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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-H₂O)⁻ 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 \Leftrightarrow Figure 4.

Optimized Anionic structure					
Structural	open chain	open chain	open chain	open chain	open chain
Polymorphism	0.00	0.01	0.17	0.25	0.58
$\Delta E (eV)$	1.64	1.73	1.51	<u> </u>	0.38
VDE (eV)	1.04	1./3	1.51	1.00	0.17
Optimized Anionic structure	ుం లు లృతి చిత్తి చిల ల లు లు				
Structural		β -pyranose (¹ C ₄ -	α -pyranose (¹ C ₄ -	α -furanose (C ₂ –	β-furanose (C ₃
Polymorphism	open chain	chair)	chair)	endo)	– endo)
$\Delta E (eV)$	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	α -pyranose (⁴ C ₁ -	β -pyranose (⁴ C ₁ -	β -furanose (C ₂ –	α-furanose (C ₃ –	
Polymorphism	chair)	chair)	endo)	endo)	
$\Delta E (eV)$	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.

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Optimized Anionic structure	૾ૢૢૢૢૢૢૢૢૢૢૢૢૢૢૢૢ૽૾૾૾૾ૢૢૢ૽૽ૢૢૢૢૺ૽૾ૢૺ	● ²		• • •	
Structural Polymorphism	open chain (C) - (4C)H	open chain (C) - (3)H	α -pyranose (¹ C ₄ - chair) - (2)H	open chain (A) - (2)H	open chain (B) - (2C)H
$\Delta E (eV)$	0.00	0.11	0.22	0.25	0.27
VDE (eV)	3.16	4.47	3.75	3.91	2.74
Optimized Anionic					1 1 1
structure	a furances (C	a furances (C	open chain (A)	open chein (P)	ß fureness (C
Structural	α -furanose (C ₂ –	α -furanose (C ₂ –	open chain (A) -	open chain (B) -	β -furanose (C ₃
Polymorphism	endo) - (1)H 0.27	endo) - (3)H 0.27	(2C)H 0.28	(2)H 0.29	- endo) - (1)H 0.29
$\frac{\Delta E (eV)}{VDE (eV)}$	<u> </u>	3.83	2.64	3.93	3.96
VDE (ev)	5.19	3.03	2.04	5.95	3.90
Optimized Anionic structure					
Structural	α-pyranose (¹ C ₄ -	open chain (A) -	open chain (C) -	open chain (C) -	open chain (C) -
Polymorphism	chair) - (1)H	(4C)H	(2)H	(2C)H	(4)H
$\Delta E (eV)$	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 ($^{1}C_{4}$ - chair) - (2)H	β-pyranose ($^{1}C_{4}$ - chair) - (4)H	β-pyranose ($^{1}C_{4}$ - chair) - (3)H	α -furanose (C ₂ – endo) - (5C)H	β -furanose (C ₃ – endo) - (1)H
$\Delta E (eV)$	0.52	0.52	0.56	0.59	0.64
VDE (eV)	3.31	3.32	3.67	3.50	3.67
VDL (CV)	0.01	0.02	0.07	0.00	5.07
Optimized Anionic structure					β-pyranose
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	$(^{1}C_{4}\text{-chair}) - (1)H$
$\Delta E (eV)$	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					

					α-pyranose
Cture atoms 1	β -furanose (C ₃ –	open chain (D) -	open chain (C) -	α -pyranose (¹ C ₄ -	$(^{1}C_{4}\text{-chair})$ -
Structural Polymorphism	endo) - $(2)H$	(2C)H	(3)H	chair) - $(3)H$	(C4-chan) = (4)H
	0.80	0.86	0.94	1.14	1.17
$\Delta E (eV)$	3.40	2.25	4.06	2.83	2.81
VDE (eV)	5.40	2.25	4.00	2.03	2.01
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Optimized Anionic	- <u>- 23</u> -2	في آن	° ₀ ?€		
structure					
Structural	open chain (B) -	open chain (A) -	β -furanose (C ₃ –	open chain (A) -	open chain (A) -
Polymorphism	(C3)H	(C3)H	endo) - (5)H	(1C)H	(5)H
$\Delta E (eV)$	1.26	1.30	1.36	1.43	1.52
VDE (eV)	3.41	3.53	2.71	2.47	2.58
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Optimized Anionic				Je 19	
structure		· · · · · · · · · · · · · · · · · · ·	- · · · · · · · · · · · · · · · · · · ·	<u> </u>	a
Structural	open chain (C) -	open chain (C) -	open chain (D) -	α -furanose (C ₂ –	β-furanose (C ₃
Polymorphism	(3C)H	(1C)H	(4C)H	endo) - (4C)H	– endo) - (4C)H
$\Delta E (eV)$	1.56	1.60	1.73	1.77	1.78
VDE (eV)	2.40	2.35	2.60	2.27	2.16
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Optimized Anionic			1		
structure	Le 7 2 2	•••	7		ی وقع
					β-pyranose
Structural	β -pyranose (¹ C ₄ -	open chain (B) -	α -furanose (C ₂ –	α -furanose (C ₂ –	$(^{1}C_{4}$ -chair) -
Polymorphism	chair) - (5C)H	(4C)H	endo) - (2C)H	endo) - (1C)H	(2C)H
$\Delta E (eV)$	1.83	2.05	2.21	2.21	2.23
VDE (eV)	2.29	1.74	1.75	2.24	2.01
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Ontimized Anioria					
Optimized Anionic structure	🧉 🎐 🚡	9 3 g			
	α -pyranose (¹ C ₄ -	β -pyranose (¹ C ₄ -	open chain (C) -	open chain (A) -	
Structural Polymorphism	chair) - $(5C)H$	chair) - $(1C)H$	(C5)H	(C5)H	
* •	2.24	2.67	2.94	3.04	
$\frac{\Delta E (eV)}{VDE (eV)}$	1.93	1.54	1.06		
VDE (eV)	1.93	1.34	1.00	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			ૢઙૢ૾૾૾૾૾ૺ૾ૢ૽૽ૼૺૢૼૺૺૺૺૢ		
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
$\Delta E (eV)$	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]
$\Delta E (eV)$	0.43	0.44	0.57	0.59	0.85
VDE (eV)	1.58	1.97	1.50	1.01	3.85
(• • •)		<u></u>	<u> </u>		
Optimized Anionic structure	e	, , , , , , , , , , , , , , , , , , ,			
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
$\Delta E (eV)$	0.94	0.94	0.94	1.02	1.03
VDE (eV)	3.86	4.08	3.90	4.00	2.84
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Optimized Anionic structure	,	9 9 ° ° °	•,•;•		
Structural Polymorphism	open chain (A) - (3C)H - (4)OH	β -pyranose (${}^{1}C_{4}$ - chair) - (5C)H - (3/4)OH	open chain (A) – [(3)H + (2)OH]	open chain (A) - (1C)H - (2)OH	β-pyranose (¹ C ₄ -chair) - (1C)H - (4)OH
$\Delta E (eV)$	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		ی بورچی ب	<u>م</u>		
Structural Polymorphism	α -pyranose (¹ C 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
$\Delta E (eV)$	1.27	1.27	1.29	1.29	1.34
VDE (eV)	3.30	1.07	2.28	0.75	3.79
Optimized Anionic				•	•

