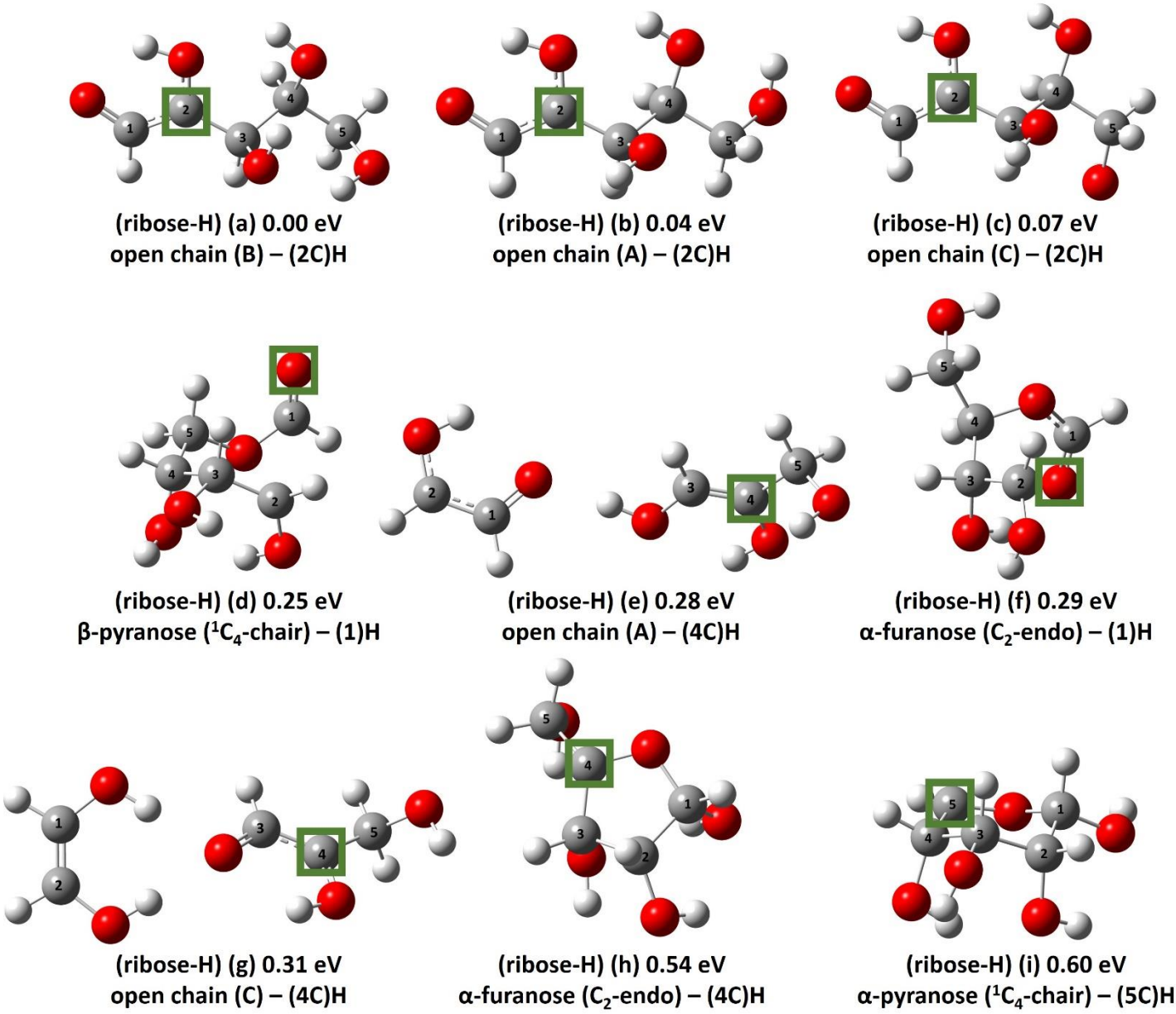


Figure S11 Optimized geometries of the typical low lying neutral isomers of (ribose-H) based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates loss of hydrogen at the indicated position. The C atom numberings are given. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction. C atom numbering for open chain structures corresponds to that in the cyclic structures, for instance (1)C ⇔ (1)C.

