Structure of the 1,N^2-Etheno-2′-deoxyguanosine Lesion in the 3'-G(εdG)T-5' Sequence Opposite a One-Base Deletion

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Supporting Information

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Running Title: Structure of 1,N^2-εdG Opposite One-Base Deletion

Table S1. Nonexchangeable Proton Chemical Shifts[a] of 1-BD duplex in D_2O[b] at pH 7.0, 25 °C.

Nucleotide	H8	H6	H1′	H2′	H2″	H3′	H5/H2/CH_3
C^1		7.66	5.79	2.00	2.44	4.73	5.93
G^2	7.99		5.93	2.70	2.78	5.01	
C^3		7.42	5.64	2.06	2.41	4.88	5.50
A^4	8.37		6.21	2.67	2.87	5.03	7.71
T^5		7.03	5.62	1.60	1.88	4.77	1.60
X^6	7.92		5.08	2.43	2.5	4.85	
G^7	7.83		5.52	2.71	2.76	4.99	
A^8	8.10		5.92	2.71	2.85	5.05	7.27
A^9	8.13		6.21	2.57	2.88	4.98	7.76
T^{10}	7.16		5.92	2.05	2.47	4.85	1.31
C^{11}		7.59	6.08	2.22	2.49	4.83	5.66
C^{12}		7.68	6.25	2.28	2.28	4.56	5.82
G^{13}	7.84		5.65	2.48	2.68	4.81	
G^{14}	7.85		5.65	2.70	2.82	5.01	
A^{15}	8.23		6.31	2.68	2.95	5.05	7.88
T^{16}		7.17	5.96	1.98	2.54	4.83	1.30
T^{17}		7.37	6.02	2.09	2.52	4.90	1.51
C^{18}		7.63	6.02	1.94	2.00	4.98	5.71
A^{19}	8.59		6.28	2.88	3.01	5.08	7.32
T^{20}		7.16	5.64	2.03	2.37	4.85	1.42
G^{21}	7.88		5.85	2.62	2.68	4.97	
C^{22}		7.34	5.77	1.90	2.37	4.81	5.43
G^{23}	7.95		6.16	2.37	2.62	4.68	

[a] Values in parts per million. [b] 10 mM phosphate buffer, 100 mM NaCl, pH 7.0. Etheno protons H7 and H6 observed at 5.84 and 5.55 ppm, respectively.

Table S2. Non-exchangeable Proton Chemical Shifts[a] of unmodified 1-BD duplex in D_2O[b] at pH 7.0, 25 °C.

Nucleotide	H8	H6	H1′	H2′	H2′′	H3′	H5/H2/CH_3
C^1		7.66	5.79	2.00	2.43	4.71	5.93
G^2	7.99		5.95	2.70	2.78	5.00	
C^3		7.42	5.65	2.09	2.43	4.87	5.48
A^4	8.35		6.24	2.68	2.88	5.03	7.71
T^5		7.07	5.69	1.70	2.05	4.79	1.49
X^6	7.76		5.44	2.47	2.50	4.90	
G^7	7.71		5.38	2.50	2.52	4.93	
A^8	8.15		5.89	2.74	2.84	5.03	7.29
A^9	8.12		6.20	2.58	2.88	4.95	7.80
T^{10}		7.19	5.95	2.07	2.48	4.85	1.29
C^{11}		7.60	6.08	2.23	2.48	4.85	5.67
C^{12}		7.71	6.26	2.27	2.27	4.56	5.83
G^{13}	7.84		5.65	2.48	2.66	4.81	
G^{14}	7.85		5.65	2.70	2.82	5.03	
A^{15}	8.23		6.31	2.70	2.95	5.05	7.91
T^{16}		7.18	5.97	1.98	2.52	4.85	1.35
T^{17}		7.38	6.12	2.09	2.31	4.89	1.59
C^{18}		7.63	-.57	2.17	2.31	4.89	5.85
A^{19}	8.41		6.26	2.78	2.95	5.05	7.73
T^{20}		7.13	5.69	1.98	2.35	4.85	1.49
G^{21}	7.87		5.85	2.60	2.66	4.97	
C^{22}		7.35	5.79	1.90	2.33	4.81	5.42

G^{23}	7.95	6.16	2.62	2.62	4.68

[a] Values in parts per million. [b] 10 mM phosphate buffer, 100 mM NaCl, pH 7.0.

Table S3. Exchangeable Proton Chemical Shifts[a] of Unmodified 1-BD and 1-BD Duplexes in H_2O[b] at pH 7.0, 7 °C.

Nucleotide	Unmodified 1-BD duplex (X^6=G^6)				1-BD duplex (X^6 = 1,N^2-εdG)			
	G(N1H)	T(N3H)	C(N^4H)$_{nhb}$	C(N^4H)$_{hb}$	G(N1H)	T(N3H)	C(N^4H)$_{nhb}$	C(N^4H)$_{hb}$
G^2•C^{22}	13.06		6.63	8.43	13.06		6.63	8.43
C^3•G^{21}	12.71		6.51	8.35	12.75		6.55	8.35
A^4•T^{20}		13.49				13.45		
T^5•A^{19}		13.49				13.33		
X^6								
G^7•C^{18}	11.68[c]		d	d	11.79		6.78	7.72
A^8•T^{17}		13.67				13.69		
A^9•T^{16}		13.59				13.67		
T^{10}•A^{15}		13.57				13.57		
C^{11}•G^{14}	12.79		6.90	8.39	12.77		6.90	8.39

[a]Values in parts per million. [b]10 mM phosphate buffer in H_2O, 100 mM NaCl, pH 7.0. nh and hb and nhb refer to the hydrogen bond and non-hydrogen bonded cytidine amino protons, respectively. [c]G^7 imino proton was broad. [d]C^{18} amino protons were broadened.

