Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Normal and Reverse Base Pairing of Iz and Oz Lesions in DNA: Structural Implications for Mutagenesis.

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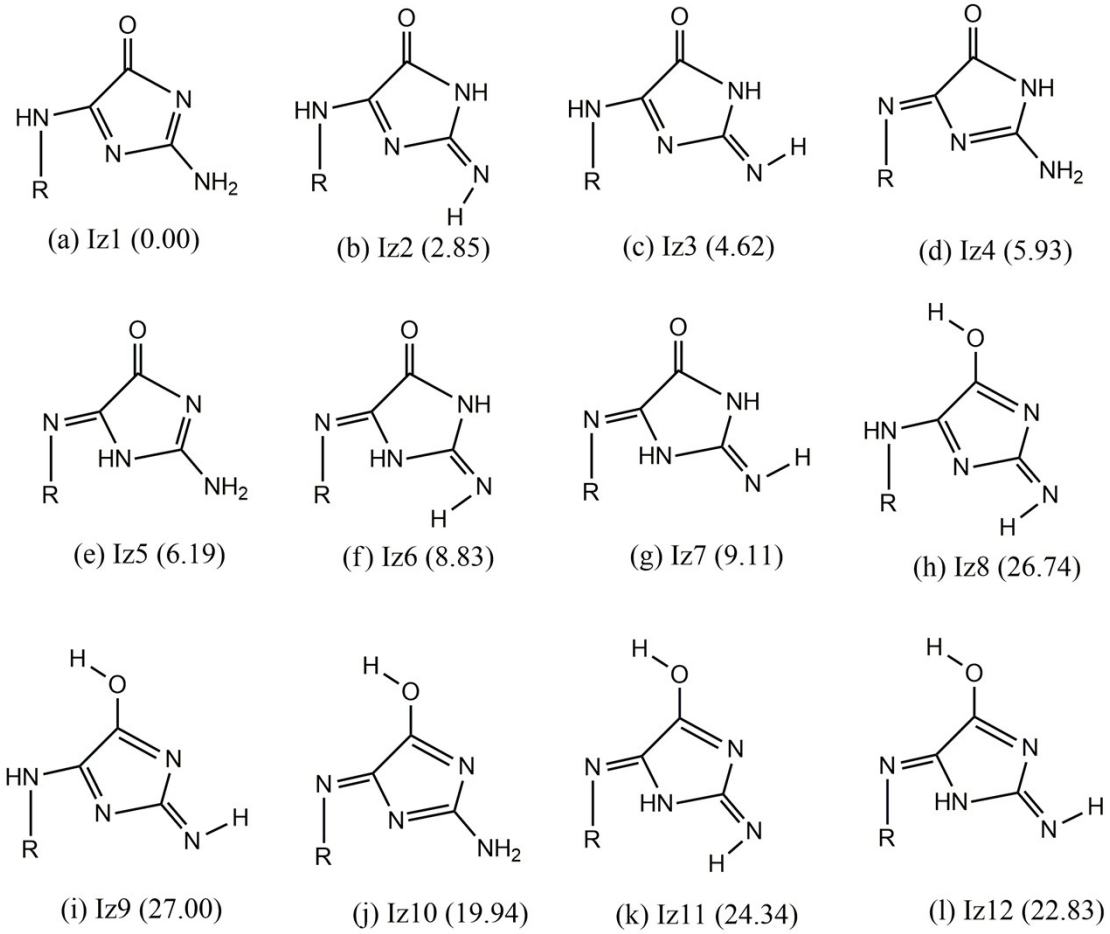


Fig. S1: Structures of different tautomers of Iz and their relative energies (kcal/mol) as obtained at the B3LYP/6-31+G* method in aqueous medium. The tautomer presented in (a) is the most stable one. Here R stands for the deoxyribose group, which was replaced by the H9 atom during geometry optimizations.