	β -furanose (C ₃ –		β -furanose (C ₃ –		
Structural	endo) - (1)H -	open chain (B) -	endo) - (1)H -	open chain (A) -	open chain (A) -
Polymorphism	(2)OH	(4C)H - (5)OH	(3)OH	(2C)H - (4)OH	(5C)H - (2)OH
$\Delta E (eV)$	1.35	1.36	1.39	1.46	1.48
VDE (eV)	4.06	1.10	3.41	2.88	3.66
			0111		0.00
Optimized Anionic structure	• • • • • • • • • • • • • • • • • • •				
Structural	open chain (A) –	open chain (C) -	open chain (C) -	β -furanose (C ₃ – endo) - (1)H -	open chain (C) -
Polymorphism	[(2)H + (4)OH]	(2C)H - (4)OH	(3)H - (4)OH	(3)OH	(3)H - (5)OH
$\Delta E (eV)$	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		* 38 [°]			
	α -furanose (C ₂ –	α -furanose (C ₂ –	α -pyranose (¹ C ₄ -	α -furanose (C ₂ –	α -furanose (C ₂
Structural Polymorphism	endo) - (1)H - (3)OH	endo) - (1)H - (4C)OH	chair) - (1)H - (3)OH	endo) - (1)H - (5)OH	- endo) - [(1)H + (5)OH]
$\Delta E (eV)$	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			α-pyranose (¹ C ₄ -		
Structural Polymorphism	open chain $(A) -$ [(2)H + (3)OH]	open chain (C) - (2C)H - (5)OH	chair) - (5C)H - (1)OH	open chain $(A) -$ [(2)H + (5)OH]	open chain (A) - (3)OH - (5)H
$\Delta E (eV)$	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	β-pyranose (¹ C ₄ -	α-pyranose (¹ C ₄ -	α-pyranose (¹ C ₄ -	β-pyranose (¹ C ₄ -	open chain (A)
Structural Polymorphism	chair) - (5C)H - (1/4)OH	chair) - (2)H - (3)OH	chair) - (2)H - (4)OH	chair) - (1)H - (4)OH	-[(4)H + (3)OH]
$\Delta E (eV)$	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		******	• <u>;</u> •;		

en chain (A) - 4)H - (3)OH 1.72 3.13 by ranose ($^{1}C_{4}$ - hair) - (2)H - (1)OH 1.79 2.67	open chain (A) - (2)OH - (5)H 1.73 4.34 4.34 α-pyranose (¹ C ₄ - chair) - (2)H -	open chain (A) - (5)H - (2)OH 1.74 4.11 α-pyranose (¹ C ₄ -	α-furanose (C ₂ – endo) - (1)H - (2)OH 1.75 3.28	β-furanose (C ₃ - endo) - (1)H - (3)OH 1.76 3.23
4)H - (3)OH 1.72 3.13 3.13 byranose (¹ C ₄ - hair) - (2)H - (1)OH 1.79	(2)OH - (5)H 1.73 4.34 α-pyranose (¹ C ₄ - chair) - (2)H -	(5)H - (2)OH 1.74 4.11	(2)OH 1.75	(3)OH 1.76
1.72 3.13 yranose (¹ C ₄ - hair) - (2)H - (1)OH 1.79	1.73 4.34 α-pyranose (¹ C ₄ - chair) - (2)H -	1.74 4.11	1.75	1.76
3.13 yranose (¹ C ₄ - hair) - (2)H - (1)OH 1.79	4.34 4.34 α-pyranose (¹ C ₄ - chair) - (2)H -	4.11		
byranose (¹ C ₄ - nair) - (2)H - (1)OH 1.79	α-pyranose (¹ C ₄ - chair) - (2)H -		3.28	3.23
nair) - (2)H - (1)OH 1.79	chair) - (2)H -			مې د چې وړې
nair) - (2)H - (1)OH 1.79	chair) - (2)H -	a puranese (¹ C)		مېر مېرېد
nair) - (2)H - (1)OH 1.79	chair) - (2)H -			
nair) - (2)H - (1)OH 1.79	chair) - (2)H -		*	
nair) - (2)H - (1)OH 1.79	chair) - (2)H -	α pyranosa (^{1}C		e 💽 🖕
nair) - (2)H - (1)OH 1.79	chair) - (2)H -		α -pyranose (¹ C ₄ -	α-pyranose
(1)OH 1.79		chair) - (1)H -	chair) - (4)H -	$({}^{1}C_{4}\text{-chair})$ -
1.79	(1)OH	(4)OH	(1)OH	(3)H - (1)OH
	1.80	1.80	1.80	1.82
	2.67	3.71	3.12	3.20
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	•	- - - - (A)	$1 \sim 1 \sim 1$	α -pyranose
. ,			A	$({}^{1}C_{4}\text{-chair}) -$
				(4)H - (3)OH 1.83
				3.07
4.27	2.90	0.20	5.20	5.07
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yranose $({}^{1}C_{4}-$	$\beta$ -furanose (C ₃ –		$\beta$ -furanose (C ₃ –	$\alpha$ -furanose (C ₂
nair) - (1)H -	endo) - (1)H -	open chain (A) -	endo) - (2)H -	– endo) - (3)H -
(2)OH	(5)OH	(3)OH - (4)H	(5)OH	(1)OH
1.83	1.84	1.85	1.86	1.86
2.96	3.40	3.03	3.54	2.81
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		$\alpha$ -furanose (C ₂ –		$\alpha$ -furanose (C ₂
en chain (C) -	open chain (C) -		open chain (A) -	- endo) - (2C)H
	· · ·			- (3)OH
				1.94
				-0.11
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uranose ( $C_2$ –	$\beta$ -pyranose ( ¹ C ₄ -	$\alpha$ -furanose (C ₂ –	· · · ·	β-pyranose
$a_1a_1o_5c_1c_2 =$		$u$ -ruranose ( $U_2$ –		p-pyranose
	chair) - (1)H -	endo - (2)H -	open chain (C) -	
do) - (1C)H - (2)OH	chair) - (1)H - (3)OH	endo) - (2)H - (1)OH	open chain (C) - (3)H - (4)OH	$({}^{1}C_{4}\text{-chair}) - (1C)H - (2)OH$
	1.83	5)H + (2)OH]       (5)OH         1.82       1.82         4.29       2.96 $4.29$ 2.96 $1.82$ $1.82$ $4.29$ 2.96 $1.82$ $1.82$ $4.29$ $2.96$ $1.82$ $1.82$ $1.82$ $2.96$ $1.81$ $1.81$ $1.83$ $1.84$ $2.96$ $3.40$ $1.83$ $1.84$ $2.96$ $3.40$ $1.83$ $1.84$ $2.96$ $3.40$ $1.83$ $1.84$ $1.83$ $1.84$ $1.88$ $1.89$	en chain (A) – (5)OH (1C)H - (3)OH (1C)H (	en chain (A) – (5)H + (2)OH] (5)OH (1C)H - (3)OH (2)H - (3)OH 1.82 1.82 1.82 1.82 1.83 4.29 2.96 0.28 3.20

