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Supporting Information

Stability of the Conformationally Locked Free Fructose: Theoretical and Computational Insights

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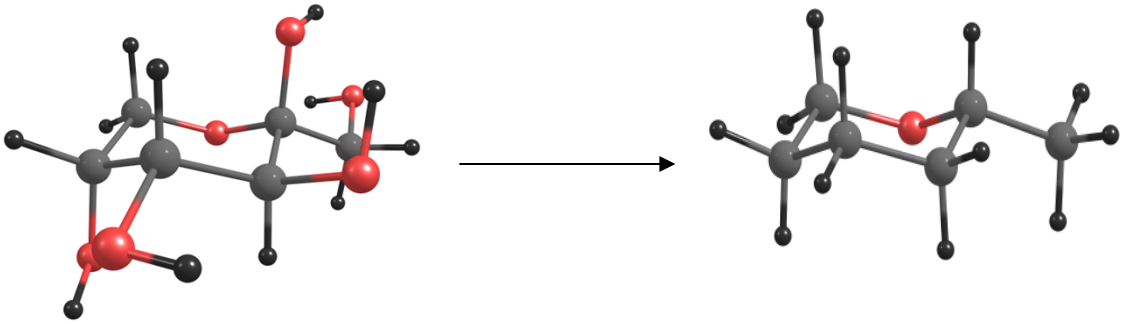

(A)
β-Fructo-Pyranose

(B)
β-Fructo-Pyranose Ring without hydroxyl groups

Supporting Information Figure S1: The structure of fructose ring (B) used for calculation of ring energy obtained by replacing hydroxyl groups on original fructose (A) by H-atoms and keeping the carbon skeleton frozen.

Supporting Information Table S1: Hyperconjugation energy obtained by deletion, E(deletion) and also perturbation E(2) methods at HF/6-311++G(d,p) level.

Conformer	$n^{O(6)} \rightarrow \sigma^{*C(2)-O(2)}$ **(Endo)**				$n^{O(2)} \rightarrow \sigma^{*C(2)-O(6)}$ **(Exo)**			
	E(deletion)[a]	E(2)[a]	Ei-Ej	Fij	E(deletion)	E(2)	Ei-Ej	Fij
α-Pry-1	11.410 LP(1)	15.4	1.08	0.116	17.572	24.23	1.03	0.141
	1.088 LP(2)	1.31	1.37	0.038				
α-Pry-2	11.915 LP(1)	15.12	1.08	0.115	17.635	24.36	1.03	0.142
	1.125 LP(2)	1.35	1.38	0.039				
α-Pry-3	11.125 LP(1)	15.36	1.05	0.114	15.396 LP(1)	21.05	1.05	0.133
	1.486 LP(2)	1.80	1.34	0.044	0.514 LP(2)	0.61	1.41	0.026
β-Pry-1	12.049 LP(1)	16.82	1.04	0.118	15.477	20.96	1.07	0.134
	1.624 LP(2)	1.98	1.33	0.046				
β-Pry-2	12.542 LP(1)	17.51	1.03	0.120	15.292	20.65	1.08	0.133
	1.666 LP(2)	2.04	1.32	0.047				
β-Pry-3	13.142 LP(1)	18.28	1.03	0.123	13.571 LP(1)	18.37	1.07	0.126
	1.052 LP(2)	1.29	1.32	0.037	0.589 LP(2)	0.69	1.43	0.028
	$n^{O(5)} \rightarrow \sigma^{*C(2)-O(2)}$ **(Endo)**				$n^{O(2)} \rightarrow \sigma^{*C(2)-O(5)}$ **(Exo)**			
	E(deletion)	E(2)	Ei-Ej	Fij	E(deletion)	E(2)	Ei-Ej	Fij
α-Fur-1	13.64 LP(1)	18.82	1.04	0.125	14.587 LP(1)	19.94	1.06	0.13
	0.459 LP(2)	0.55	1.35	0.025	0.581 LP(2)	0.68	1.42	0.028
α-Fur-2	13.387	18.39	1.05	0.124	14.926 LP(1)	20.47	1.05	0.131
					0.536 LP(2)	0.63	1.41	0.027
αFur-3	13.57 LP(1)	18.69	1.04	0.125	14.699 LP(1)	20.04	1.06	0.13
	0.618 LP(2)	0.74	1.36	0.029	0.531 LP(2)	0.62	1.42	0.027
β-Fur-1	14.973	20.47	1.03	0.13	14.756	20.33	1.07	0.132
β-Fur-2	14.343	19.78	1.04	0.128	15.764	21.36	1.07	0.135
β-Fur-3	11.521	15.71	1.05	0.116	11.314	15.65	1.06	0.115

[a] Two lone pair (LP) →**σ*(C-O)** interactions, ie LP(1) and LP(2) are presented in the NBO output; both of these are presented here.