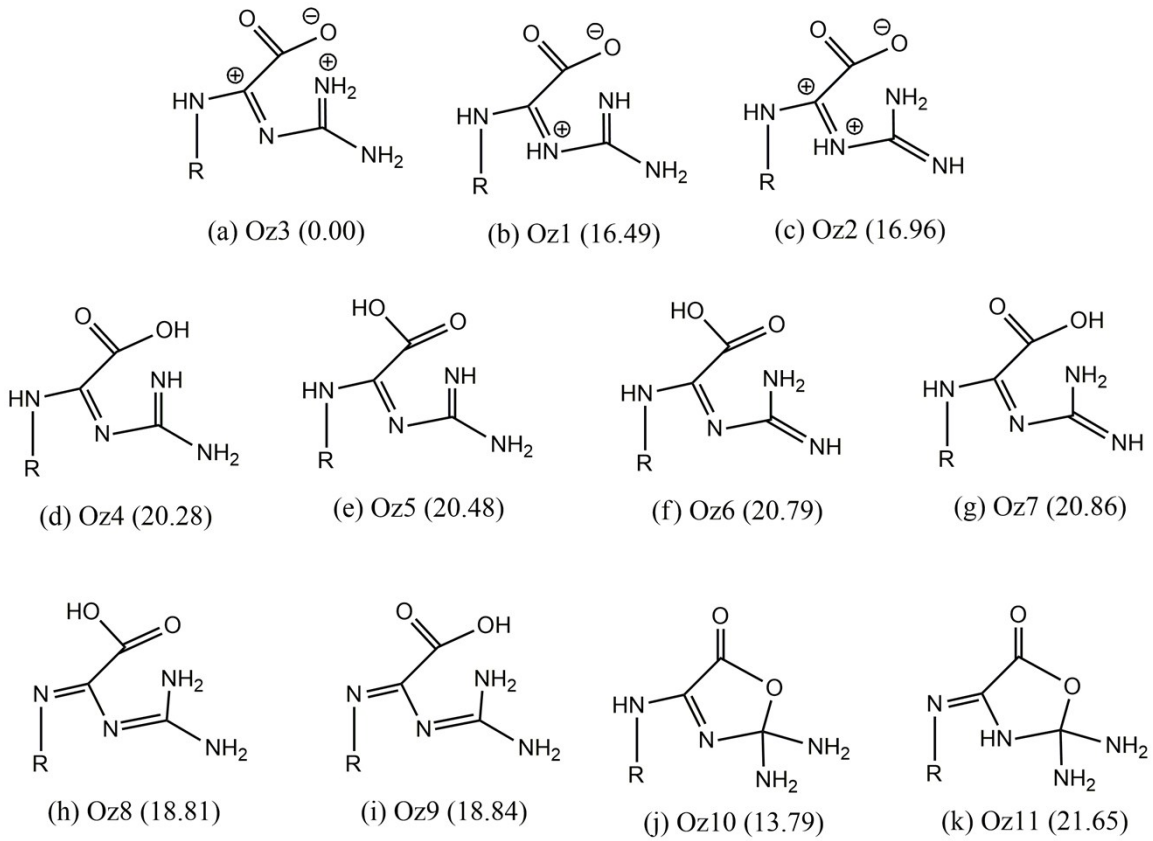
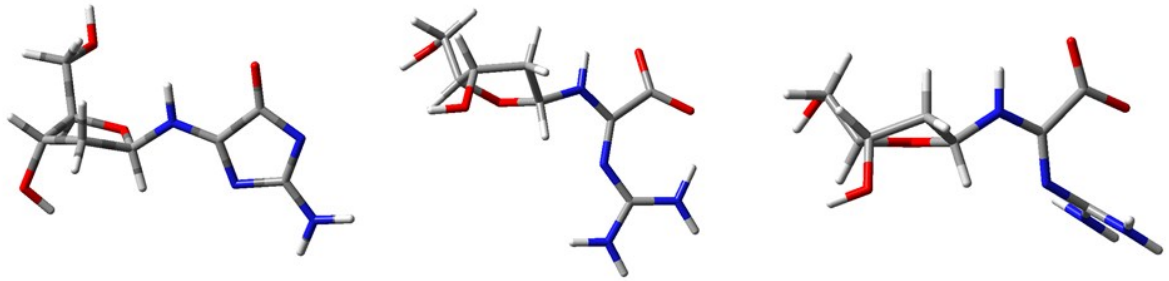


Fig. S2: Structures of different tautomers of Oz and their relative energies (kcal/mol) as obtained at the B3LYP/6-31+G* method in aqueous medium. The tautomer presented in (a) is the most stable one. Here R stands for the deoxyribose group, which was replaced by the H9 atom during geometry optimizations.



(a) dIz (planar)
O4'-C1'-N9-C4' = -101.0 deg
E = -831.804994 hartree

(b) dOz (planar)
O4'-C1'-N9-C4' = -91.2 deg
E = -908.227972 hartree

(c) dOz (non-planar)
O4'-C1'-N9-C4' = -94.0 deg
E = -908.228947 hartree

Fig.S3: Optimized structures of (a) planar 2'-deoxyimidazolone (dIz) and (b) planar and (c) non-planar 2'-deoxyoxazolone (dOz) obtained at the B3LYP/6-31+G* level of theory. Important geometric parameters and total energies (hartree) are shown for comparison of structures and stabilities.

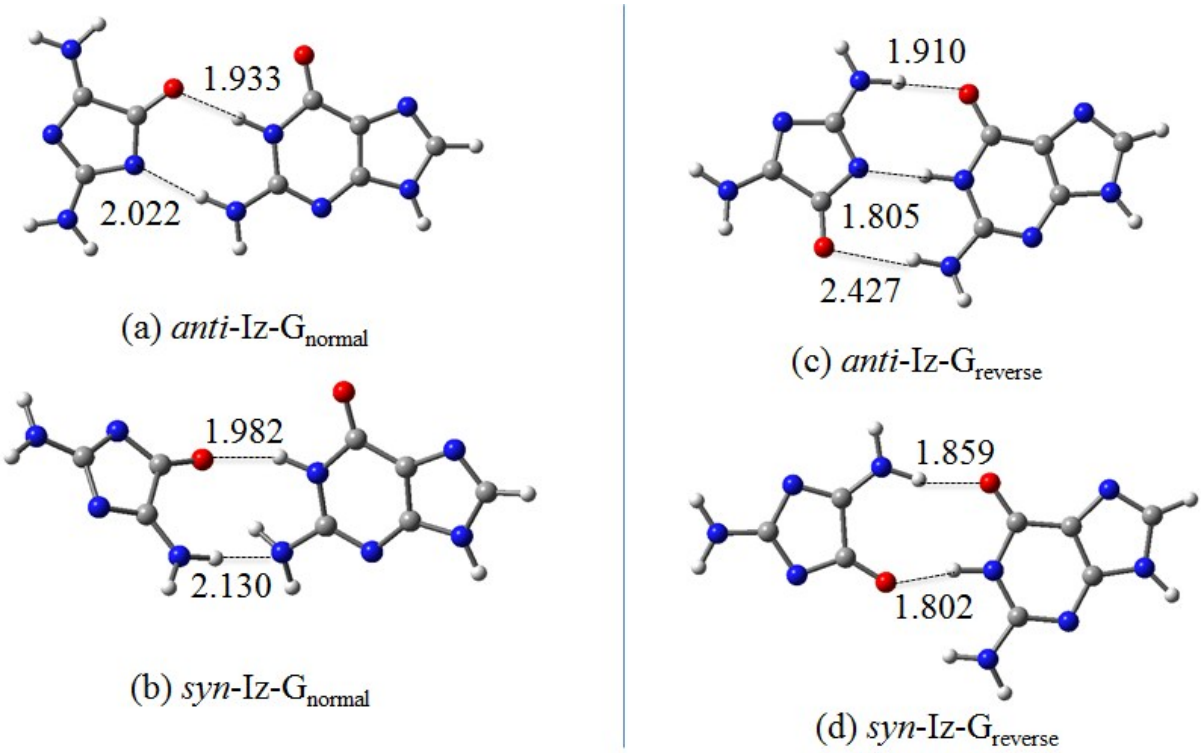


Fig. S4: Optimized structures of Iz:G complexes in the normal (a,b) and reverse (c,d) base pairing orientations obtained at the B3LYP/6-31+G* level of theory.

