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Supporting information

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A New Insight on the 5-Carboxycytosine and 5-Formylcytosine under Typical Bisulfite Conditions: A Deamination Mechanism Studies

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Table S1 The Relevant Energy Information[a] (in kJ·mol^{-1}) of Different 5-caCytN3^{+}-SO_3^{-} Isomers Both in the Gas and Aqueous Phases

Species	ΔE^{g} /(kJ·mol^{-1})	ΔG^{g} /(kJ·mol^{-1})	ΔG^{s} /(kJ·mol^{-1})
R1	0.00	0.00	0.00
R2	8.69	8.55	-2.53
R3	14.77	14.99	-1.28
R4	11.12	12.38	-3.27

[a] ΔG^{g}, relative free energy in the gas phase; ΔE^{g}, relative free energy in the gas phase; ΔG^{s}, relative free energy in the aqueous phase.

Table S2 Relative Energies [a] (in kJ·mol^{-1}) for the Hydrolytic Deamination Reaction of Different 5-caCytN3^{+}-SO_3^- Isomers (R1, R2 and R4) and HSO_3^- group (R1-paths A-B, R2-paths A-B and R4-paths A-B) Both in the Gas and Aqueous Phases

System	MP2//B3LYP method [b]			PCM[c]	
	ΔE^g	ΔG^g	$\Delta G^{g\neq}$	ΔG^s	$\Delta G^{s\neq}$
R1-path A					
R1+HSO_3^-+H_2O	0.00	0.00	0.00	0	
R1-A-RC	-283.96	-201.20		-34.90	
R1-A-TS1	-207.86	-112.76		63.03	
R1-A-IM1	-255.63	-160.82		12.81	
R1-A-TS2	-247.38	-150.62		27.29	
R1-A-IM2	-251.74	-156.58		20.32	
R1-A-TS3	-258.13	-163.26		7.31	
R1-A-IM3	-259.31	-165.81		-1.27	
R1-A-TS4	-216.38	-125.17		47.20	
R1-A-P	-295.65	-209.99		-18.75	
R1-A-RC→R1-A-IM1			88.44		97.93
R1-A-IM1→R1-A-IM2			10.2		14.48
R1-A-IM2→R1-A-IM3			-6.68		-13.01
R1-A-IM4→R1-A-P			40.64		48.47
R1-path B					
R1-R+HSO_3^-+H_2O	0.00	0.00		0.00	
R1-B-RC	-282.97	-200.12		-22.04	
R1-B-TS1	-209.13	-111.44		67.93	
R1-B-IM1	-246.77	-151.12		34.95	
R1-B-IM2	-238.45	-144.80		39.09	
R1-B-TS2	-125.88	-31.06		146.49	
R1-B-P	-295.68	-210.10		140.07	
R1-B-RC→R1-B-IM1			88.68		89.97
R1-B-IM2→R1-B-P			113.74		107.4
R2-path A					
R2+HSO_3^-+H_2O	0.00	0.00		0.00	
R2-A-RC	-314.35	-226.28		-29.24	
R2-A-TS1	-213.40	-118.80		63.22	
R2-A-IM1	-275.30	-177.05		17.61	
R2-A-TS2	-248.50	-153.40		26.97	
R2-A-IM2	-252.65	-158.59		15.34	
R2-A-TS3	-257.90	-163.51		17.15	
R2-A-IM3	-255.75	-163.01		2.57	
R2-A-TS4	-245.62	-156.93		54.74	
R2-A-P	-295.20	-211.12		-11.46	
R2-A-RC→R2-A-IM1			107.48		92.46
R2-A-IM1→R2-A-IM2			23.65		9.36
R2-A-IM2→R2-A-IM3			-4.92		1.81
R2-A-IM4→R2-A-P			6.08		52.17
R2-path B					
R2+HSO_3^-+H_2O	0.00	0.00		0.00	