Supporting Information Table S2: The relative stability of various fructose conformers calculated as sum of different contributing factors. Energy values are presented in kcal mol^{-1}. The strain energies were evaluated with group equivalence homodesmic method and the hyperconjugation energies were evaluated with deletion method, E(deletion).

Conformer	Sum of all the H-bond energies	Strain Energy [a]	Hyperconjugation [b]	Total Energetic Stabilization	Relative Energy
α-Pry-1	-12.98	27.02	30.070	-16.03	0.328
α-Pry-2	-12.80	27.25	29.995	-15.55	0.810
α-Pry-3	-12.55	25.21	28.521	-15.86	0.492
β-Pry-1	**-12.92**	**25.71**	**29.150**	**-16.36**	**0.000**
β-Pry-2	-10.27	25.03	29.500	-14.74	1.615
β-Pry-3	-12.35	25.43	28.350	-15.272	1.085
α-Fur-1	-12.24	27.70	29.267	-13.81	2.548
α-Fur-2	-11.52	27.86	28.849	-12.51	3.844
αFur-3	-9.41	27.93	29.418	-10.90	5.454
β-Fur-1	-11.3	27.90	29.729	-13.13	3.226
β-Fur-2	-8.93	27.74	30.107	-11.30	5.059
β-Fur-3	-20.26	29.30	22.835	-13.80	2.559

[a] Positive value of strain energy represents destabilization

[b] Negative values of hyperconjugation represents stabilization and these negative values were used in valuation of total energetic stabilization.

Supporting Information Table S3: The relative stability of various fructose conformers calculated as sum of different contributing factors. Energy values are presented in kcal mol^{-1}. The strain energies were evaluated with conventional homodesmic method and the hyperconjugation energies were evaluated perturbation method, E(2).

Sum of all the H-bond energies	Strain Energy [a]	Hyperconjugation [b]	Total Energetic Stabilization	Relative Energy
-12.98	21.17	40.94	-32.75	0.068
-12.8	21.40	40.84	-32.24	0.575
-12.55	19.36	38.82	-32.01	0.803
-12.92	**19.87**	**39.76**	**-32.81**	**0.000**
-10.27	19.18	40.2	-31.29	1.525
-12.35	19.58	38.63	-31.40	1.415
-12.24	21.85	39.99	-30.38	2.435
-11.52	22.01	39.49	-29.00	3.813
-9.41	22.08	40.09	-27.42	5.392
-11.3	22.05	40.8	-30.05	2.765
-8.93	21.89	41.14	-28.18	4.636
-20.26	23.45	31.36	-28.17	4.644

[a] Positive value of strain energy represents destabilization

[b] Negative values of hyperconjugation represents stabilization and these negative values were used in valuation of total energetic stabilization.

Supporting Information Table S4: The relative stability of various fructose conformers calculated as sum of different contributing factors. Energy values are presented in kcal mol^{-1}. The strain energies were evaluated with conventional homodesmic method and the hyperconjugation energies were evaluated with deletion method, E(deletion).

Conformer	Sum of all the H-bond energies	Strain Energy [a]	Hyperconjugation [b]	Total Energetic Stabilization	Relative Energy
α-Pry-1	-12.98	21.17	30.070	-21.88	0.328
α-Pry-2	-12.8	21.40	29.995	-21.39	0.810
α-Pry-3	-12.55	19.36	28.521	-21.71	0.492
β-Pry-1	**-12.92**	**19.87**	**29.150**	**-22.20**	**0.000**
β-Pry-2	-10.27	19.18	29.500	-20.59	1.615
β-Pry-3	-12.35	19.58	28.350	-21.12	1.085
α-Fur-1	-12.24	21.85	29.267	-19.66	2.548
α-Fur-2	-11.52	22.01	28.849	-18.36	3.844
αFur-3	-9.41	22.08	29.418	-16.75	5.454
β-Fur-1	-11.3	22.05	29.729	-18.98	3.226
β-Fur-2	-8.93	21.89	30.107	-17.14	5.059
β-Fur-3	-20.26	23.45	22.835	-19.65	2.559

[a] Positive value of strain energy represents destabilization

[b] Negative values of hyperconjugation represents stabilization and these negative values were used in valuation of total energetic stabilization.