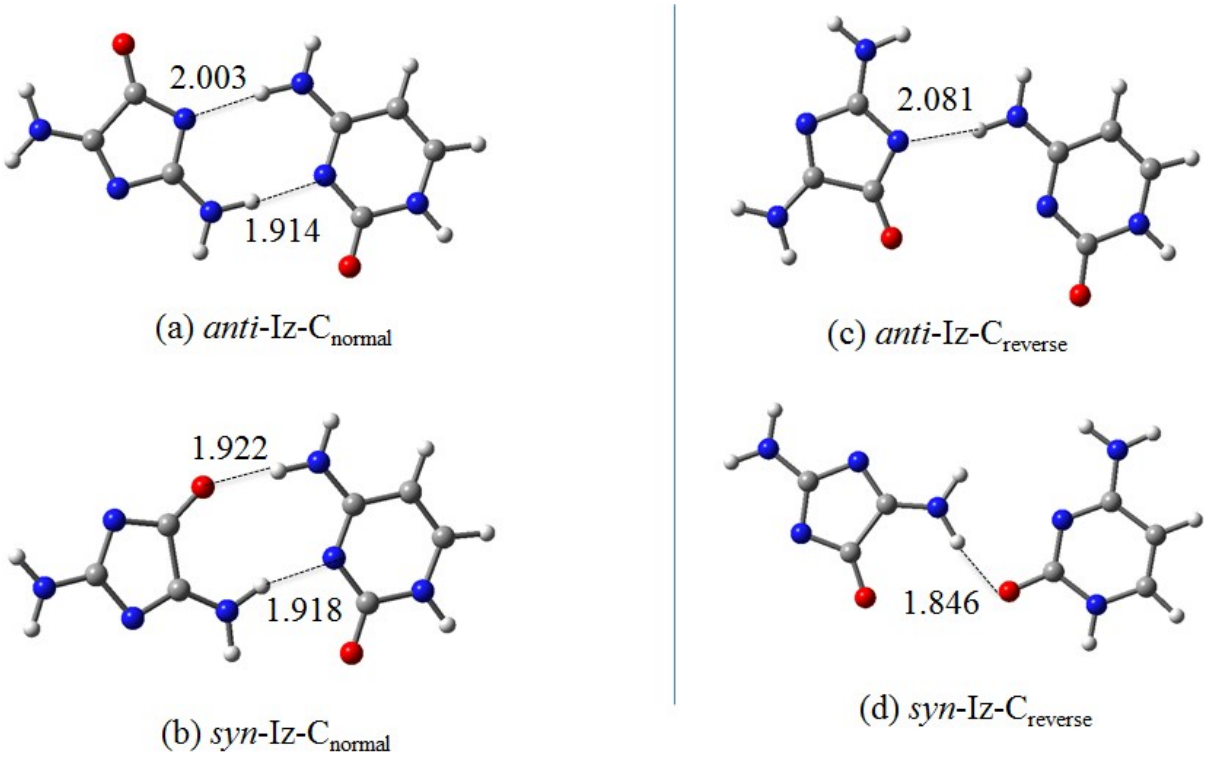


Fig. S5: Optimized structures of Iz:C complexes in the normal (a,b) and reverse (c,d) base pairing orientations obtained at the B3LYP/6-31+G* level of theory.