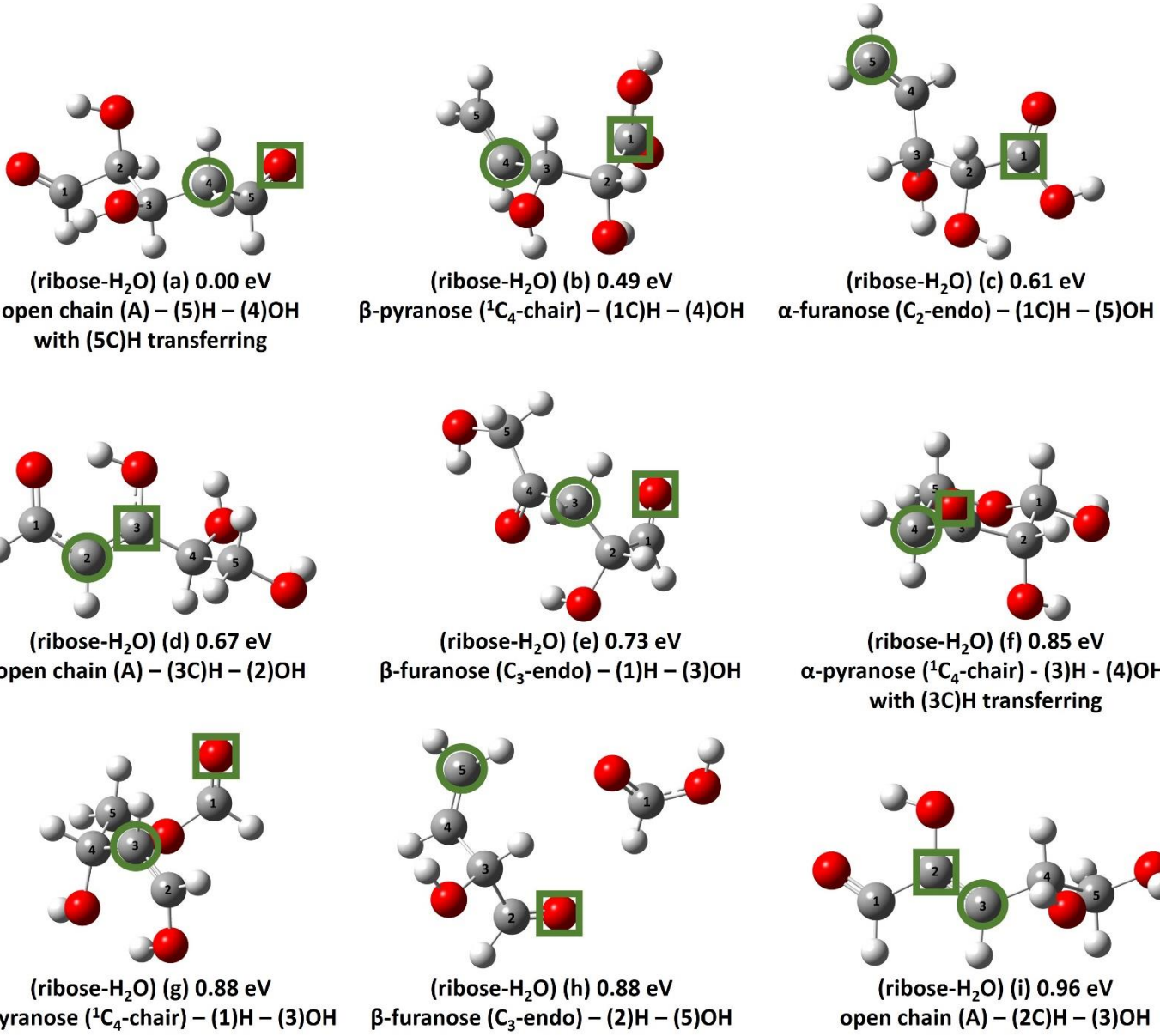


Figure S12 Optimized geometries of the typical low lying neutral isomers of (ribose-H_2O) based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates loss of hydrogen and the green circle indicates loss of an OH group at the marked positions. The C atom numberings are given. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction. C atom numbering for open chain structures corresponds to that in the cyclic structures, for instance (1)C ⇔ (1)C.

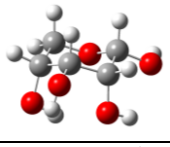
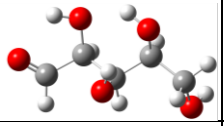
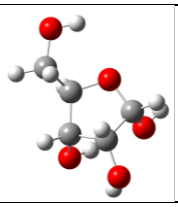
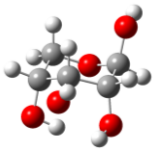
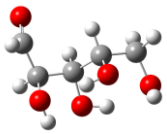
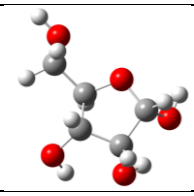
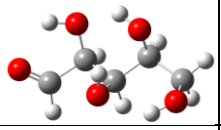
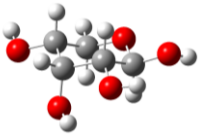
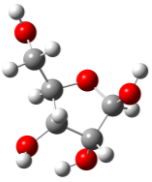
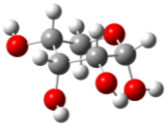
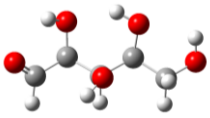
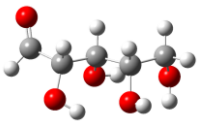
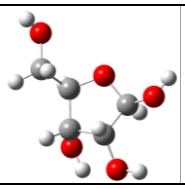
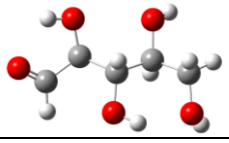
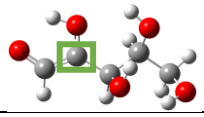
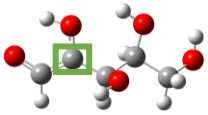
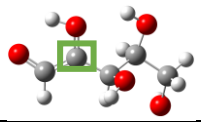
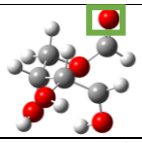
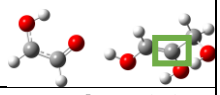
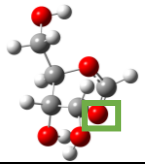
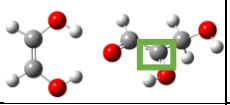
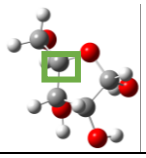
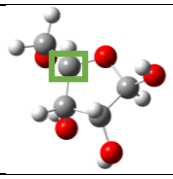
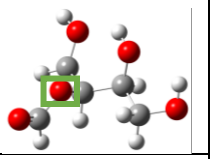
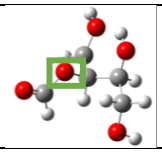
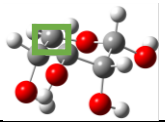
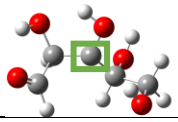
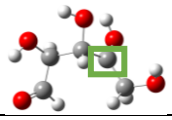
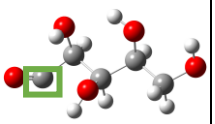
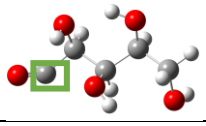
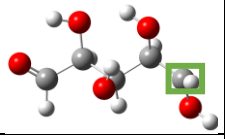
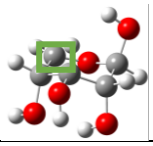
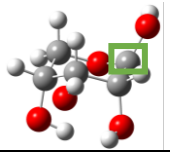
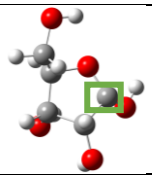
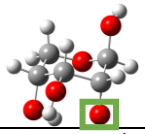
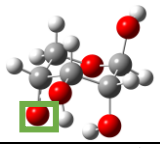
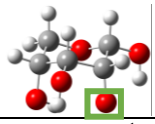
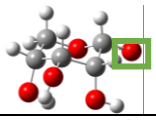
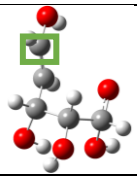
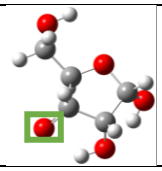
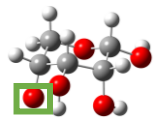
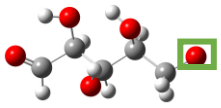
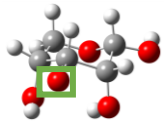
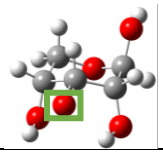
Optimized neutral structure					
Structural Polymorphism	α-pyranose ($^1C_4$-chair)	open chain	α-furanose (C_2 – endo)	β-pyranose ($^1C_4$-chair)	open chain
ΔE (eV)	0.00	0.10	0.11	0.13	0.13
Optimized neutral structure					
Structural Polymorphism	α-furanose (C_3 – endo)	open chain	β-pyranose ($^4C_1$-chair)	β-furanose (C_3 – endo)	α-pyranose ($^4C_1$-chair)
ΔE (eV)	0.16	0.16	0.17	0.26	0.27
Optimized neutral structure					
Structural Polymorphism	open chain	open chain	β-furanose (C_2 – endo)	open chain	
ΔE (eV)	0.29	0.31	0.32	0.43	

Figure S13 Optimized geometries of the typical low lying neutral isomers of ribose based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The structural presentation is the same as those in the main text Figures 4-6 as well as SI Figures S10-12. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