R2-B-RC	-318.65	-227.26		-61.05	
R2-B-TS1	-230.32	-131.72		36.18	
R2-B-IM1	-259.40	-163.55		6.08	
R2-B-TS2	-256.59	-160.75		15.18	
R2-B-IM2	-261.78	-165.33		8.97	
R2-B-TS3	-256.51	-161.57		9.106	
R2-B-IM3	-259.69	-163.43		26.00	
R2-B-TS4	-138.42	-41.43		112.70	
R2-B-P	-322.82	-234.95		-39.08	
R2-B-RC→R2-B-IM1			95.54		97.23
R2-B-IM1→R2-B-IM2			2.80		9.10
R2-B-IM2→R2-B-IM3			3.76		0.14
R2-B-IM3→R2-B-P			122.00		86.70
R4-path A					
R4+HSO_3^-+H_2O	0.00	0.00		0.00	
R4-A-RC	-283.44	-200.95		-11.94	
R4-A-TS1	-200.84	-107.84		71.23	
R4-A-IM1	-255.23	-161.22		27.33	
R4-A-TS2	-256.16	-160.10		--	
R4-A-IM2	-254.07	-160.01		3.46	
R4-A-TS3	-257.54	-165.67		15.43	
R4-A-IM3	-260.20	-168.52		10.84	
R4-A-TS4	-221.86	-125.16			
R4-A-P	-342.46	-251.64		-64.80	
R4-A-RC→R4-A-IM1			93.11		83.17
R4-A-IM1→R4-A-IM2			1.12		
R4-A-IM2→R4-A-IM3			-5.66		11.97
R4-A-IM4→R4-A-P			43.36		--
R4-path B					
R4+HSO_3^-+H_2O	0.00	0.00		0.00	
R4-B-RC	-282.39	-191.16		-43.58	
R4-B-TS1	-212.31	-113.72		38.30	
R4-B-IM1	-271.14	-176.31		-2.03	
R4-B-TS2	-266.29	-172.17		7.43	
R4-B-IM2	-279.15	-185.85		-5.10	
R4-B-TS3	-149.58	-53.33		125.54	
R4-B-P	-327.05	-239.81		-57.75	
R4-B-RC→R4-B-IM1			77.44		81.88
R4-B-IM1→R4-B-IM2			4.14		9.46
R4-B-IM2→R4-B-P			132.52		130.64

[a] ΔG^{g}, relative free energy in the gas phase; ΔE^{g}, relative free energy in the gas phase; $\Delta G^{g\neq}$, activation free energy in the gas phase; ΔG^{s}, relative free energy in the aqueous phase; $\Delta G^{s\neq}$, activation free energy in the aqueous phase. [b] MP2/6-311++G(3df,3pd)//B3LYP/ 6-311++G(d,p) level. [c] MP2/6-311++G(3df,3pd)//B3LYP/6-311++G(d,p) with PCM model.

Table S3 The Relevant Information[a] (in kJ·mol^{-1}) of Different 5-O^{+}fCytN3^{+}-SO_3^{-} Isomers Both in the Gas and Aqueous Phases

Species	ΔE^{g} /(kJ·mol^{-1})	ΔG^{g} /(kJ·mol^{-1})	ΔG^{s} /(kJ·mol^{-1})
R1′	23.59	24.17	25.35
R2′	28.07	29.47	26.94
R3′	0.00	0.00	0.00
R4′	1.40	1.48	-2.63

[a] ΔG^{g}, relative free energy in the gas phase; ΔE^{g}, relative free energy in the gas phase; ΔG^{s}, relative free energy in the aqueous phase.