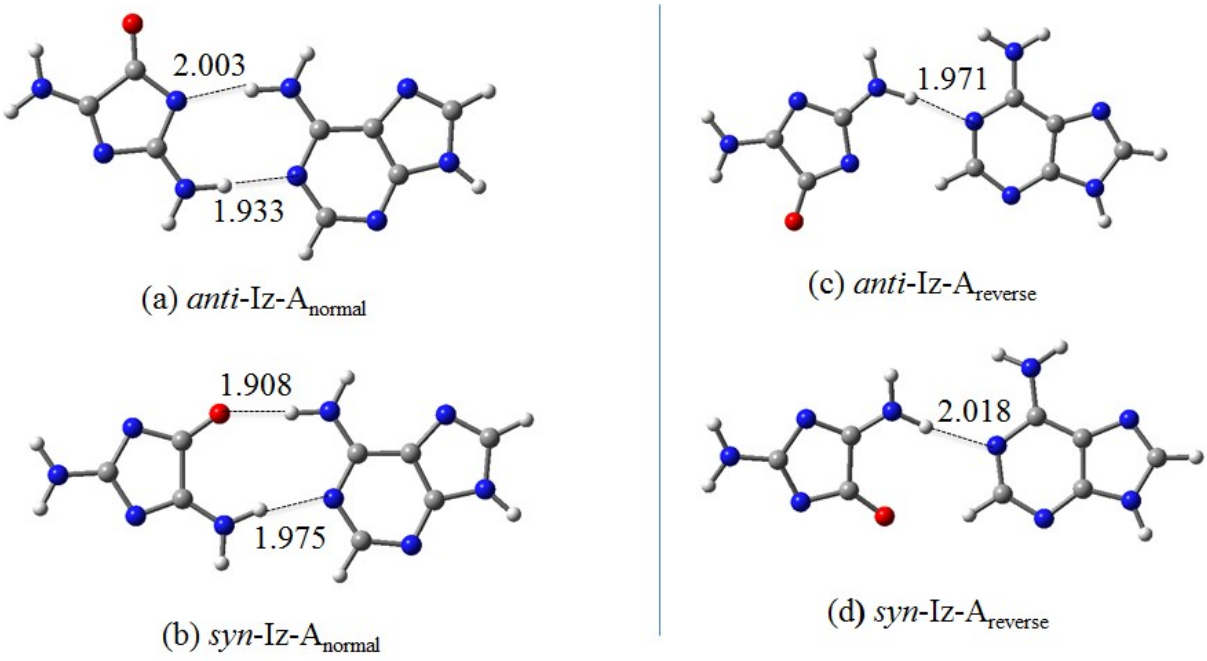


Fig. S6: Optimized structures of Iz:A complexes in the normal (a,b) and reverse (c,d) base pairing orientations obtained at the B3LYP/6-31+G* level of theory.

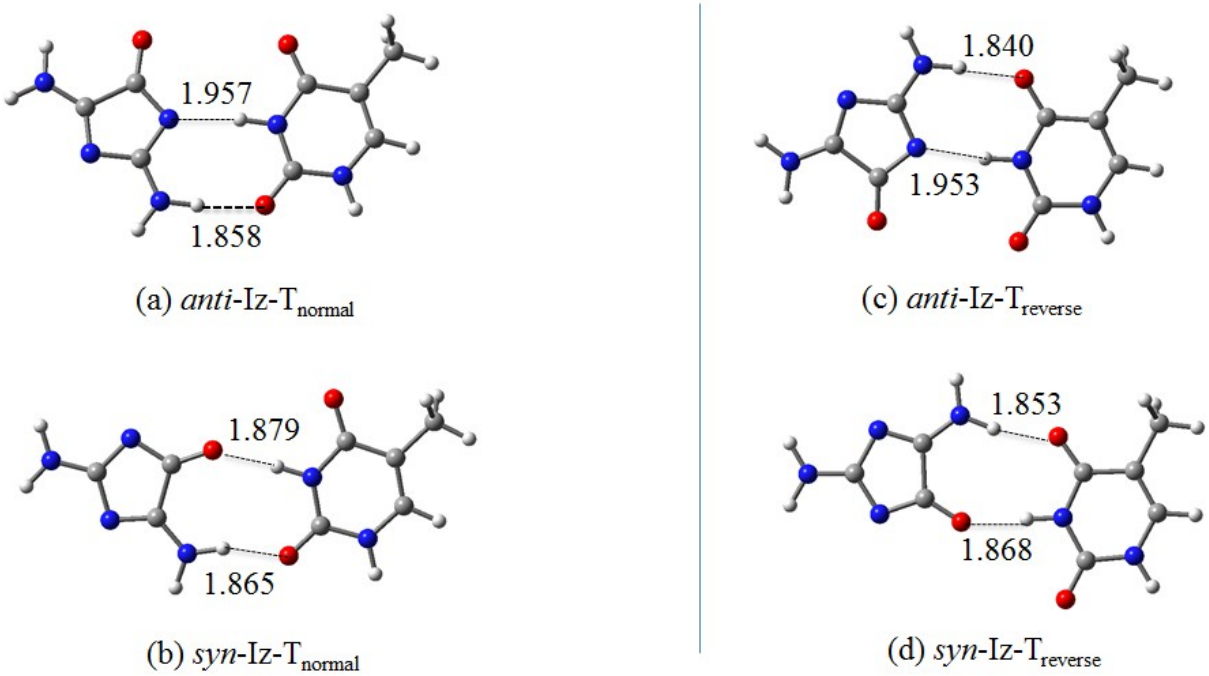


Fig. S7: Optimized structures of Iz:T complexes in the normal (a,b) and reverse (c,d) base pairing orientations obtained at the B3LYP/6-31+G* level of theory.

Table S1: Zero-Point energy-corrected binding energies of different complexes involving Iz as obtained in aqueous medium. For comparison, zero-point energy-corrected binding energies of G:C and A:T complexes are shown in parentheses. Absent of entry indicates that the corresponding structure does not exist. Structures of these complexes are shown in Figs S1-S4.

Base Pair	Method	Normal base pairing		Reverse base pairing	
		anti-Iz	*syn*-Iz	*anti*-Iz	*syn*-Iz
Iz:G (T:G)[a]	B3LYP	-6.62 (-7.41)	-4.09	-9.74	-7.94
	ωB97XD	-9.48 (-10.82)	-6.96	-14.10	-10.79
	B3LYP-D3	-10.04 (-11.82)		-15.23	
Iz:C (G:C)[a]	B3LYP	-7.37 (-11.63)	-6.64	-2.03	-4.42
	ωB97XD	-10.77 (-16.26)	-9.50	-3.92	-6.27
	B3LYP-D3	-11.70 (-17.01)			
Iz:A (T:A)[a]	B3LYP	-6.90 (-6.57)	-6.04	-3.75	-3.25
	ωB97XD	-9.97 (-10.30)	-8.49	-6.03	-5.34
	B3LYP-D3	-10.78			
Iz:T	B3LYP	-7.15	-6.23	-7.30	-6.50
	ωB97XD	-10.18	-8.26	-10.38	-8.58
	B3LYP-D3	-11.21		-11.55	

[a][Ref 49,50]