Optimized neutral structure					
Structural Polymorphism	open chain (B) - (2C)H	open chain (A) - (2C)H	open chain (C) - (2C)H	β-pyranose ($^1C_4$-chair) - (1)H	open chain (A) - (4C)H
ΔE (eV)	0.00	0.04	0.07	0.25	0.28
Optimized neutral structure					
Structural Polymorphism	α-furanose (C_2 – endo) - (1)H	open chain (C) - (4C)H	α-furanose (C_2 – endo) - (4C)H	β-furanose (C_3 – endo) - (4C)H	open chain (A) - (3)H
ΔE (eV)	0.29	0.31	0.54	0.56	0.57
Optimized neutral structure					
Structural Polymorphism	open chain (C) - (3)H	α-pyranose ($^1C_4$-chair) - (5C)H	open chain (C) - (3C)H	open chain (B) - (4C)H	open chain (A) - (1C)H
ΔE (eV)	0.57	0.60	0.60	0.63	0.65
Optimized neutral structure					
Structural Polymorphism	open chain (C) - (1C)H	open chain (C) - (C5)H	β-pyranose ($^1C_4$-chair) - (5C)H	β-pyranose ($^1C_4$-chair) - (1C)H	α-furanose (C_2 – endo) - (1C)H
ΔE (eV)	0.65	0.68	0.73	0.81	0.86
Optimized neutral structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (2)H	β-pyranose ($^1C_4$-chair) - (4)H	α-pyranose ($^1C_4$-chair) - (2)H	α-pyranose ($^1C_4$-chair) - (1)H	α-furanose (C_2 – endo) - (6C)H
ΔE (eV)	0.86	0.87	0.91	0.92	0.94
Optimized neutral structure					
Structural Polymorphism	α-furanose (C_2 – endo) - (3)H	α-pyranose ($^1C_4$-chair) - (4)H	open chain (A) - (5)H	α-pyranose ($^1C_4$-chair) - (3)H	β-pyranose ($^1C_4$-chair) - (4)H
ΔE (eV)	1.00	1.02	1.05	1.08	1.09

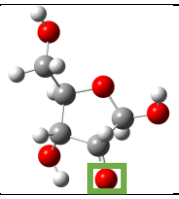
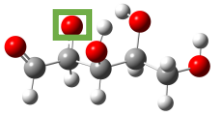
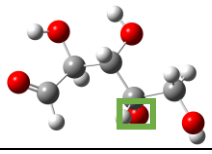
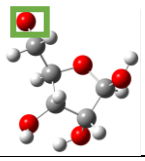
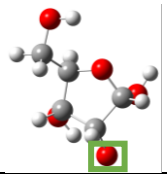
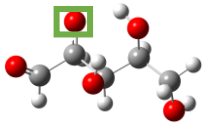
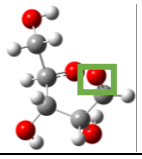
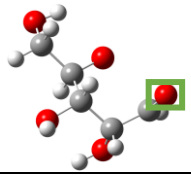
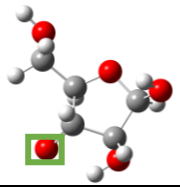
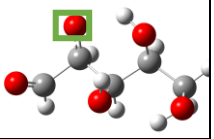
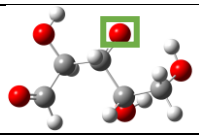
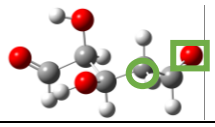
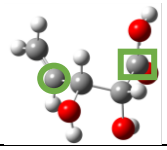
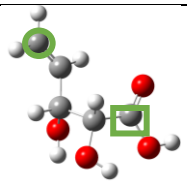
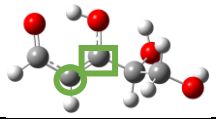
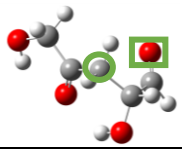
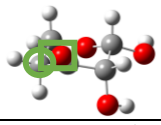
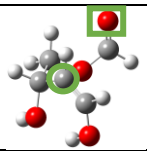
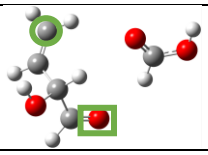
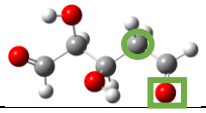
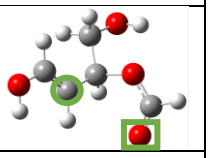
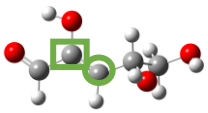
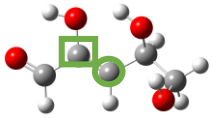
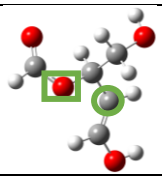
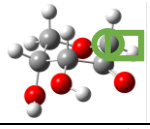
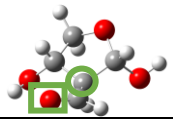
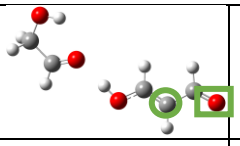
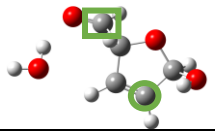
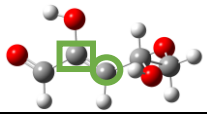
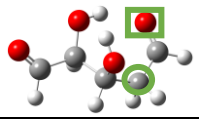
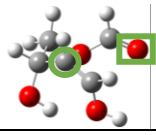
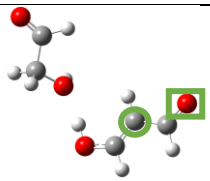
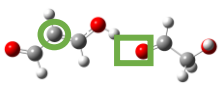
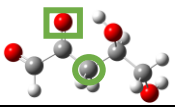
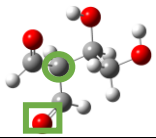
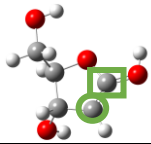
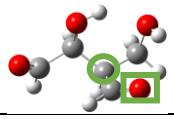
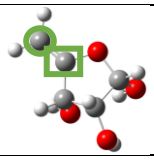
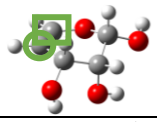
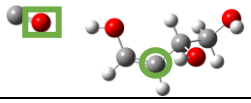
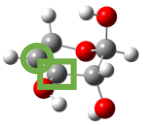
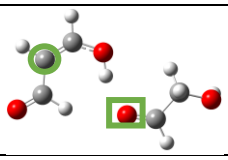
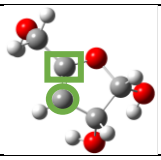
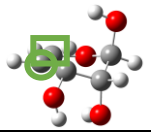
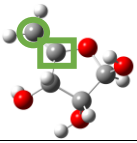
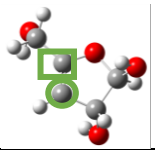
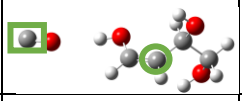
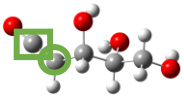
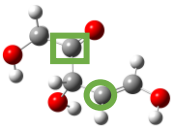
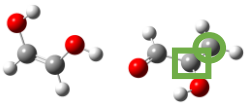
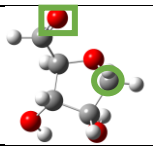
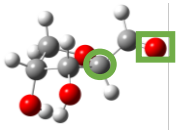
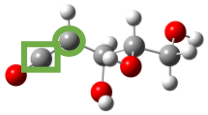
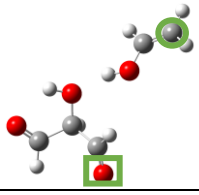
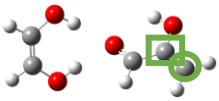
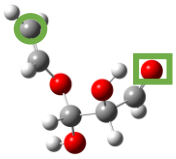
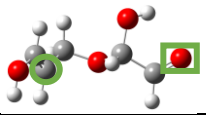
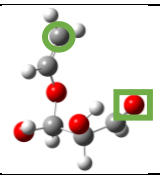
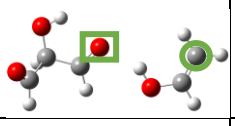
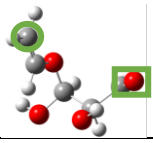
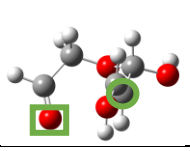
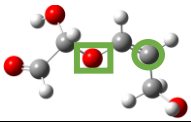
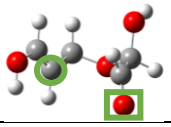
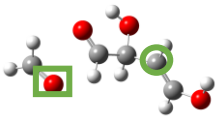
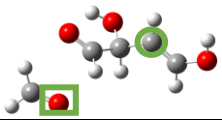
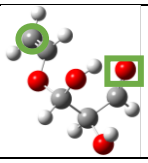
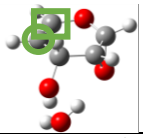
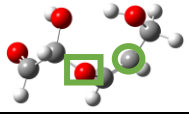
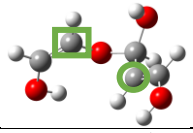
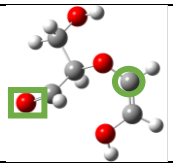
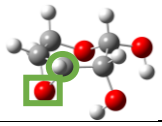
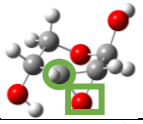
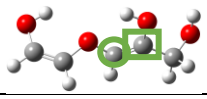
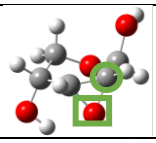
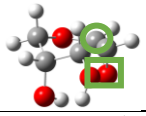
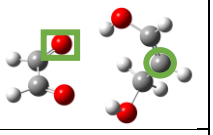
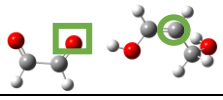
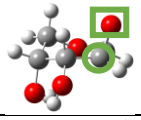
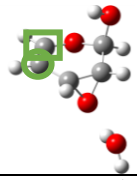
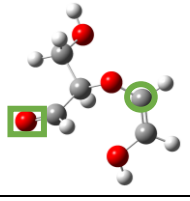
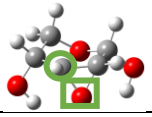
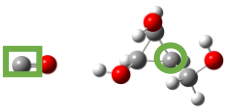
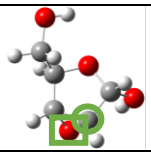
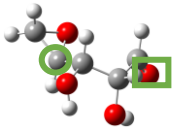
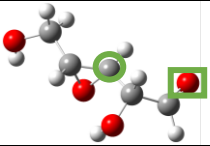
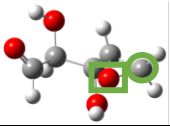
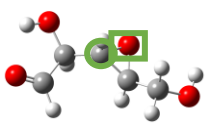
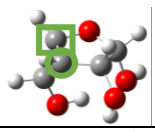
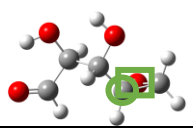
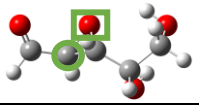
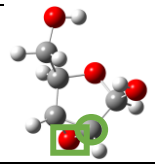
Optimized neutral structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (2)H	open chain (A) - (2)H	open chain (A) - (4)H	β-furanose (C_3 – endo) - (5)H	α-furanose (C_2 – endo) - (2)H
ΔE (eV)	1.11	1.12	1.13	1.13	1.15
Optimized neutral structure					
Structural Polymorphism	open chain (C) - (2)H	β-furanose (C_3 – endo) - (1)H	β-furanose (C_3 – endo) - (1)H	β-furanose (C_3 – endo) - (3)H	open chain (B) - (2)H
ΔE (eV)	1.16	1.17	1.20	1.20	1.24
Optimized neutral structure					
Structural Polymorphism	open chain (C) - (3)H				
ΔE (eV)	1.25				