Table S4 Relative Energies [a] (in kJ·mol^{-1}) for the Hydrolytic Deamination Reaction of 5-O^{+}fCytN3^{+}-SO_3^- Isomer (R4′) and HSO_3^- group (R4′-paths C-D) Both in the Gas and Aqueous Phases

System	MP2//B3LYP method [b]			PCM[c]	
	ΔE^{g}	ΔG^{g}	$\Delta G^{g\neq}$	ΔG^{s}	$\Delta G^{s\neq}$
R4′-path C					
R4′+HSO_3^- +H_2O	0.00	0.00		0.00	
R4′-C-RC	-560.15	-474.74		-20.02	
R4′-C-TS1	-497.92	-404.03		58.18	
R4′-C-IM1	-524.96	-434.00		33.38	
R4′-C-TS2	-507.90	-416.62		--	
R4′-C-IM2	-521.04	-432.60		43.73	
R4′-C-TS3	-515.56	-423.31		--	
R4′-C-IM3	-533.62	-443.67		29.93	
R4′-C-TS4	-422.68	-329.58		138.04	
R4′-C-P	-596.72	-510.65		-35.35	
R4′-C-RC→R4′-C-IM1			70.71		78.2
R4′-C-IM1→R4′-C-IM2			17.38		
R4′-C-IM2→R4′-C-IM3			9.29		
R4′-C-IM4→R4′-C-P			114.09		108.11
R4′-path D					
R4′+HSO_3^- +H_2O	0.00	0.00		0.00	
R4′-D-RC	-567.94	-480.13		-45.59	
R4′-D-TS1	-495.38	-403.56		31.09	
R4′-D-IM1	-546.46	-450.53		11.24	
R4′-D-TS2	-535.56	-439.43		23.06	
R4′-D-IM2	-552.37	-458.33		4.82	
R4′-D-TS3	-414.27	-318.80		120.50	
R4′-D-P	-597.20	-515.89		-54.07	
R4′-D-RC→R4′-D-IM1			76.57		76.68
R4′-D-IM1→R4′-D-IM2			11.10		11.82
R4′-D-IM2→R4′-D- P			139.53		115.68

[a] ΔG^{g}, relative free energy in the gas phase; ΔE^{g}, relative free energy in the gas phase; $\Delta G^{g\neq}$, activation free energy in the gas phase; ΔG^{s}, relative free energy in the aqueous phase; $\Delta G^{s\neq}$, activation free energy in the aqueous phase. [b] MP2/6-311++G(3df,3pd)//B3LYP/ 6-311++G(d,p) level. [c] MP2/6-311++G(3df,3pd)//B3LYP/6-311++G(d,p) with PCM model.

Table S5 The Chelpg Charge on O5 of Reaction Complexes for Path A and Water-mediated Paths A Both in the Gas and Aqueous Phases

path A	ρ	1w-path A	ρ	2w-Path A	ρ
A-RC	-0.7186	1w-A-RC	-0.6778	2w-A-RC	-0.9432
(A-RC)[a]	-0.8427	(1w-A-RC)	-0.7916	(2w-A-RC)	-0.9460

[a] in brackets Chelpg charge on O5 of reaction complexes for path A and water-mediated paths A in the aqueous phase.

As for 5-caCytN3$^+$-SO_3^-, two diastereomers are formed: one has 5-H *trans* to 6-SO_3^-(*trans* isomer), and another, 5-H *cis* to 6-SO_3^-(*cis* isomer). The two diastereomers are respectively divided into two isomers based on the torsion and the angles of the OH group in 5-caCytN3$^+$-SO_3^-, denoted as R1, R2, R3, and R4, respectively.