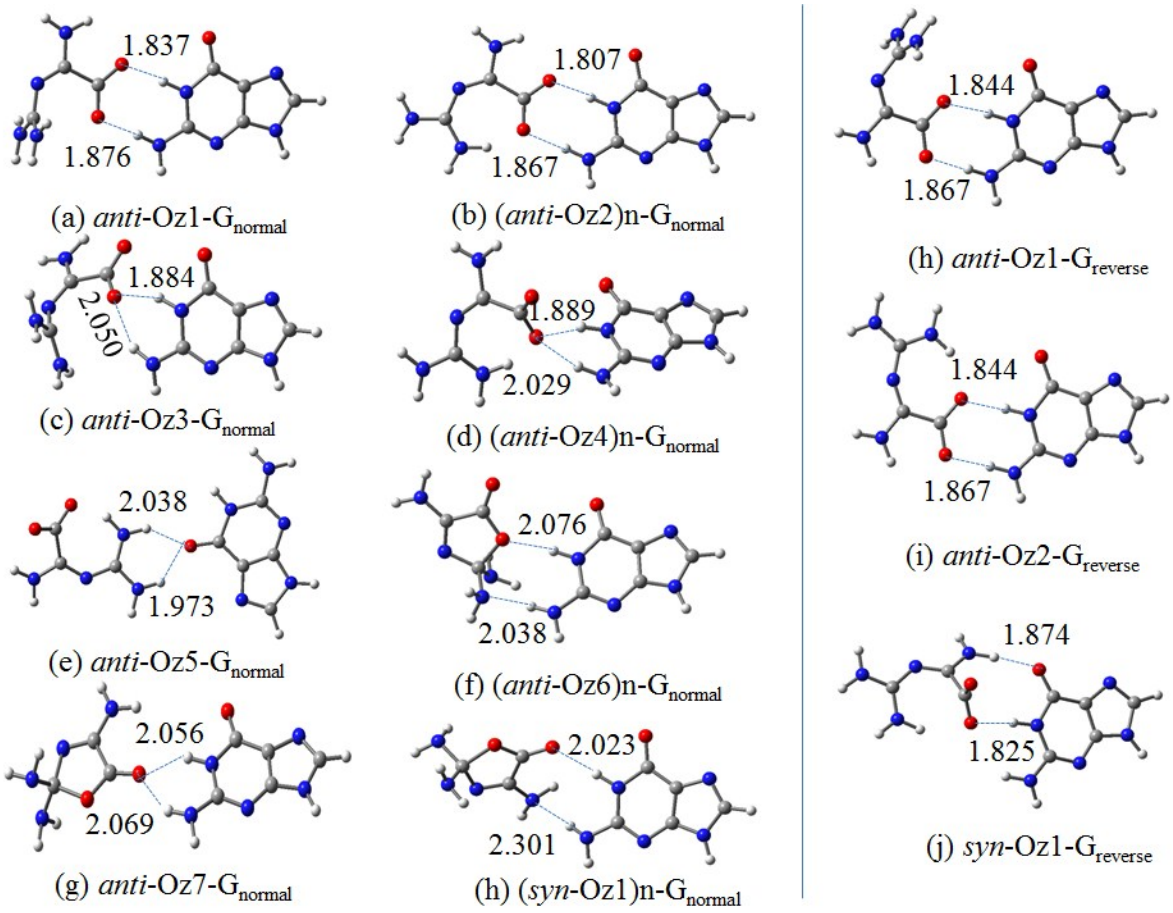


Fig. S8: Optimized structures of Oz:G complexes in the normal (a-f) and reverse (g-i) base pairing orientations obtained at the B3LYP/6-31+G* level of theory.