Figure S14 Optimized geometries of the typical low lying neutral isomers of (ribose-H) based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates loss of hydrogen at the indicated position. The green labels indicate loss of hydrogen from carbon atom. The structural presentation is the same as those in the main text Figures 4-6 as well as SI Figures S10-12. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

Optimized neutral structure					
Structural Polymorphism	open chain (A) – [(5)H + (4)OH] with (5C)H transferring	β-pyranose ($^1C_4$-chair) - (1C)H - (4)OH	α -furanose (C_2 – endo) - (1C)H - (5)OH	open chain (A) - (3C)H - (2)OH	β-furanose (C_3 – endo) - (1)H - (3)OH
ΔE (eV)	0.00	0.49	0.61	0.67	0.73
Optimized neutral structure					
Structural Polymorphism	α-pyranose ($^1C_4$-chair) - (3)H - (4)OH with (3C)H transferring	β-pyranose ($^1C_4$-chair) - (1)H - (3)OH	β-furanose (C_3 – endo) - (5)OH - (2)H	open chain (A) - (5)H - (4)OH with (5C)H transferring	α -furanose (C_2 – endo) - (1)H - (3)OH
ΔE (eV)	0.85	0.88	0.88	0.89	0.95
Optimized neutral structure					
Structural Polymorphism	open chain (A) - (2C)H - (3)OH	open chain (B) - (2C)H - (3)OH	open chain (C) - (4)H - (3)OH	α-pyranose ($^1C_4$-chair) - (2)H - (1)OH	α-pyranose ($^1C_4$-chair) - (3)H - (2)OH
ΔE (eV)	0.96	0.99	1.01	1.02	1.04
Optimized neutral structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (1)H - (2)OH	β-furanose (C_3 – endo) - (5C)H - (2/3)OH	open chain (C) - (2C)H - (3)OH	open chain (A) – [(4)H + (5)OH]	α-pyranose ($^1C_4$-chair) - (1)H - (3)OH
ΔE (eV)	1.06	1.08	1.08	1.11	1.14
Optimized neutral structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (1)H - (2)OH	open chain (A) – [(4)H + (2)OH]	open chain (C) - (2)H - (3)OH with (2C)H transferring	open chain (A) – [(2)H + (3)OH]	α-furanose (C_2 – endo) - (1C)H - (2)OH
ΔE (eV)	1.16	1.16	1.17	1.18	1.19