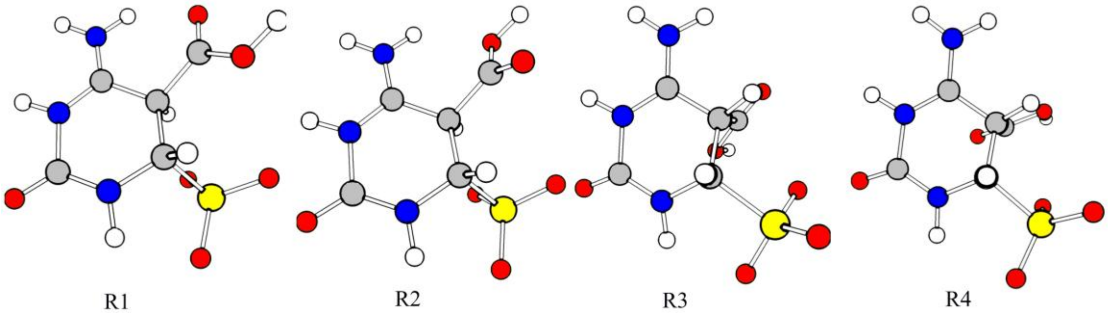

Fig. S1

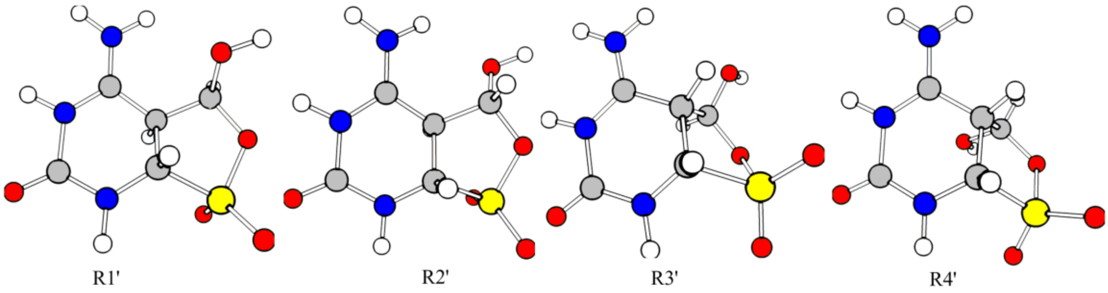

Fig. S2

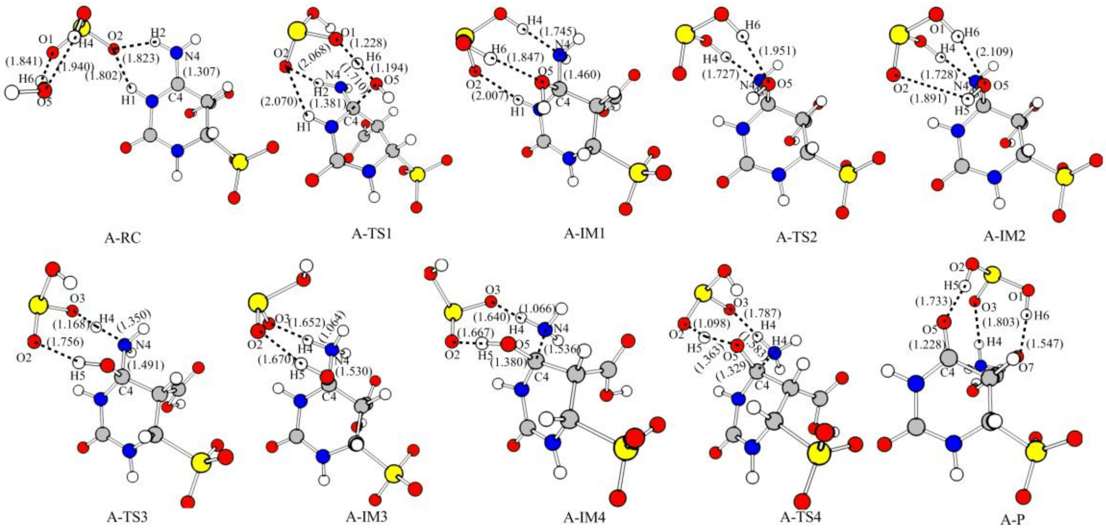