VDE (eV)	-0.25	3.02	2.72	3.44	-0.32
Optimized Anionic					
structure		<b>.</b>	🗨 🔶	• 🎍	
		$\alpha$ -furanose (C ₂ –			
_	$\beta$ -pyranose ( ¹ C ₄ -	endo) - (5)OH -	$\alpha$ -pyranose ( ¹ C ₄ -	$\alpha$ -furanose (C ₂ –	$\alpha$ -furanose (C ₂
Structural	chair) - (2C)H - (3)OH	(2)H with (1)OH transferring	chair) - (5C)H - (4)OH	endo) - (4C)H -	- endo) - [(3)H
Polymorphism ΔE (eV)	1.97	1.99	1.99	(5)OH 2.00	+ (5)OH] 2.01
VDE (eV)	-0.24	4.44	-0.19	-0.03	2.97
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		»». O	<b>*</b>		9
Optimized Anionic structure					
structure	β-pyranose ( $^{1}C_{4}$ -	$\beta$ -furanose (C ₃ –	$\beta$ -furanose (C ₃ –	β-pyranose ( $^{1}C_{4}$ -	$\alpha$ -furanose (C ₂
Structural	chair) - (3)H -	endo) - (1)H -	endo) - (3)H -	chair) - (4)H -	– endo) - (4C)H
Polymorphism	(2)OH	(5)OH	(1)OH	(3)OH	- (3)OH
$\Delta E (eV)$	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		38 3 3 3 3 3 3			
	0 (17	$\alpha$ -furanose (C ₂ – endo) - (5C)H -	4.6	$\alpha$ -furanose (C ₂ –	
~ .	$\beta$ -pyranose ( ¹ C ₄ -	(5)OH with	$\alpha$ -pyranose ( ¹ C ₄ -	endo) - (5)OH - (3)H with (1)OH	$\beta$ -pyranose
Structural Polymorphism	chair) - (2)H - (3)OH	(1)OH transferring	chair) - (4)H - (2)OH	(3)H with (1)OH transferring	$(^{1}C_{4}\text{-chair}) - (2)H - (4)OH$
$\Delta E (eV)$	2.05	2.06	2.06	2.07	2.07
VDE (eV)	2.84	4.62	2.84	4.55	2.81
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Optimized Anionic structure					• <u>;</u>
	$\alpha$ -furanose (C ₂ –	$\alpha$ -furanose (C ₂ –	β-pyranose ( $^{1}C_{4}$ -	β-furanose (C ₃ –	
Structural	endo) - (2)H -	endo) – [(2)H +	chair) - (2C)H -	endo) - (5)OH -	open chain (A)
Polymorphism	(5)OH	(5)OH	(1)OH	(3)H	(2C)H - (2)OH
$\Delta E (eV)$	2.08	2.08	2.09	2.09	2.09
VDE (eV)	3.45	3.45	-0.03	4.28	3.54
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Optimized Anionic					
structure					

Structural Polymorphism	$\beta$ -furanose (C ₃ – endo) - (3)H - (2)OH	β-furanose (C ₃ – endo) - (4C)H - (3)OH	β-pyranose ( ¹ C ₄ - chair) - (3)H - (4)OH	$\alpha$ -furanose (C ₂ – endo) - (5)OH - (1)H with (1)O transferring	α-pyranose ( ¹ C ₄ -chair) - (3)H - (2)OH
$\Delta E (eV)$	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			್ರಿ ಿ ಶಿ	ۣ ؋ ٳ	,
Structural Polymorphism	open chain (C) - (4C)H - (2)OH	$\beta$ -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
$\Delta E (eV)$	2.14	2.14	2.14	2.14	2.15
VDE (eV)	3.94	2.83	3.94	2.69	3.84
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Optimized Anionic structure				<b>.</b>	
Structural	$\beta$ -furanose (C ₃ – endo) - (2)H -	$\beta$ -pyranose ( ¹ C ₄ - chair) - (5C)H -	open chain (A) -	open chain (C) -	open chain (A) -[(5)H +
Polymorphism	(1)OH	(4)OH	(3)H - (2)OH	(2C)H - (2)OH	(3)OH]
$\Delta E (eV)$	2.15 2.37	2.19 - <b>0.37</b>	2.23 <b>3.61</b>	2.25 <b>3.41</b>	2.27 2.64
VDE (eV)	2.37	-0.37	3.01	3.41	2.04
Optimized Anionic structure	, <b>9</b> •3 •3 ,9 <b>4</b>				
Structural Polymorphism	open chain (A) - (5)H - (3)OH	$\beta$ -furanose (C ₃ – endo) - (4C)H - (5)OH	$\alpha$ -furanose (C ₂ – endo) - (2C)H - (1)OH	open chain (A) – [(4)H + (5)OH]	$\beta$ -furanose (C ₃ - endo) - (5)OH - (1)H
$\Delta E (eV)$	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				<u>می می می او</u>	
Structural Polymorphism	open chain (A) - (4C)H - (4)OH	$\alpha$ -furanose (C ₂ – endo) - (4C)H - (2)OH	open chain (C) - (3)H - (2)OH	open chain (A) - (5)H - (4)OH	$\alpha$ -furanose (C ₂ - endo) - (3)H - (4)OH
$\Delta E (eV)$	2.38	2.40	2.43	2.46	2.54
VDE (eV)	3.86	2.35	3.44	2.82	2.68