Optimized neutral structure					
Structural Polymorphism	open chain (C) - (3)H - (4)OH	α-furanose (C_2 – endo) - (4C)H - (5)OH	α-pyranose ($^1C_4$-chair) - (5C)H - (4)OH	open chain (A) - (1C)H - (3)OH	β-pyranose ($^1C_4$-chair) - (3C)H - (4)OH
ΔE (eV)	1.21	1.22	1.24	1.27	1.29
Optimized neutral structure					
Structural Polymorphism	open chain (A) – [(4)H + (2)OH]	α-furanose (C_2 – endo) - (4C)H - (3)OH	β-pyranose ($^1C_4$-chair) - (5C)H - (4)OH	β-furanose (C_3 – endo) - (4C)H - (5)OH	β-furanose (C_3 – endo) - (4C)H - (3)OH
ΔE (eV)	1.30	1.30	1.33	1.33	1.38
Optimized neutral structure					
Structural Polymorphism	open chain (C) - (1C)H - (3)OH	open chain (A) - (1C)H - (2)OH	α-furanose (C_2 – endo) - (4C)H - (2)OH	open chain (A) - (4C)H - (5)OH	β-furanose (C_3 – endo) - (5)H - (1)OH with (5C)H transferring
ΔE (eV)	1.36	1.39	1.39	1.39	1.40
Optimized neutral structure					
Structural Polymorphism	α-pyranose ($^1C_4$-chair) - (1)H - (2)OH	open chain (C) - (1C)H - (2)OH	open chain (A) - (3)H - (5)OH	open chain (C) - (4C)H - (5)OH	β-furanose (C_3 – endo) - (1)H - (5)OH
ΔE (eV)	1.40	1.43	1.47	1.48	1.51
Optimized neutral structure					
Structural Polymorphism	α-pyranose ($^1C_4$-chair) - (2)H - (4)OH	α -furanose (C_2 – endo) - (1)H - (5)OH	open chain (C) - (3)H - (5)OH	α-furanose (C_2 – endo) – [(1)H + (5)OH]	α-pyranose ($^1C_4$-chair) - (4)H - (2)OH
ΔE (eV)	1.51	1.57	1.57	1.64	1.66

Optimized neutral structure					
Structural Polymorphism	open chain (A) - (3)H - (4)OH	β-pyranose ($^1C_4$-chair) - (2)H - (4)OH	open chain (A) - (5)H - (3)OH	open chain (A) – [(5)H + (3)OH]	α-furanose (C_2 – endo) - (1)H - (5)OH
ΔE (eV)	1.66	1.71	1.75	1.75	1.78
Optimized neutral structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (5C)H - (1/4)OH	open chain (C) - (3)H - (4)OH	β-pyranose ($^1C_4$-chair) - (5C)H - (2)OH	α-furanose (C_2 – endo) - (3)H - (1)OH	α-pyranose ($^1C_4$-chair) - (4)H - (3)OH
ΔE (eV)	1.83	1.87	1.92	1.92	1.94
Optimized neutral structure					
Structural Polymorphism	β-pyranose ($^1C_4$-chair) - (2)H - (3)OH	open chain (C) - (4C)H - (3)OH	β-pyranose ($^1C_4$-chair) - (3)H - (2)OH	β-pyranose ($^1C_4$-chair) - (2)H - (1)OH	open chain (A) – [(2)H + (4)OH]
ΔE (eV)	1.95	1.95	1.95	1.95	1.96
Optimized neutral structure					
Structural Polymorphism	open chain (C) - (2)H - (4)OH	β-pyranose ($^1C_4$-chair) - (1)H - (2)OH	β-pyranose ($^1C_4$-chair) - (5C)H - (3/4)OH	β-furanose (C_3 – endo) - (3)H - (1)OH	α-pyranose ($^1C_4$-chair) - (2)H - (3)OH
ΔE (eV)	1.97	1.98	1.99	2.00	2.00
Optimized neutral structure					
Structural Polymorphism	open chain (A) - (1C)H - (4)OH	α-furanose (C_2 – endo) - (3)H - (2)OH	α-pyranose ($^1C_4$-chair) - (1)H - (4)OH	β-furanose (C_3 – endo) - (1)H - (3)OH	open chain (C) - (4)H - (5)OH
ΔE (eV)	2.02	2.03	2.03	2.04	2.04
Optimized neutral structure					
Structural Polymorphism	open chain (A) - (3)OH - (4)H	α-pyranose ($^1C_4$-chair) - (5C)H - (3)OH	open chain (A) – [(4)H + (5)OH]	open chain (C) - (3)H - (2)OH	β-furanose (C_3 – endo) - (3)H - (2)OH

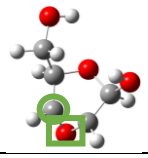
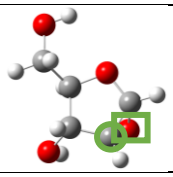
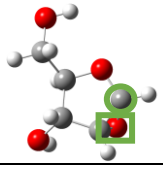
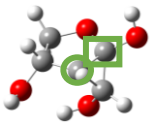
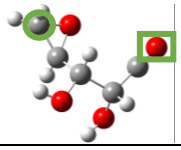
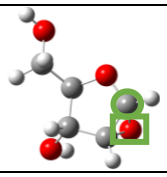
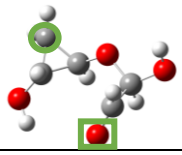
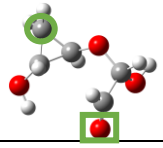
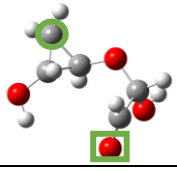
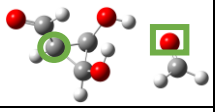
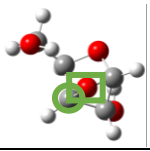
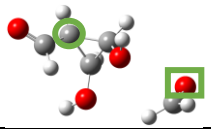
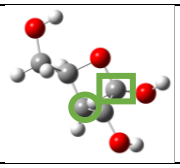
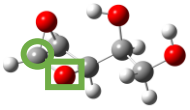
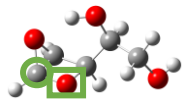
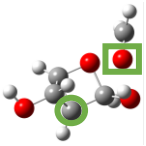
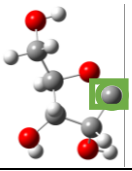
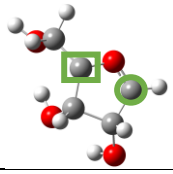
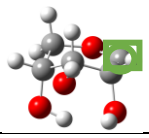
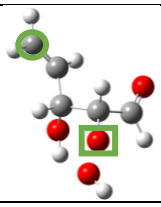
ΔE (eV)	2.05	2.06	2.07	2.07	2.07
Optimized neutral structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (2)H - (3)OH	α-furanose (C_2 – endo) - (1)H - (2)OH	α-furanose (C_2 – endo) - (2)H - (1)OH	β-pyranose ($^1C_4$-chair) - (1C)H - (3)OH	β-furanose (C_3 – endo) - (1)H - (5)OH
ΔE (eV)	2.07	2.09	2.09	2.18	2.18
Optimized neutral structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (2)H - (1)OH	β-furanose (C_3 – endo) - (2)H - (5)OH	α-furanose (C_2 – endo) – [(2)H + (5)OH	α-furanose (C_2 – endo) - (2) H - (5)OH	open chain (A) - (5)H - (2)OH
ΔE (eV)	2.19	2.24	2.31	2.31	2.33
Optimized neutral structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (1)H - (3)OH	open chain (A) – [(5)H + (2)OH]	α-furanose (C_2 – endo) - (1C)H - (3)OH	open chain (A) - (3)H - (2)OH	open chain (C) - (3)H - (2)OH
ΔE (eV)	2.50	2.51	3.07	3.16	3.21
Optimized neutral structure					
Structural Polymorphism	β-furanose (C_3 – endo) - (5)H - (2)OH	α-furanose (C_2 – endo) - (1C)H - (1)OH	α-furanose (C_2 – endo) - (4C)H - (1)OH	β-pyranose ($^1C_4$-chair) - (1C)H - (1)OH	α-furanose (C_2 – endo) - (5)OH - (2)H with (1)OH transferring
ΔE (eV)	3.27	3.45	3.55	3.85	4.13