Fig. S3

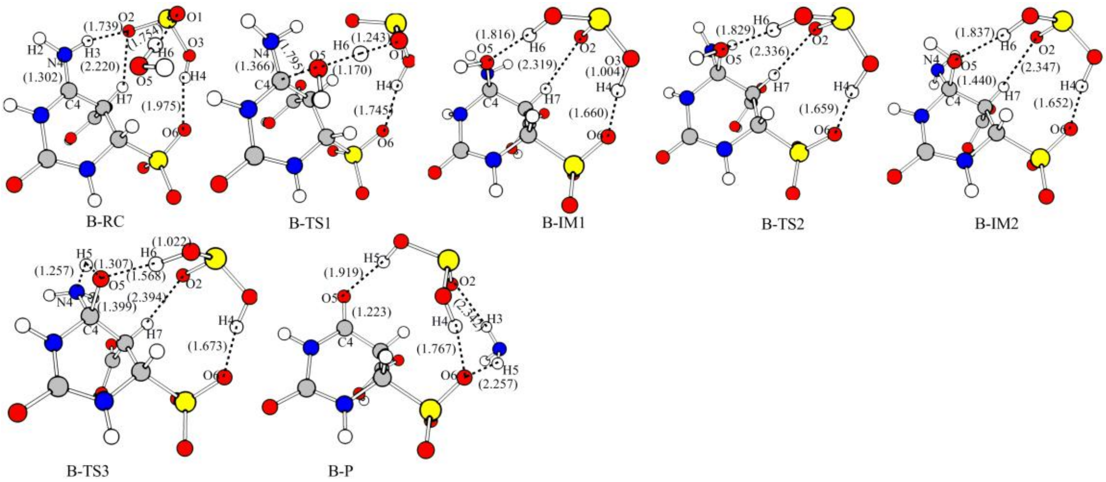

Fig. S4

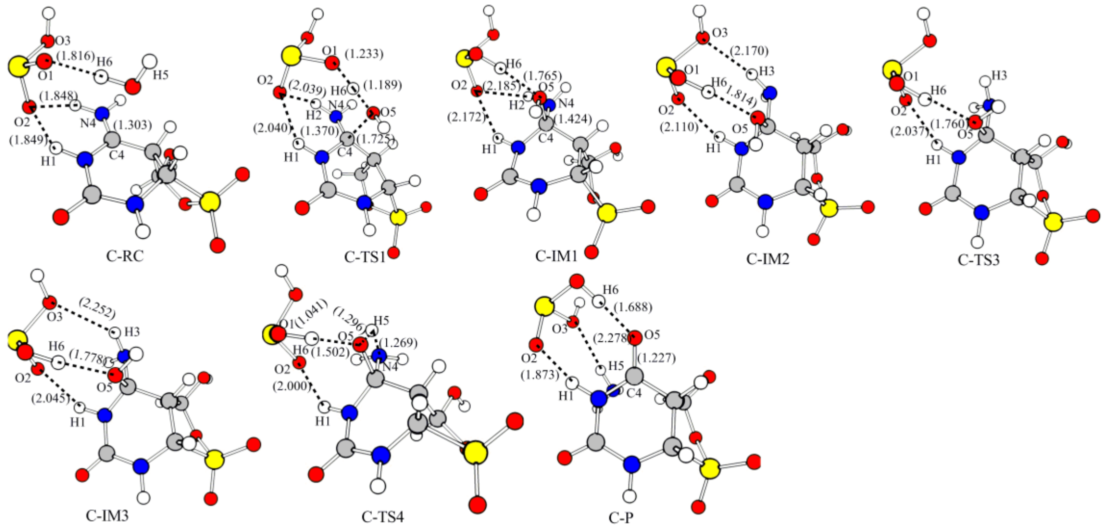

Fig. S5