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Optimized Anionic structure	3 <b>0</b> 33				<b>*</b>
	$\beta$ -furanose (C ₃ –		β-furanose (C ₃ –		open chain (A)
Structural	endo) - (5)H -	open chain (A) -	endo) - (5)H -	open chain (A) -	- [(5)H +
Polymorphism	(1)OH	(1C)H - (4)OH	(2)OH	(3C)H - (5)OH	(4)OH]
$\Delta E (eV)$	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				<b>`</b>	
		$\alpha$ -pyranose ( ¹ C ₄ -			$\alpha$ -furanose (C ₂
Structural	open chain (C) -	chair) - (3)H -	open chain (A) -	open chain (A) -	– endo) - (4C)H
Polymorphism	(1C)H - (4)OH	(4)OH	(4C)H - (3)OH	(1C)H - (5)OH	- (1)OH
$\Delta E (eV)$	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					
	β-furanose (C ₃ –	$\beta$ -pyranose ( ¹ C ₄ -	$\alpha$ -furanose (C ₂ –	β-pyranose ( ¹ C ₄ -	α-furanose (C ₂
Structural	endo) - (4C)H -	chair) - (1C)H -	endo) - (1C)H -	chair) - (5C)H -	– endo) - (2C)H
Polymorphism	(1)OH	(3)OH	(1)OH	(2)OH	- (2)OH
$\Delta E (eV)$	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			ġ.		
	$\beta$ -pyranose ( $^{1}C_{4}$ -	$\alpha$ -pyranose ( ¹ C ₄ -	$\beta$ -pyranose ( $^{1}C_{4}$ -	$\alpha$ -pyranose ( ¹ C ₄ -	$\alpha$ -furanose (C ₂
Structural	chair) - (2C)H -	chair) - (5C)H -	chair) - (2C)H -	chair) - (5C)H -	- endo) - (2C)H
Polymorphism	(2)OH	(3)OH	(4)OH	(1)OH 3.42	- (5)OH 3.44
$\frac{\Delta E (eV)}{VDE (eV)}$	3.20 2.24	3.26 <b>1.92</b>	3.32 1.62	2.05	<b>2.01</b>
VDE (ev)	2.24	1.92	1.02	2.03	2.01
Optimized Anionic structure					
	$\alpha$ -furanose (C ₂ –	β-pyranose ( $^{1}C_{4}$ -	_		
Structural	endo) - (1C)H -	chair) - (1C)H -	open chain (C) -		
Polymorphism	(3)OH	(1)OH	(5C)H - (5)OH		
$\Delta E (eV)$	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-H₂O)⁻ 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 left to right.

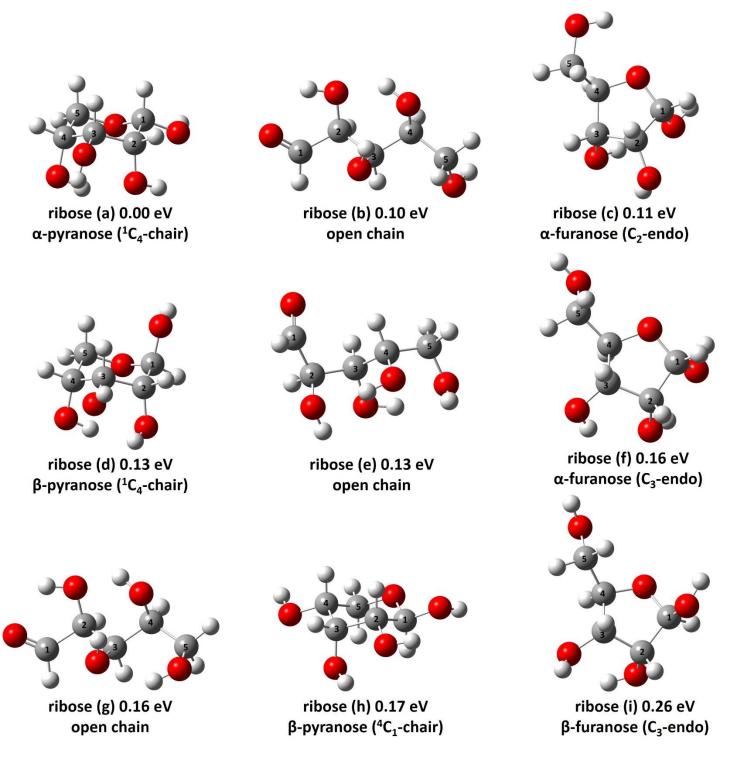


Figure S10 Optimized geometries of the typical low lying neutral isomers of ribose based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The C atom numberings are given. For open chain structures (1)C to (5)C is ordered from left to right. For both 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  $\Leftrightarrow$  (1)C.

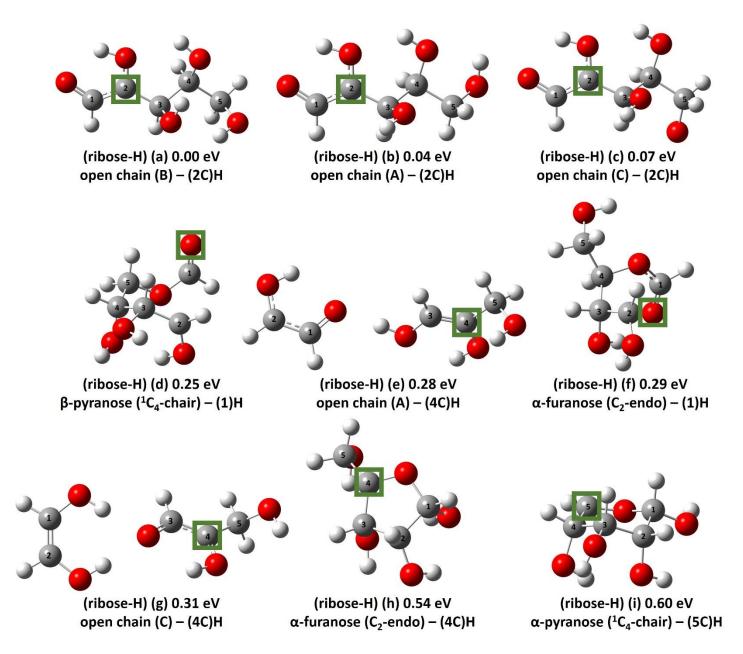
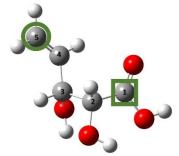
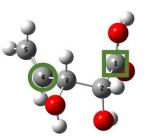


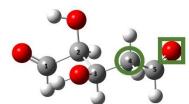
Figure S11 Optimized geometries of the typical low lying neutral isomers of (ribose-H) based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The green square indicates loss of hydrogen at the indicated position. The C atom numberings are given. For 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  $\Leftrightarrow$  (1)C.