Figure S15 Optimized geometries of the typical low lying neutral isomers of (ribose-H_2O) based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates loss of hydrogen and the green circle indicates loss of an OH group. The structural presentation is the same as those in the main text Figures 4-6 as well as SI Figures S10-12. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

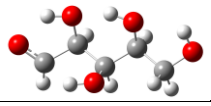
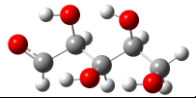
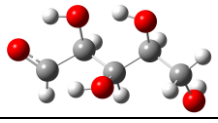
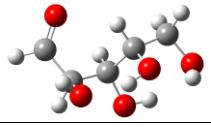
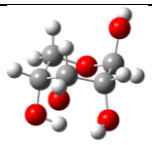
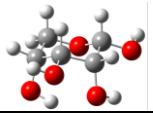
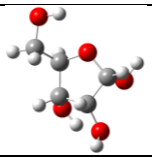
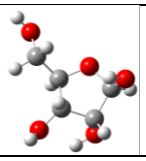
Optimized anionic structure					
Structural polymorphism	ribose$^-$ (A) open chain	ribose$^-$ (B) open chain	ribose$^-$ (C) open chain	ribose$^-$ (D) open chain	ribose$^-$ (E) β-pyranose ($^1C_4$-chair)
ΔE	0.00	0.01	0.19	0.29	0.64
VDE(eV)	1.48	1.57	1.37	0.92	-0.52
Optimized anionic structure					
Structural polymorphism	ribose$^-$ (F) α-pyranose ($^1C_4$-chair)	ribose$^-$ (G) α-furanose (C_2-endo)	ribose$^-$ (H) β-furanose (C_3-endo)		
ΔE	0.66	0.78	0.79		
VDE(eV)	-0.45	-0.34	-0.21		

Figure S16 Optimized geometries of the typical low lying anionic isomers of ribose$^-$ based on M062X/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The isomers have nearly identical structures with respect to the corresponding isomers optimized from B3LYP/6-311++G(d,p) level of theory.

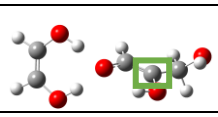
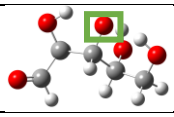
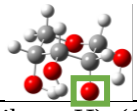
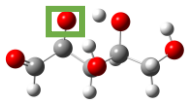
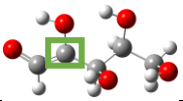
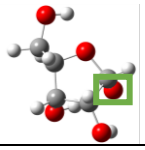
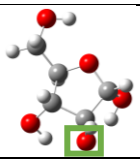
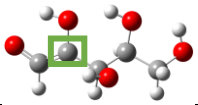
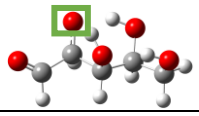
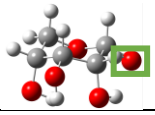
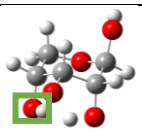
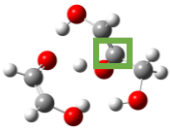
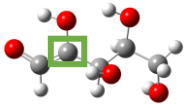
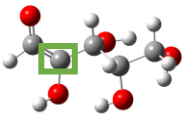
Optimized anionic structure					
Structural polymorphism	(ribose-H)$^-$ (A) open chain (C) – (4C)H	(ribose-H)$^-$ (B) open chain (C) – (3)H	(ribose-H)$^-$ (C) α-pyranose ($^1C_4$-chair) – (2)H	(ribose-H)$^-$ (D) open chain (A) – (2)H	(ribose-H)$^-$ (E) open chain (B) – (2C)H
ΔE	0.38	0.19	0.00	0.30	0.37
VDE(eV)	3.51	4.63	3.87	4.17	2.73
Optimized anionic structure					
Structural polymorphism	(ribose-H)$^-$ (F) α-furanose (C_2-endo) – (1)H	(ribose-H)$^-$ (G) α-furanose (C_2-endo) – (3)H	(ribose-H)$^-$ (H) open chain (A) – (2C)H	(ribose-H)$^-$ (I) open chain (B) – (2)H	(ribose-H)$^-$ (J) α-pyranose ($^1C_4$-chair) – (1)H
ΔE	0.14	0.00	0.37	0.34	0.17
VDE(eV)	3.86	4.16	2.65	4.11	3.75
Optimized anionic structure					
Structural polymorphism	(ribose-H)$^-$ (K) β-pyranose ($^1C_4$-chair) – (4)H	(ribose-H)$^-$ (L) open chain (A) – (4C)H	(ribose-H)$^-$ (M) open chain (C) – (2C)H	(ribose-H)$^-$ (N) open chain (D) – (2C)H	
ΔE	0.29	0.36	0.54	0.94	
VDE(eV)	3.48	3.53	2.55	2.25	

Figure S17 Optimized geometries of the typical low lying anionic isomers of (ribose-H)$^-$ based on M062X/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates the position from which the H atom of ribose is removed.