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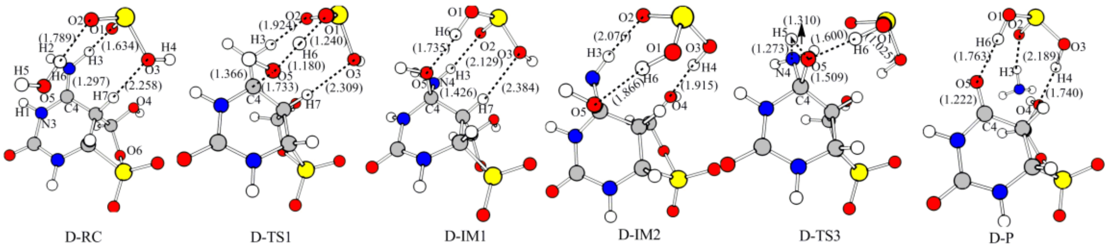
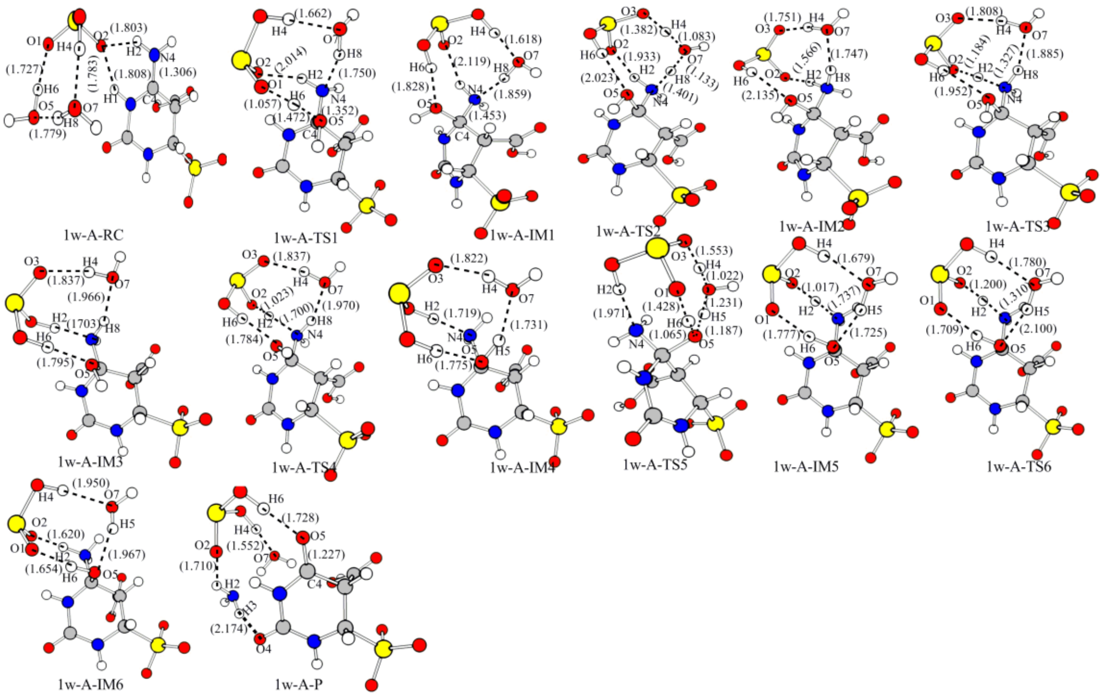