Figure S1. The partial charges assigned to the 1,N^2-εdG adduct, calculated using the RESP protocol.

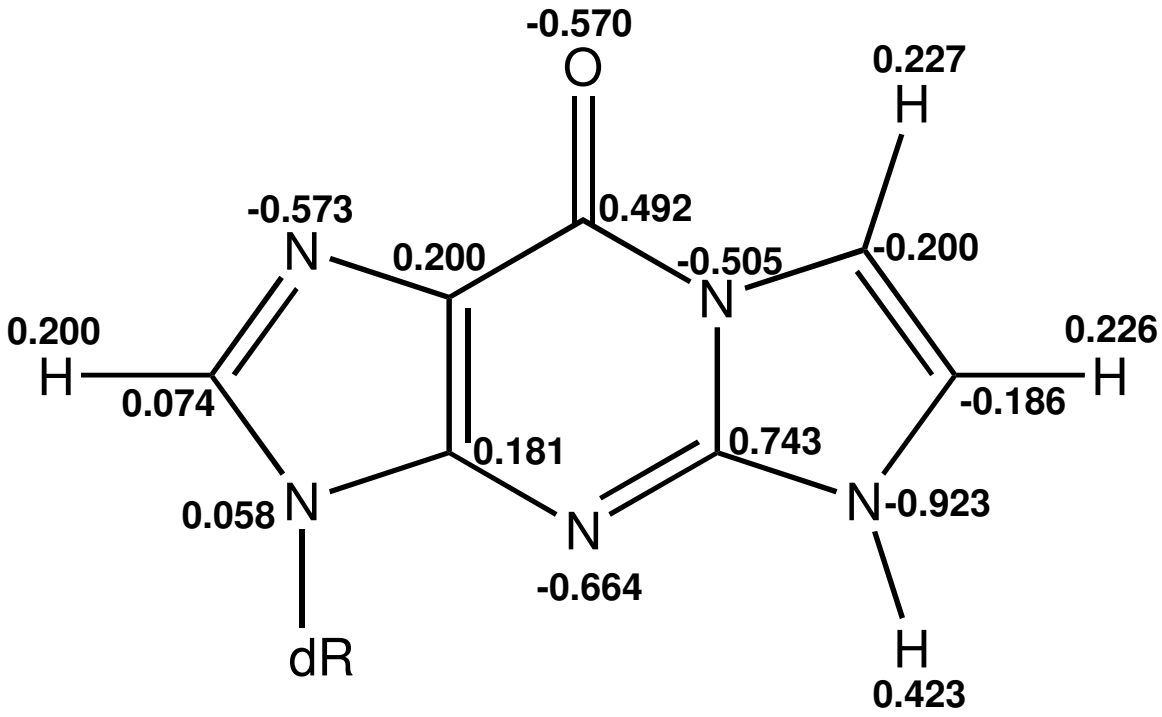

Figure S2. Proton-decoupled ^{31}P NMR spectrum of the 1-BD duplex. Labeled peak G^7 was identified from the two-dimensional H3′-^{31}P spectrum showing cross- peak for X^6 H3′- G^7 ^{31}P. The spectrum was recorded at 25 °C in 10 mM NaH_2PO_4, 100 mM NaCl, and 5 μM Na_2EDTA (pH 7).

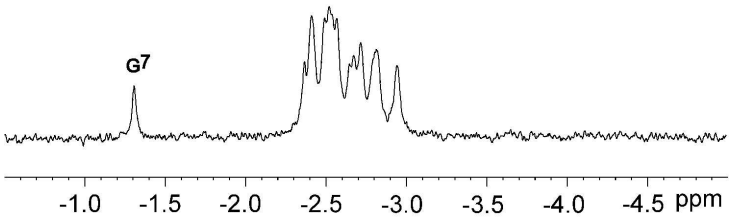

Figure S3. Superposition of structures emergent from rMD calculations for the 1-BD duplex. A. Using a B-form DNA starting structure. B. Using A-form DNA starting structure.

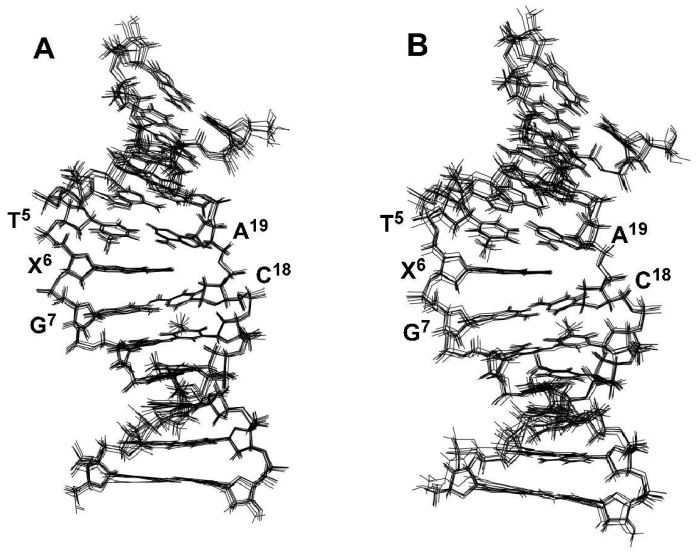

Figure S4. Intra- (black) and inter-nucleotide (gray) sixth root R_1^x factors as a function of nucleotide position in the 1-BD duplex. A. The modified strand. B. The complimentary strand.