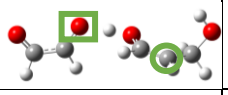
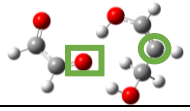
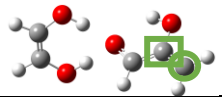
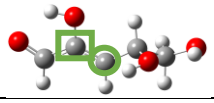
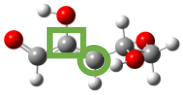
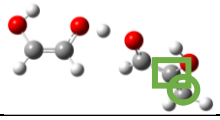
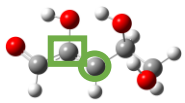
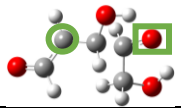
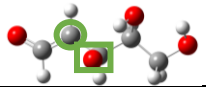
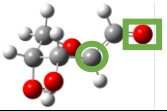
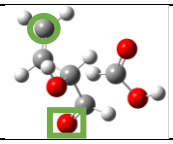
Optimized anionic structure					
Structural polymorphism	(ribose-H_2O)$^-$ (A) open chain (C) – (2)H– (4)OH	(ribose-H_2O)$^-$ (B) open chain (A) – (2)H– (4)OH	(ribose-H_2O)$^-$ (C) open chain (C) – (4C)H– (5)OH	(ribose-H_2O)$^-$ (D) open chain (A) – (2C)H– (3)OH	(ribose-H_2O)$^-$ (E) open chain (C) – (2C)H– (3)OH
ΔE	0.03	0.00	0.26	0.13	0.13
VDE(eV)	3.17	3.03	2.13	1.41	1.51
Optimized anionic structure					
Structural polymorphism	(ribose-H_2O)$^-$ (F) open chain (A) – (4C)H– (5)OH	(ribose-H_2O)$^-$ (G) open chain (B) – (2C)H– (3)OH	(ribose-H_2O)$^-$ (H) open chain (A) – (4)H– (2)OH	(ribose-H_2O)$^-$ (I) open chain (A) – (3)H– (2)OH	(ribose-H_2O)$^-$ (J) α-pyranose ($^1C_4$-chair) – (1)H– (2)OH
ΔE	0.37	0.19	0.71	0.81	1.09
VDE(eV)	2.02	1.26	4.11	3.89	3.05
Optimized anionic structure					
Structural polymorphism	(ribose-H_2O)$^-$ (K) β-furanose (C_3-endo) – (2)H– (5)OH				
ΔE	1.27				
VDE(eV)	1.32				

Figure S18 Optimized geometries of the typical low lying anionic isomers of (ribose-H_2O)$^-$ based on M062X/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates the position from which the H atom is removed and the green circle indicates the position from which an OH group is removed.

(ribose-H)$^-$

ribose$^-$ ⟶ (ribose-H)$^-$ + H	
Isomers of (ribose-H)$^-$	ΔH (kcal/mol)
(A)	28.35
(B)	29.90
(C)	17.07
(E)	37.84

(ribose-H)$^-$	
ribose^0 ⟶ (ribose-H)^0 + H $\xrightarrow{e}$ (ribose-H)$^-$ + H	
Isomers of (ribose-H)$^-$	ΔH (kcal/mol)
(A)	19.22
(B)	20.76
(C)	25.32
(E)	23.50

Figure S19 (a) Calculated ΔH values for different possible pathways for generating specific (ribose-H)$^-$ anionic isomers. Red color indicates an anionic mechanism. Black color indicates a neutral mechanism. When we calculate the ΔH values for generating every specific isomer, the reactant that has the most similar structure to that of final product is chosen.

$(ribose\text{-}H_2O)^-$

$ribose^- \rightarrow (ribose\text{-}OH)^- + OH \rightarrow (ribose\text{-}H_2O)^- + H + OH$	
$ribose^- \rightarrow (ribose\text{-}H)^- + H \rightarrow (ribose\text{-}OH)^- + O + H \rightarrow (ribose\text{-}H_2O)^- + H + O + H$	
$ribose^- \rightarrow (ribose\text{-}H_2O)^- + H_2O$	
Isomers of $(ribose\text{-}H_2O)^-$	ΔH (kcal/mol)
(C)	96.07 261.87 **-18.70**
(D)	101.87 267.66 **-12.91**

$ribose^0 \rightarrow (ribose\text{-}OH)^0 + OH \rightarrow (ribose\text{-}H_2O)^0 + H + OH \xrightarrow{e} (ribose\text{-}H_2O)^- + H + OH$	
$ribose^0 \rightarrow (ribose\text{-}H)^0 + H \rightarrow (ribose\text{-}OH)^0 + O + H \rightarrow (ribose\text{-}H_2O)^0 + H + O + H \xrightarrow{e} (ribose\text{-}H_2O)^- + H + O + H$	
$ribose^0 \rightarrow (ribose\text{-}H_2O)^- + H_2O \xrightarrow{e} (ribose\text{-}H_2O)^- + H_2O$	
Isomers of $(ribose\text{-}H_2O)^-$	ΔH (kcal/mol)
(C)	86.94 252.73 **-27.84**
(D)	84.14 249.94 **-30.63**

Figure S19 (b) Calculated ΔH values for different possible pathways for generating specific $(ribose\text{-}H_2O)^-$ anionic isomers. Red color indicates an anionic mechanism. Black color indicates a neutral mechanism. When we calculate the ΔH values for generating every specific isomer, the reactant that has the most similar structure to that of final product is chosen.

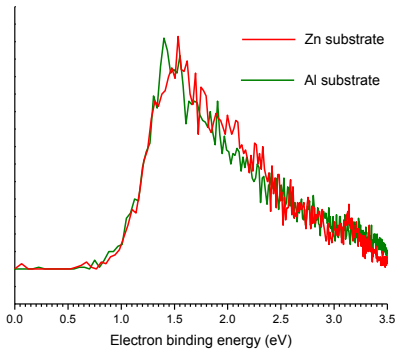


Figure S20 Photoelectron spectrum of (ribose-H_2O)$^-$ recording using 355 nm photons with sample (D-ribose/DCM) spayed on different absorption substrates.