Fig. S6


1w-A-RC
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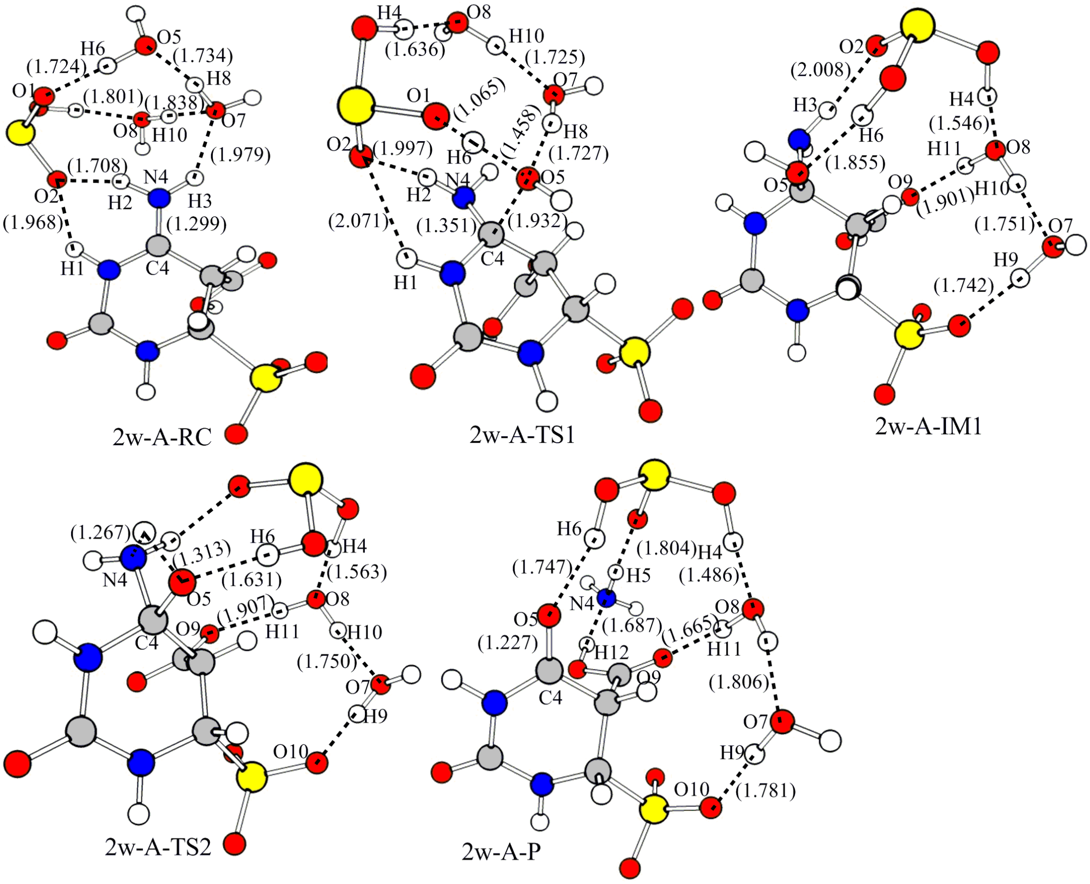
1w-A-IM1
1w-A-TS2
1w-A-IM2
1w-A-TS3
1w-A-IM3
1w-A-TS4
1w-A-IM4
1w-A-TS5
1w-A-IM5
1w-A-TS6
1w-A-IM6
1w-A-P

Fig. S7


H6
O5
(1.724)
(1.734)
H8
O1
(1.801)
(1.838)
O8
H10
O7
(1.979)
(1.708)
N4
O2
H2
H3
(1.968)
(1.299)
H1
C4
2w-A-RC
H4
O8
(1.636)
H10
(1.725)
O7
O1
(1.065)
(1.458)
H8
O2
(1.997)
H6
(1.727)
N4
O5
H2
(2.071)
(1.351)
(1.932)
C4
H1
2w-A-TS1
O2
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H3
H4
H6
(1.546)
H11
O8
(1.855)
O5
O9
H10
(1.901)
(1.751)
O7
H9
(1.742)
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H6
H4
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(1.563)
N4
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O5
O8
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O9
H11
H10
C4
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O7
H9
O10
2w-A-TS2
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H4
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H5
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N4
O8
O5
(1.687)
(1.665)
(1.227)
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H11
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C4
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O7
H9
O10
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2w-A-P