(ribose-H₂O) (c) 0.61 eV α-furanose (C₂-endo) – (1C)H – (5)OH

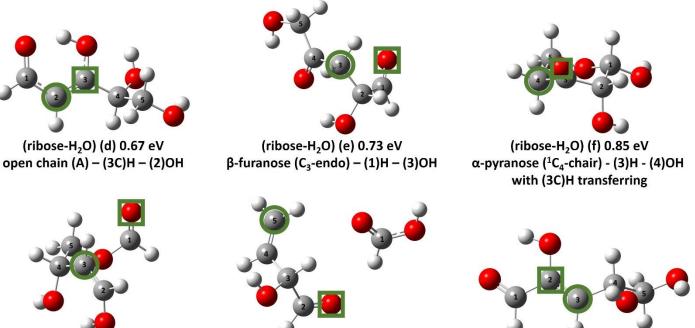


(ribose-H₂O) (b) 0.49 eV  $\beta$ -pyranose (¹C₄-chair) – (1C)H – (4)OH



(ribose-H₂O) (a) 0.00 eV open chain (A) - (5)H - (4)OH with (5C)H transferring

(ribose-H₂O) (g) 0.88 eV



(ribose-H₂O) (i) 0.96 eV open chain (A) - (2C)H - (3)OH

β-furanose (C₃-endo) – (2)H – (5)OH β-pyranose ( ${}^{1}C_{4}$ -chair) – (1)H – (3)OH Figure S12 Optimized geometries of the typical low lying neutral isomers of (ribose-H₂O) 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  $(1)C \Leftrightarrow (1)C$ .

(ribose-H2O) (h) 0.88 eV

Optimized neutral structure					
Structural	$\alpha$ -pyranose ( ¹ C ₄ -		$\alpha$ -furanose (C ₂ –	$\beta$ -pyranose ( ¹ C ₄ -	
Polymorphism	chair)	open chain	endo)	chair)	open chain
$\Delta E (eV)$	0.00	0.10	0.11	0.13	0.13
Optimized neutral structure	α-furanose (C ₃ –		β-pyranose ( ⁴ C ₁ -	β-furanose (C ₃ –	α-pyranose
Structural Polymorphism	endo)	open chain	chair)	endo)	$({}^{4}C_{1}$ -chair)
$\Delta E (eV)$	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	
$\Delta E (eV)$	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.

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Optimized neutral structure		್ರತ್ಯತ್ಯಕ್			وتصفر مهمر
Structural Polymorphism	open chain (B) - (2C)H	open chain (A) - (2C)H	open chain (C) - (2C)H	β-pyranose ( $^{1}C_{4}$ - chair) - (1)H	open chain (A) - (4C)H
$\Delta E (eV)$	0.00	0.04	0.07	0.25	0.28
	<b>.</b>				
Optimized neutral		್ಟ್ ಕಿದ್ದಾಳಿ			
structure	$\alpha$ -furanose (C ₂ –	open chain (C) -	$\alpha$ -furanose (C ₂ –	$\beta$ -furanose (C ₃ –	open chain (A) -
Structural Polymorphism	endo) - (1)H	(4C)H	endo) - $(4C)H$	endo) - $(4C)H$	(3)H
$\Delta E (eV)$	0.29	0.31	0.54	0.56	0.57
	•				
Optimized neutral structure					
Structural	open chain (C) -	$\alpha$ -pyranose ( ¹ C ₄ -	open chain (C) -	open chain (B) -	open chain (A) -
Polymorphism ΔE (eV)	(3)H 0.57	chair) - (5C)H 0.60	(3C)H 0.60	(4C)H 0.63	(1C)H 0.65
	0.07	0.00	0.00	0.00	
Optimized neutral structure					
Structural Polymorphism	open chain (C) - (1C)H	open chain (C) - (C5)H	β-pyranose ( $^{1}C_{4}$ - chair) - (5C)H	$\beta$ -pyranose ( ¹ C ₄ - chair) - (1C)H	$\alpha$ -furanose (C ₂ - endo) - (1C)H
$\Delta E (eV)$	0.65	0.68	0.73	0.81	0.86
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Optimized neutral structure					ାହାଁ କୁନ୍ଦି କୁନ୍ଦି କୁନ୍ଦି କୁନ୍ଦି
Structural Polymorphism	$\beta$ -pyranose ( $^{1}C_{4}$ - chair) - (2)H	β-pyranose ( ¹ C ₄ - chair) - (4)H	$\alpha$ -pyranose ( $^{1}C_{4}$ - chair) - (2)H	α-pyranose ( ¹ C ₄ - chair) - (1)H	$\alpha$ -furanose (C ₂ - endo) - (6C)H
$\frac{\Delta E \text{ (eV)}}{\Delta E \text{ (eV)}}$	0.86	0.87	0.91	0.92	0.94
Optimized neutral structure					
Structural Polymorphism	$\alpha$ -furanose (C ₂ – endo) - (3)H	α-pyranose ( ¹ C ₄ - chair) - (4)H	open chain (A) - (5)H	$\alpha$ -pyranose ( ¹ C ₄ - chair) - (3)H	$\beta$ -pyranose ( ¹ C ₄ -chair) - (4)H
$\Delta E (eV)$	1.00	1.02	1.05	1.08	1.09
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Optimized neutral structure			30 9 9 9 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		
Structural	$\beta$ -furanose (C ₃ –	open chain (A) -	open chain (A) -	β-furanose (C ₃ –	$\alpha$ -furanose (C ₂
Polymorphism	endo) - (2)H	(2)H	(4)H	endo) - (5)H	– endo) - (2)H
$\Delta E (eV)$	1.11	1.12	1.13	1.13	1.15
Optimized neutral structure					
Structural	open chain (C) - $(2)$ L	$\beta$ -furanose (C ₃ – endo) - (1)H	$\beta$ -furanose (C ₃ – endo) - (1)H	$\beta$ -furanose (C ₃ – endo) - (3)H	open chain (B) -
Polymorphism	(2)H 1.16	1.17	1.20	1.20	(2)H 1.24
ΔE (eV)		1.17	1.20	1.20	1.24
Structural Polymorphism ΔE (eV)	open chain (C) - (3)H 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 ΔE (eV)	open chain (A) – [(5)H + (4)OH] with (5C)H transferring 0.00	β-pyranose ( ¹ C ₄ - chair) - (1C)H - (4)OH 0.49	α -furanose (C ₂ – endo) - (1C)H - (5)OH 0.61	open chain (A) - (3C)H - (2)OH 0.67	β-furanose (C ₃ – endo) - (1)H - (3)OH 0.73
Optimized neutral structure					99999 0
Structural Polymorphism ΔE (eV)	α-pyranose ( ¹ C ₄ - chair) - (3)H - (4)OH with (3C)H transferring 0.85	β-pyranose ( ¹ C ₄ - chair) - (1)H - (3)OH 0.88	β-furanose (C ₃ – endo) - (5)OH - (2)H 0.88	open chain (A) - (5)H - (4)OH with (5C)H transferring 0.89	α -furanose (C ₂ – endo) - (1)H - (3)OH 0.95
Optimized neutral structure	• <b>,</b> • <b>,</b> • <b>,</b> •,•,•,•,•,•,•,•,•,•,•,•,•,•				
Structural Polymorphism ΔE (eV)	open chain (A) - (2C)H - (3)OH 0.96	open chain (B) - (2C)H - (3)OH 0.99	open chain (C) - (4)H - (3)OH 1.01	α-pyranose ( ¹ C ₄ - chair) - (2)H - (1)OH 1.02	α-pyranose ( ¹ C ₄ -chair) - (3)H - (2)OH 1.04
Optimized neutral structure	,		م م م م		
Structural Polymorphism ΔE (eV)	β-furanose (C ₃ – endo) - (1)H - (2)OH 1.06	β-furanose (C ₃ – endo) - (5C)H - (2/3)OH 1.08	open chain (C) - (2C)H - (3)OH 1.08	open chain (A) – [(4)H + (5)OH] 1.11	α-pyranose ( ¹ C ₄ -chair) - (1)H - (3)OH 1.14
Optimized neutral structure		• رُ <mark>بُو</mark> وَ	<b>٩</b>		
Structural Polymorphism ΔE (eV)	β-furanose (C ₃ – endo) - (1)H - (2)OH 1.16	open chain (A) – [(4)H + (2)OH] 1.16	open chain (C) - (2)H - (3)OH with (2C)H transferring 1.17	open chain (A) – [(2)H + (3)OH] 1.18	α-furanose (C ₂ – endo) - (1C)H - (2)OH 1.19