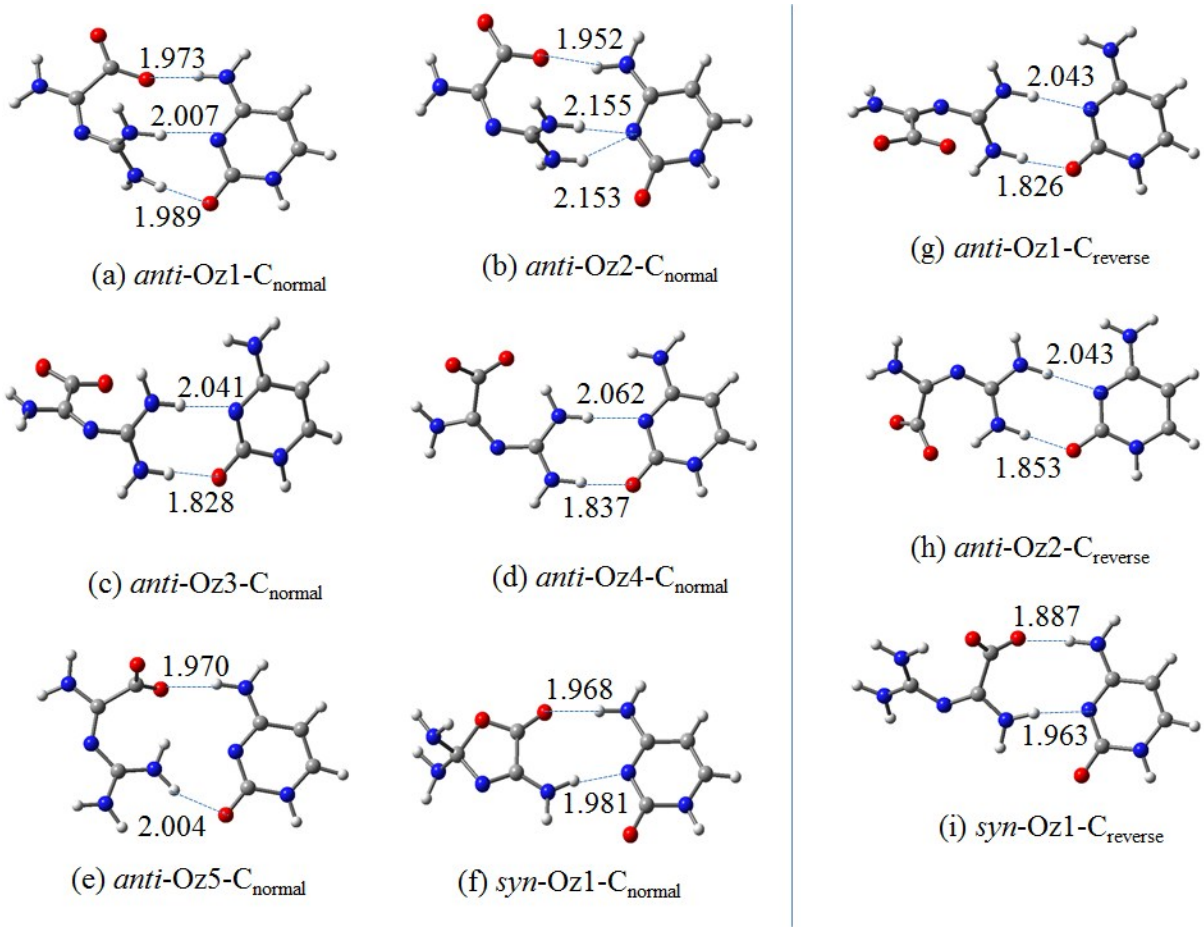


Fig. S9: Optimized structures of Oz:C complexes in the normal (a-e) and reverse (f-h) base pairing orientations obtained at the B3LYP/6-31+G* level of theory.

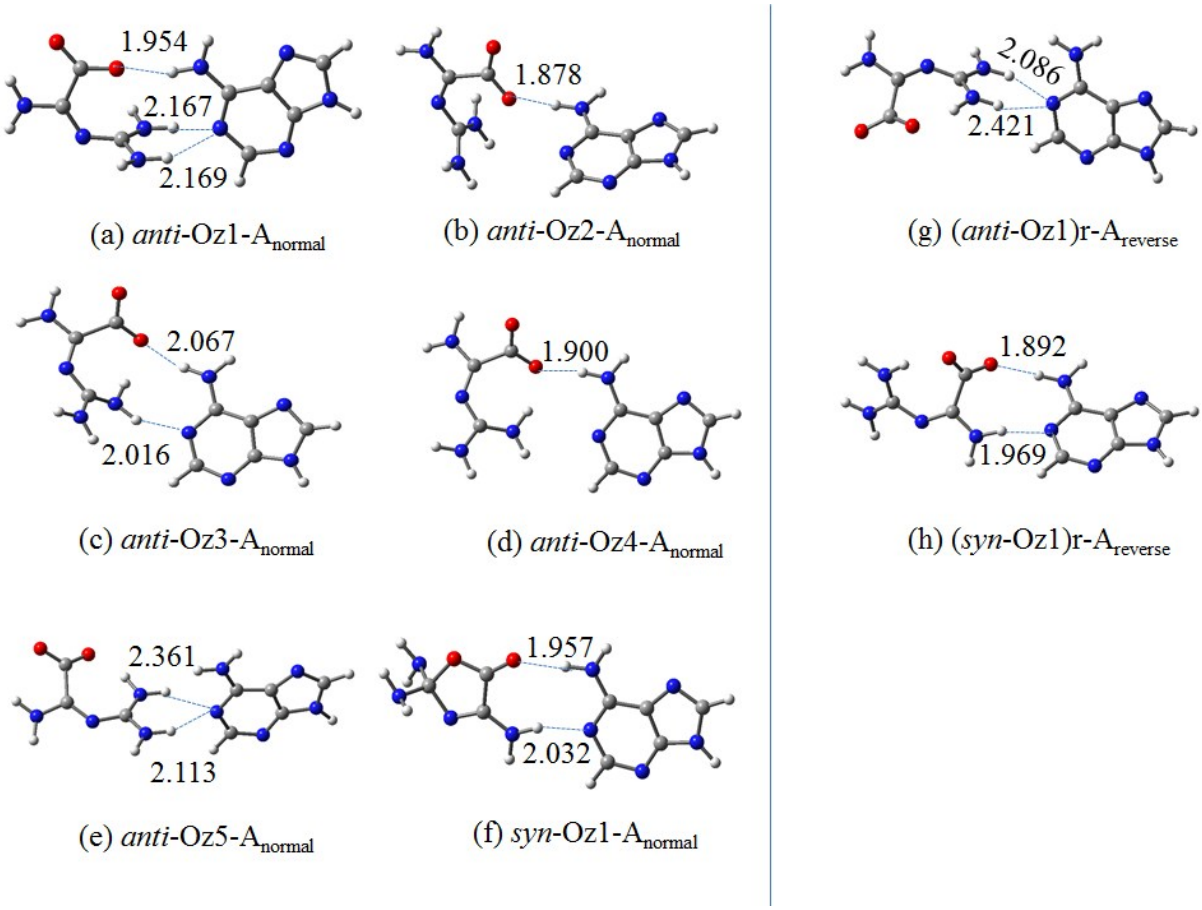


Fig. S10: Optimized structures of Oz:A complexes in the normal (a-f) and reverse (g-h) base pairing orientations obtained at the B3LYP/6-31+G* level of theory.