Fig. S8

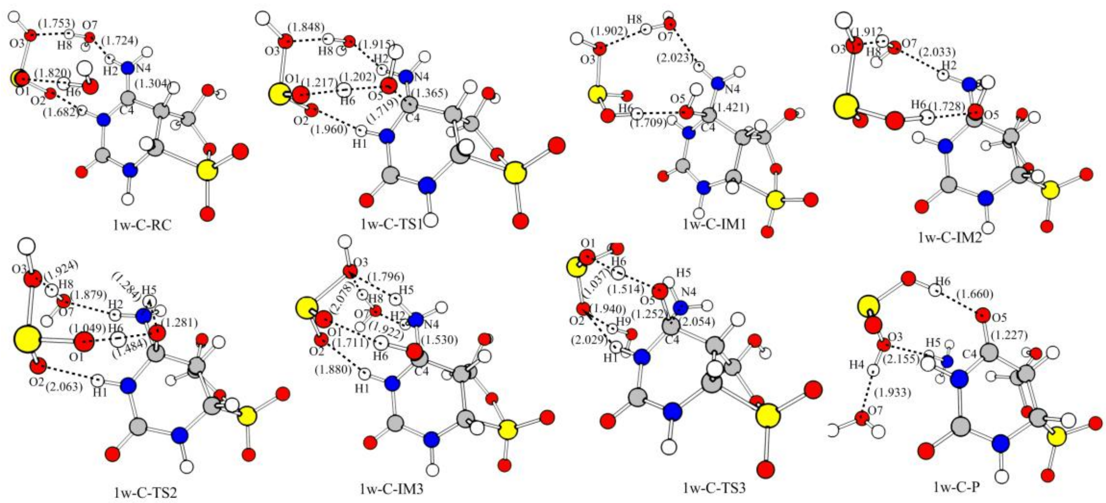

Fig. S9

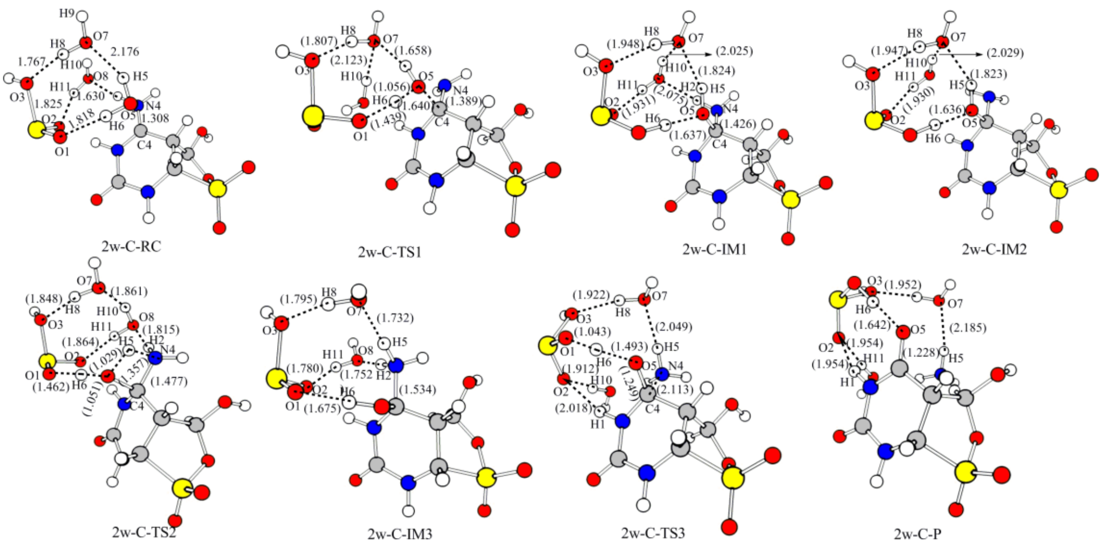

Fig. S10