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Optimized neutral structure				ಁ಄ೢೢೢಁೢೢ	
Structural Polymorphism	open chain (C) - (3)H - (4)OH	α-furanose (C ₂ – endo) - (4C)H - (5)OH	$\alpha$ -pyranose ( $^{1}C_{4}$ - chair) - (5C)H - (4)OH	open chain (A) - (1C)H - (3)OH	β-pyranose ( ¹ C ₄ -chair) - (3C)H - (4)OH
$\Delta E (eV)$	1.21	1.22	1.24	1.27	1.29
Optimized neutral		, , , , , , , , ,			
structure Structural Polymorphism ΔE (eV)	open chain (A) – [(4)H + (2)OH] 1.30	α-furanose (C ₂ – endo) - (4C)H - (3)OH 1.30	β-pyranose ( ¹ C ₄ - chair) - (5C)H - (4)OH 1.33	β-furanose (C ₃ – endo) - (4C)H - (5)OH 1.33	β-furanose (C ₃ – endo) - (4C)H - (3)OH 1.38
Optimized neutral structure		ڰ <b>ؚ</b>	,	م بالان من	
Structural Polymorphism	open chain (C) - (1C)H - (3)OH	open chain (A) - (1C)H - (2)OH	$\alpha$ -furanose (C ₂ – endo) - (4C)H - (2)OH	open chain (A) - (4C)H - (5)OH	$\beta$ -furanose (C ₃ - endo) - (5)H - (1)OH with (5C)H transferring
$\Delta E (eV)$	1.36	1.39	1.39	1.39	1.40
Optimized neutral structure		Jan and a geo			
Structural Polymorphism ΔE (eV)	α-pyranose ( ¹ C ₄ - chair) - (1)H - (2)OH 1.40	open chain (C) - (1C)H - (2)OH 1.43	open chain (A) - (3)H - (5)OH 1.47	open chain (C) - (4C)H - (5)OH 1.48	β-furanose (C ₃ – endo) - (1)H - (5)OH 1.51
			I		I
Optimized neutral structure	999 er ja				
Structural Polymorphism	$\alpha$ -pyranose ( $^{1}C_{4}$ - chair) - (2)H - (4)OH	$\alpha$ -furanose (C ₂ – endo) - (1)H - (5)OH	open chain (C) - (3)H - (5)OH	$\alpha$ -furanose (C ₂ – endo) – [(1)H + (5)OH]	$\alpha$ -pyranose ( ¹ C ₄ -chair) - (4)H - (2)OH
$\Delta E (eV)$	1.51	1.57	1.57	1.64	1.66

Optimized neutral structure				,	
Structural Polymorphism	open chain (A) - (3)H - (4)OH	β-pyranose ( ¹ C ₄ - chair) - (2)H - (4)OH	open chain (A) - (5)H - (3)OH	open chain (A) – [(5)H + (3)OH]	$\alpha$ -furanose (C ₂ - endo) - (1)H - (5)OH
$\Delta E (eV)$	1.66	1.71	1.75	1.75	1.78
Optimized neutral structure		ೢೢೢೢೲೣೢೢ಄ೢ			
Structural	$\beta$ -pyranose ( ¹ C ₄ - chair) - (5C)H -	open chain (C) - $(2)H$ (4)OH	$\beta$ -pyranose ( ¹ C ₄ - chair) - (5C)H -	$\alpha$ -furanose (C ₂ – endo) - (3)H -	$\alpha$ -pyranose ( ¹ C ₄ -chair) - (4)H - (3)OH
Polymorphism	(1/4)OH 1.83	(3)H - (4)OH 1.87	(2)OH 1.92	(1)OH 1.92	1.94
$\Delta E (eV)$	1.03	1.0/	1.92	1.92	1.94
Optimized neutral structure	β-pyranose ( ¹ C ₄ -		β-pyranose ( ¹ C ₄ -	β-pyranose ( ¹ C ₄ -	open chain (A)
Structural Polymorphism	chair) - (2)H - (3)OH	open chain (C) - (4C)H - (3)OH	chair) - (3)H - (2)OH	chair) - (2)H - (1)OH	-[(2)H + (4)OH]
$\Delta E (eV)$	1.95	1.95	1.95	1.95	1.96
Optimized neutral structure	•		9-3-3 		
Structural Polymorphism	open chain (C) - (2)H - (4)OH	β-pyranose ( ¹ C ₄ - chair) - (1)H - (2)OH	β-pyranose ( ¹ C ₄ - chair) - (5C)H - (3/4)OH	β-furanose (C ₃ – endo) - (3)H - (1)OH	$\alpha$ -pyranose ( $^{1}C_{4}$ -chair) - (2)H - (3)OH
$\Delta E (eV)$	1.97	1.98	1.99	2.00	2.00
Optimized neutral structure	<b></b>				
Structural Polymorphism	open chain (A) - (1C)H - (4)OH	$\alpha$ -furanose (C ₂ – endo) - (3)H - (2)OH	α-pyranose ( ¹ C ₄ - chair) - (1)H - (4)OH	β-furanose (C ₃ – endo) - (1)H - (3)OH	open chain (C) - (4)H - (5)OH
$\Delta E (eV)$	2.02	2.03	2.03	2.04	2.04
Optimized neutral structure					B furances (C
Structural Polymorphism	open chain (A) - (3)OH - (4)H	α-pyranose ( ¹ C 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