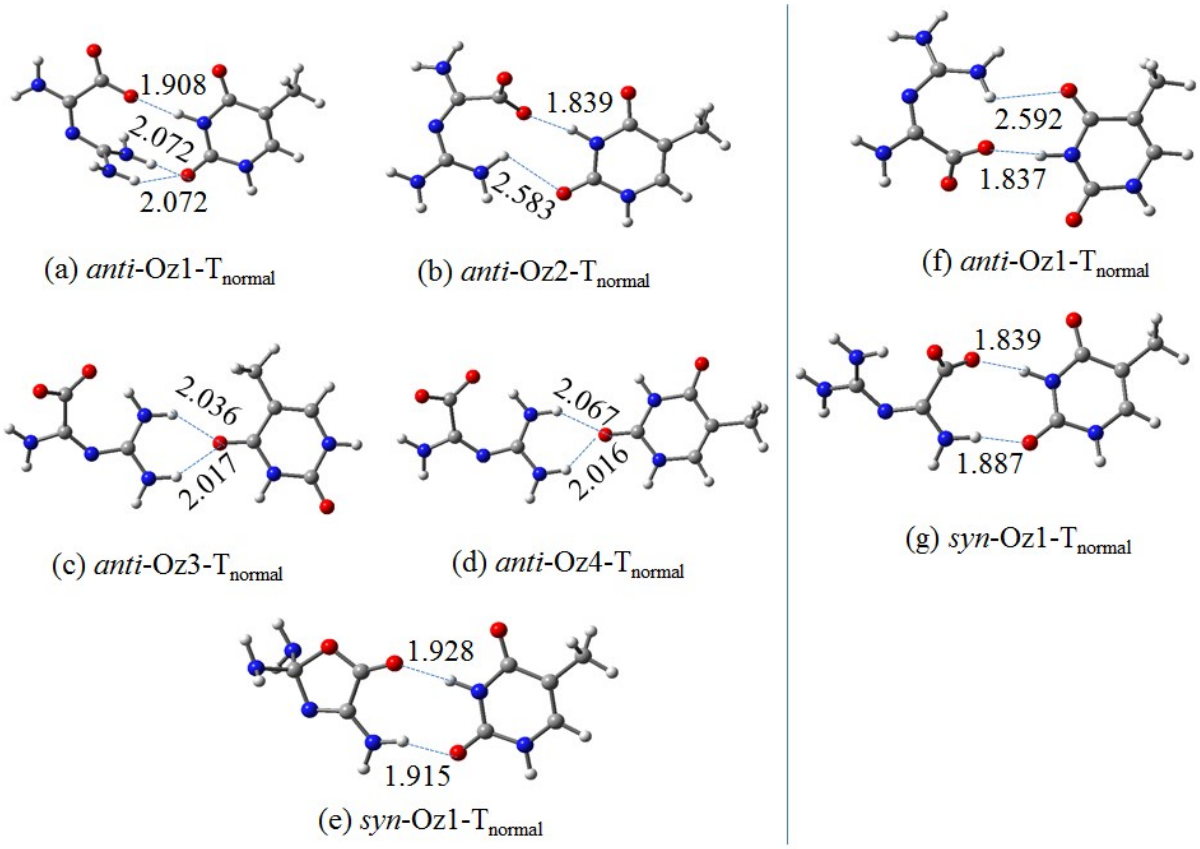


Fig. S11: Optimized structures of Oz:T complexes in the normal (a-c) and reverse (d,e) base pairing orientations obtained at the B3LYP/6-31+G* level of theory.

Table S2: Zero-Point energy-corrected binding energies of different complexes involving Oz as obtained in aqueous medium. Absent of entries indicate that the corresponding structures do not exist. Structures of these complexes are shown in Figs S5-S8.

Base Pair	Method	Normal base pairing							Reverse base pairing		
		anti-Oz1	*anti*-Oz2	*anti*-Oz3	*anti*-Oz4	*anti*-Oz5	*anti*-Oz6	*syn*-Oz1	*anti*-Oz1	*anti*-Oz2	*syn*-Oz1
Oz:G	B3LYP	-9.43	-8.46	-6.88	-5.97	-4.80	-4.06	-0.97	-8.51	-8.50	-6.63
	ωB97XD	**-12.20**	-10.88	-10.01	-8.16	-7.68	-5.64	-3.52	**-12.22**	-10.97	-10.57
	B3LYP-D3	**-12.81**	-11.29						**-12.91**	-11.74	
Oz:C	B3LYP	-7.65	-7.35	-8.53	-7.72			-3.54	-8.52	-7.57	-6.49
	ωB97XD	**-11.58**	**-11.54**	-11.25	-10.73			-6.31	**-11.16**	-10.53	-9.85
	B3LYP-D3	**-13.02**	**-12.67**						**-12.06**		
Oz:A	B3LYP	-6.57	-3.55	-2.79	-3.09	-4.35		-3.14	-4.36		-6.23
	ωB97XD	**-10.62**	-4.78	-5.85	-5.28	-7.12		-5.54	-7.11		-9.06
	B3LYP-D3	**-11.68**									
Oz:T	B3LYP	-6.31	-4.04					-3.29	-4.19		-6.38
	ωB97XD	**-9.67**	-6.53					-5.21	-6.67		-8.87
	B3LYP-D3	**-11.05**									

Table S3: XYZ-coordinates of anti-Iz:G reverse complex

N	-5.48317700	0.50050600	-0.00191600
C	-4.28356600	-0.04954900	-0.00103700
C	-2.99298500	0.80393200	0.00084400
O	-2.94141500	2.03214200	0.00164900
N	-1.97895700	-0.09255900	0.00139300
C	-2.58540400	-1.30989000	-0.00014000
N	-3.97910300	-1.33126100	-0.00156400
N	-1.87947100	-2.42175800	-0.00032600
H	-2.35558600	-3.31369600	-0.00159800
H	-0.84793700	-2.36920500	0.00055000
H	-6.32810300	-0.05660000	-0.00325300
H	-5.56187800	1.50973900	-0.00143300
N	4.70975900	0.63209600	-0.00167300
C	5.07293400	-0.70092700	-0.00132200
C	3.33949400	0.67895300	-0.00074200
H	6.11427400	-1.00359800	-0.00194200
N	4.03720500	-1.50895200	-0.00019300
C	2.93514100	-0.66422800	0.00023700
N	2.57031000	1.79004200	-0.00074700
C	1.53477100	-0.94290400	0.00143300
C	1.27256200	1.50694400	0.00030400
N	0.77502200	0.22928600	0.00149600
H	5.33621400	1.42675000	-0.00250100
O	0.96350900	-2.05496600	0.00232300
N	0.35992500	2.50938200	0.00053400
H	0.69336200	3.46068100	-0.00072000
H	-0.64032000	2.34090400	0.00086800
H	-0.26506300	0.10614500	0.00174400