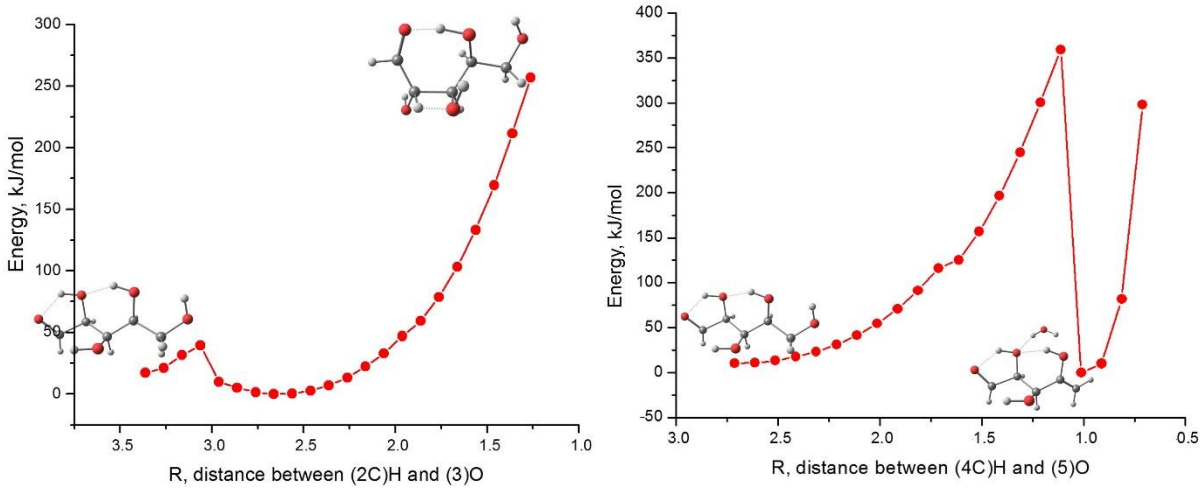


Figure S21. (left) Relaxed Potential Energy Surface scan of ribose$^-$ parent open chain (A) through forming of an H_2O unit. R(Å): distance between (2C)H and (3)O. (right) Relaxed Potential Energy Surface scan of ribose$^-$ parent open chain (A) through forming of an H_2O unit. R(Å): distance between (4C)H and (5)O.

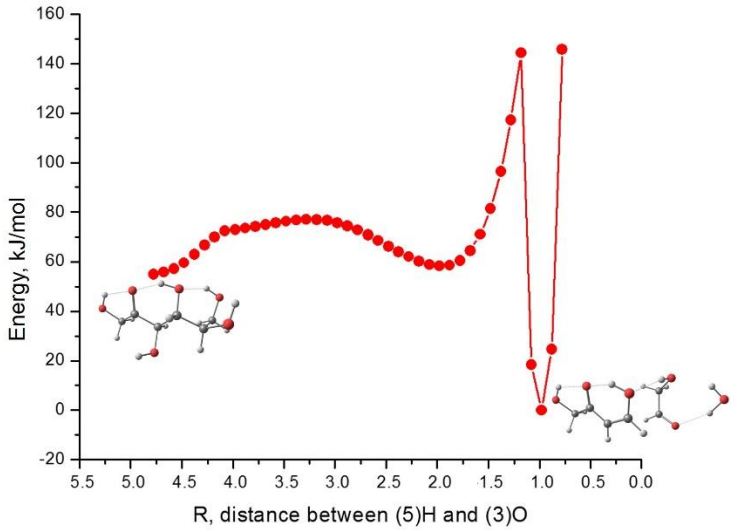


Figure S22. Relaxed Potential Energy Surface scan of fructose$^-$ parent open chain (A) through forming of an H_2O unit. R(Å): distance between (5)H and (3)O.

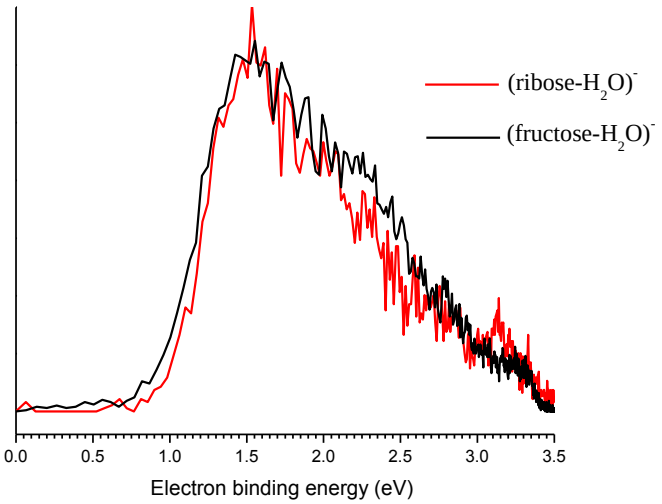


Figure 23 Photoelectron spectra of $(ribose\text{-}H_2O)^-$ and $(fructose\text{-}H_2O)^-$ recording with 355 nm photons with sample (D-ribose/DCM) spayed on a Zn substrate.

Table S1 The calculated VDEs and their relative energies (ΔE) of lower lying isomers of (ribose-H_2O)$^-$ based on B3LYP/6-311++G(d,p), M062X/6-311++G(d,p), ωB97XD/6-311++G(d,p), and MP2/6-311++G(d,p). Experimental results are given in the right hand column. All energies are in eV.

		B3LYP/6-311++G(d,p)	M062X/6-311++G(d,p)	ωB97XD/6-311++G(d,p)	MP2/6-311++G(d,p)	MP2/Aug-CC-PVTZ	experimental measurement
(ribose-H_2O)$^-$ (A)	ΔE	0.00	0.03	0.04	0.05	0.00	
	VDE	3.13	3.17	3.04	2.22	2.50	
(ribose-H_2O)$^-$ (B)	ΔE	0.04	0.00	0.00	0.00		
	VDE	3.09	3.03	3.04	2.16		
(ribose-H_2O)$^-$ (C)	ΔE	0.32	0.26	0.33	0.42	0.00	
	VDE	2.16	2.13	2.12	1.50	1.13	~1.98
(ribose-H_2O)$^-$ (D)	ΔE	0.41	0.13	0.24	0.10		
	VDE	1.50	1.41	1.40	0.84		~1.53
(ribose-H_2O)$^-$ (E)	ΔE	0.43	0.13	0.23	0.08	0.27	
	VDE	1.58	1.51	1.50	0.96	1.68	
(ribose-H_2O)$^-$ (F)	ΔE	0.44	0.37	0.48	0.56		
	VDE	1.97	2.02	1.90	1.25		

Table S2 Bond strengths (kJ/mol) of O—H, C—H and C—OH bonds for the lowest energy open chain isomer of ribose$^-$ and fructose$^-$.

	O—H bond strength						C—OH bond strength					
	(1)H	(2)H	(3)H	(4)H	(5)H	(6)H	(1)OH	(2)OH	(3)OH	(4)OH	(5)OH	(6)OH
ribose$^-$ open chain (A)	—	155	201	202	280	—	—	151	241	279	377	—
fructose$^-$ open chain (A)	250	—	191	163	242	261	143	—	129	272	264	145

		C—H bond strength			
		(1C)H	(2C)H	(3C)H	(4C)H
ribose$^-$	open chain (A)	—	160	256	174
	open chain (B)	—	158	252	332
	open chain (C)	—	176	285	136
fructose$^-$	open chain (A)	166	—	173	319
	open chain (B)	204	—	206	333
	open chain (C)	207	—	223	

Table S3 Bond strengths (kJ/mol) of O—H bond for the lowest energy furanose isomers of ribose$^-$ and fructose$^-$.

	O—H bond strength					
	(1)H	(2)H	(3)H	(4)H	(5)H	(6)H
ribose$^-$ (G)	77	127	77	—	190	—
fructose$^-$ (K)	133	122	112	141	—	183