$\Delta E (eV)$	2.05	2.06	2.07	2.07	2.07
					1
Optimized neutral structure			္ စိုရာ, ခ်.လို. ³ . ရ		
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 ( ¹ C ₄ - chair) - (1C)H - (3)OH	$\beta$ -furanose (C ₃ - endo) - (1)H - (5)OH
$\Delta E (eV)$	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	$\alpha$ -furanose (C ₂ – endo) – [(2)H + (5)OH	α-furanose (C ₂ – endo) - (2) H - (5)OH	open chain (A) - (5)H - (2)OH
$\Delta E (eV)$	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]	$\alpha$ -furanose (C ₂ – endo) - (1C)H - (3)OH	open chain (A) - (3)H - (2)OH	open chain (C) - (3)H - (2)OH
$\Delta E (eV)$	2.50	2.51	3.07	3.16	3.21
Optimized neutral structure					
Structural Polymorphism ΔE (eV)	β-furanose (C ₃ – endo) - (5)H - (2)OH 3.27	$\alpha$ -furanose (C ₂ – endo) - (1C)H - (1)OH 3.45	$\alpha$ -furanose (C ₂ – endo) - (4C)H - (1)OH 3.55	β-pyranose ( ¹ C ₄ - chair) - (1C)H - (1)OH 3.85	$\alpha$ -furanose (C ₂ - endo) - (5)OH - (2)H with (1)OH transferring 4.13

Figure S15 Optimized geometries of the typical low lying neutral isomers of (ribose-H₂O) 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 ( ¹ C ₄ - chair)
ΔE VDE(eV)	0.00	0.01	0.19	0.29 0.92	0.64 -0.52
VDE(CV)	1.40	1.57	1.57	0.92	-0.32
Optimized anionic structure					
Structural polymorphism	ribose ⁻ (F) α-pyranose ( ¹ C ₄ - chair)	ribose ⁻ (G) α-furanose (C ₂ - endo)	ribose ⁻ (H) β-furanose (C ₃ - endo)		
ΔΕ	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					
	(ribose-H) ⁻ (A)	(ribose-H) ⁻ (B)	(ribose-H) ⁻ (C)	(ribose-H) ⁻ (D)	(ribose-H) ⁻ (E)
Structural	open chain (C) –	open chain (C) –	$\alpha$ -pyranose ( ¹ C ₄ -	open chain (A) –	open chain (B) –
polymorphism	(4C)H	(3)H	chair) $-(2)H$	(2)H	(2C)H
$\Delta E$	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					
	(ribose-H) ⁻ (F)	(ribose-H) ⁻ (G)	(ribose-H) ⁻ (H)	(ribose-H) ⁻ (I)	(ribose-H) ⁻ (J)
Structural	α-furanose (C ₂ -	α-furanose (C ₂ -	open chain (A) –	open chain (B) –	$\alpha$ -pyranose ( ¹ C ₄ -
polymorphism	endo) - (1)H	endo) – $(3)H$	(2C)H	(2)H	chair) $-(1)H$
$\Delta E$	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		دي.€ر رځي⊆ي د دي. د دي.ور	್ಕಿ ವ್ಯಾತ್ಮೇ ಕ್ರಿ ವ್ಯಾತ್ಮೇ ಕ್ರಿ ವ್ಯಾತ್ಮೇ ಕ್ರಿ ವ್ಯಾತ್ಮೇ ಕ್ರಿ ವ್ಯಾತ್ಮೇ ಕ್ರಿ ವ್ಯಾತ್ಮೇ ಕ್ರಿ ವ್ಯಾತ್ಮೇ ಕ್ರಿ ವ್ಯಾತ್ಮೇ ಕ್ರಿ ವ್ಯಾತ್ಮ ಕ್ರಿ ವ್ಯಾತ್ಮ ಕ್ರಿ ವ್ಯಾತ್ಮ ಕ್ರಿ ವ್ಯಾತ್ಮ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಾ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಾ ವ್ಯಾತ್ ಕ್ರಿ ವ್ಯಾತ್ ಕ್ರಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾತ್ ಕ್ರಾ ವ್ಯಾತ ಕ್ರಾ ಕ್ರಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾ ಕ್ರಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾ ವ್ಯಾತ ಕ್ರಾ ಕ್ರಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾ ವ್ಯಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾ ವ್ಯಾ ವ್ಯಾ ವ್ಯಾ ವ್ಯಾತ ಕ್ರಾ ವ್ಯಾ ವ್ಯಾ ವ		
	(ribose-H) ⁻ (K)	(ribose-H) ⁻ (L)	(ribose-H) ⁻ (M)	(ribose-H) ⁻ (N)	
Structural	$\beta$ -pyranose ( $^{1}C_{4}$ -	open chain (A) –	open chain (C) –	open chain (D) –	
polymorphism	chair) $- (4)H$	(4C)H	(2C)H	(2C)H	
ΔΕ	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	ೢೢ಄ೢೲೲ	ۣ ڔ ڡ ٳ ڡ ٳ	္ရခုိ ုခဲ့ ၂၀.၂ ိုခဲ့သြား	• <b>3 1 1 1 1 1 1 1 1 1 1</b>	۹۶ ۲۵۹۹ کور ۲۹۹۹ کور
	$(ribose-H_2O)^-(A)$	$(ribose-H_2O)^-(B)$	$(ribose-H_2O)^-(C)$	$(ribose-H_2O)^-(D)$	$(ribose-H_2O)^-(E)$
Structural	open chain (C) –	open chain (A) –	open chain (C) –	open chain (A) –	open chain (C) –
polymorphism	(2)H–(4)OH	(2)H-(4)OH	(4C)H– (5)OH	(2C)H–(3)OH	(2C)H-(3)OH
ΔΕ	0.03	0.00	0.26	0.13	0.13
VDE(eV)	3.17	3.03	2.13	1.41	1.51
					1
Optimized anionic structure	૾૽૾૾ૺ૾૾૾૾			૾ૢૡૼૢૢૢૢૢૼ૾	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
	(ribose-H ₂ O) ⁻ (F)	(ribose-H ₂ O) ⁻ (G)	(ribose-H ₂ O) ⁻ (H)	(ribose-H ₂ O) ⁻ (I)	$(ribose-H_2O)^{-}(J)$
	open chain $(A) -$	open chain $(B)$ –	open chain $(A) -$	open chain $(A) -$	$\alpha$ -pyranose ( ¹ C ₄ -
Structural	(4C)H-(5)OH	(2C)H-(3)OH	(4)H-(2)OH	(3)H-(2)OH	chair) $-(1)H-$
polymorphism					(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					
	$(ribose-H_2O)^-(K)$				
	β-furanose (C ₃ -				
Structural	endo) – (2)H–				
polymorphism	(5)OH				
ΔΕ	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 o	f (ribose-H) ⁻	∆H (kcal/mol)
(	A)	28.35
(	В)	29.90
(	C)	17.07
(	E)	37.84
	(ribose-H) ⁻	
ribose ⁰ —	→ (ribose-H) ⁰ + H —	e (ribose-H)⁻ + H
Isomers of	f (ribose-H) ⁻	ΔH (kcal/mol)
()	A)	19.22
(1	3)	20.76
(1	C)	25.32
(		23.50

Figure S19 (a) Calculated  $\Delta H$  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  $\Delta H$  values for generating every specific isomer, the reactant that has the most similar structure to that of final product is chosen.