Table-S4: XYZ-coordinates of *anti*-Oz1:G non-planar normal complex

C	-2.12730300	0.54432700	-0.04646800
C	-4.79338800	-0.75223300	0.05816900
C	-3.52478300	1.23567200	-0.02543800
O	-2.14057300	-0.70724300	-0.06044200
N	-4.65403700	0.59537100	0.00415000
N	-5.04187500	-1.43121300	-1.06469600
N	-4.89235300	-1.36126800	1.24315900
H	-5.22895300	-2.42408600	-1.06475300
H	-4.94189000	-0.96207400	-1.95252800
H	-5.04568600	-2.35650400	1.32549400
H	-4.67994600	-0.84027900	2.08089900
N	-3.48854300	2.57099100	-0.05024800
H	-4.33526400	3.12202100	-0.03928300
H	-2.58352300	3.02086300	-0.07641800
O	-1.13969400	1.32187600	-0.04891600
N	5.16127800	-1.21059500	0.00857000
C	5.87313300	-0.02678300	0.04580300
H	6.95742200	-0.01786700	0.06381800
N	5.09402600	1.03131200	0.05574400
C	3.80399100	0.51696100	0.02324100
C	2.53213900	1.17599000	0.01668300
O	2.29488800	2.39356400	0.03977300
N	1.47232900	0.25011800	-0.02140100
H	0.51579700	0.65269600	-0.03106400
C	1.60917400	-1.12045600	-0.04874700
N	0.47153300	-1.84614700	-0.08602500
H	-0.46523500	-1.42286800	-0.07728600
H	0.56427500	-2.85019400	-0.09665800
N	2.78709300	-1.74034000	-0.04220900
C	3.82911600	-0.88169300	-0.00656800
H	5.54740600	-2.14558100	-0.00488900

Table S5: XYZ-coordinates of *anti*-Oz1:G non-planar reverse complex

N	-4.59454900	1.90939600	-0.12561100
C	-3.85964800	0.79560300	-0.05700300
C	-2.32000500	1.03227600	0.00525900
O	-1.61953500	-0.00475300	0.07543200
N	-3.59352000	-2.16338400	1.19707500
C	-3.75367900	-1.55940600	0.01674900
N	-4.41634600	-0.37725400	-0.04309100
N	-3.45953100	-2.20998500	-1.11224800
H	-3.00879700	-3.11434700	-1.10903200
H	-5.60325600	1.87430700	-0.17005600
H	-4.11105800	2.79716200	-0.13308500
O	-1.94978300	2.23144800	-0.02173100
H	-3.80053900	-1.65050000	2.04114100
H	-3.54915800	-1.72517300	-1.99284200
H	-3.15908100	-3.07145500	1.28254300
N	5.14775500	0.41163900	-0.01485400
C	5.45207100	-0.93578300	-0.04878200
C	3.77964800	0.51746400	0.00503200
H	6.47886000	-1.28419100	-0.06961600
N	4.38037200	-1.69619800	-0.05227000
C	3.31687600	-0.80297300	-0.01869000
N	3.05997000	1.66003000	0.03833100
C	1.90247200	-1.02928900	-0.00630800
C	1.74719300	1.44094800	0.05057000
N	1.18764000	0.18255000	0.03102200
H	5.80811000	1.17813100	-0.00679800
O	1.29387900	-2.11045600	-0.02415600
N	0.89365600	2.48638000	0.09058200
H	1.29565400	3.41112200	0.07800600
H	-0.12802300	2.37836600	0.05295800
H	0.15309800	0.10140100	0.04691100

Table S6: XYZ-coordinates of *anti*-Oz1:C non-planar normal complex

N	-4.68746800	-0.31006800	0.03967200
C	-3.35422300	-0.27971500	-0.01879900
C	-2.75491700	1.15861400	-0.24440800
O	-3.56304900	2.09950800	-0.08018300
N	-0.71692000	-0.90522700	1.30079200
C	-1.31785900	-1.41063300	0.20402700
N	-2.66418200	-1.38725000	0.03976700
N	-0.57476600	-2.11427400	-0.65007000
H	0.43715000	-2.21543000	-0.51575900
H	-5.18999900	-1.17439800	0.18790200
H	-5.18276700	0.56934400	-0.02637900
O	-1.54637200	1.19259400	-0.57999300
H	-1.27861800	-0.27503100	1.85687300
H	-1.00942500	-2.47151700	-1.48760200
H	0.25278300	-0.60425800	1.13228500
N	4.00993700	-0.62416100	-0.09389600
C	4.39884700	0.68164900	-0.03793000
C	2.66617500	-1.00073700	-0.05769000
H	5.46951000	0.87021900	-0.06828500
C	3.47053200	1.67419600	0.04064800
N	1.73532700	-0.02261000	0.05562800
O	2.35919300	-2.20901000	-0.13033900
H	3.76365600	2.71957400	0.07087600
C	2.09082600	1.27051700	0.06553700
N	1.09879900	2.17497000	0.10644900
H	0.12785800	1.87682300	-0.03255000
H	1.31258400	3.16070700	0.07963900
H	4.69772900	-1.36377600	-0.16957800