		(ribose-H ₂ O) ⁻			
	ribose ⁻ —	→ (ribose-OH) ⁻ + OH →	→ (ribose-H ₂ 0	D) ⁻ + H + OH	
	ribose⁻ → (ribose	e-H)⁻ + H → (ribose-O	→ (ribose-H ₂ O) ⁻ + H +	O + H	
		ribose⁻ ───→ (ri	bose-H ₂ O) ⁻ + H ₂ O		
	Isome	rs of (ribose-H ₂ O) ⁻	∆H (kcal/mol	)	
			96.07		
		(C)	261.87		
			-18.70		
		(5)	101.87		
		(D)	267.66		
			-12.91	0	
		ribose-OH)⁰ + OH ───→(			
ribose ⁰ —					$\rightarrow$ (ribose-H ₂ O) ⁻ + H + O + H
	ribose ⁰ —	$\rightarrow$ (ribose-H ₂ O) ⁻ + H ₂ O -	e → (ribose-H	₂ O) ⁻ + H ₂ O	
	Isom	ers of (ribose-H ₂ O) ⁻	ΔH (kcal/mo	ol)	
			86.94		
		(C)	252.73		
			-27.84		
		(=)	84.14		
		(D)	249.94		
			-30.63		

Figure S19 (b) Calculated  $\Delta H$  values for different possible pathways for generating specific (ribose-H₂O)⁻ anionic isomers. Red color indicates an anionic mechanism. Black color indicates a neutral mechanism. When we calculate the  $\Delta H$  values for generating every specific isomer, the reactant that has the most similar structure to that of final product is chosen.

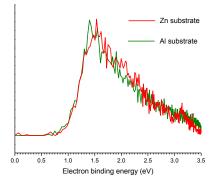


Figure S20 Photoelectron spectrum of (ribose- $H_2O$ )⁻ recording using 355 nm photons with sample (D-ribose/DCM) spayed on different absorption substrates.

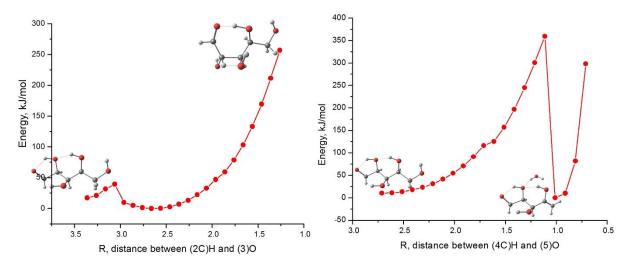


Figure S21. (left) Relaxed Potential Energy Surface scan of ribose⁻ parent open chain (A) through forming of an H₂O unit. R(Å): distance between (2C)H and (3)O. (right) Relaxed Potential Energy Surface scan of ribose⁻ parent open chain (A) through forming of an H₂O unit. R(Å): distance between (4C)H and (5)O.

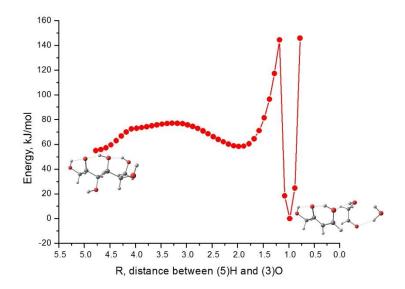


Figure S22. Relaxed Potential Energy Surface scan of fructose⁻ parent open chain (A) through forming of an  $H_2O$  unit. R(Å): distance between (5)H and (3)O.

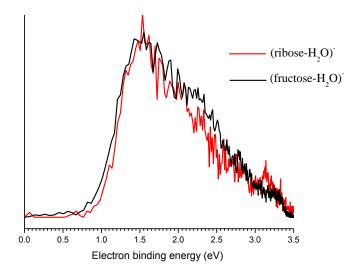


Figure 23 Photoelectron spectra of (ribose- $H_2O$ )⁻ and (fructose- $H_2O$ )⁻ recording with 355 nm photons with sample (D-ribose/DCM) spayed on a Zn substrate.

Table S1 The calculated VDEs and their relative energies ( $\Delta E$ ) of lower lying isomers of (ribose-H₂O)⁻ based on B3LYP/6-311++G(d,p), M062X/6-311++G(d,p),  $\omega$ B97XD/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-	M062X/6-	ωB97XD/6-	MP2/6-	MP2/Aug-	experimental
		311 + + G(d,p)	CC-PVTZ	measurement			
(ribose-H ₂ O) ⁻	ΔΕ	0.00	0.03	0.04	0.05	0.00	
(A)	VDE	3.13	3.17	3.04	2.22	2.50	
(ribose-H ₂ O) ⁻	ΔΕ	0.04	0.00	0.00	0.00		
(B)	VDE	3.09	3.03	3.04	2.16		
(ribose-H ₂ O) ⁻	ΔΕ	0.32	0.26	0.33	0.42	0.00	
(C)	VDE	2.16	2.13	2.12	1.50	1.13	~1.98
(ribose-H ₂ O) ⁻	ΔΕ	0.41	0.13	0.24	0.10		
(D)	VDE	1.50	1.41	1.40	0.84		~1.53
(ribose-H ₂ O) ⁻	ΔΕ	0.43	0.13	0.23	0.08	0.27	
(E)	VDE	1.58	1.51	1.50	0.96	1.68	
(ribose-H ₂ O) ⁻	ΔΕ	0.44	0.37	0.48	0.56		
(F)	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 bor	nd strength	1				C—OH bo	nd 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 bon	d strengt	h
		(1C)H	(2C)H	(3C)H	(4C)H
	open chain (A)	_	160	256	174
ribose⁻	open chain (B)	_	158	252	332
	open chain (C)	_	176	285	136
	open chain (A)	166	_	173	319
fructose-	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