Structure of the 1,N^2-Etheno-2′-deoxyguanosine Adduct in Duplex DNA at pH 8.6†

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Supporting Information

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Running Title: 1,N^2-εdG Adduct in Duplex DNA

†We congratulate Professor Lawrence J. Marnett upon the occasion of his sixtieth birthday.

Table S1. Non-exchangeable Proton Chemical Shifts[a] of 1,N^2-εdG duplex in D_2O[b] at pH 8.6, 7 °C.

Nucleotide	H8	H6	H1′	H2′	H2″	H3′	H5/H2/CH_3
C^1		7.68	5.78	2.03	2.46	4.75	5.94
G^2	8.02		5.94	2.72	2.79	5.02	
C^3		7.44	5.65	2.13	2.44	4.89	5.49
A^4	8.37		6.24	2.68	2.91	5.02	7.22
T^5		7.06	5.78	1.74	2.09	4.79	1.50
X^6	7.94		5.12	2.34	2.14	4.83	
G^7	7.84		5.45	2.74	2.77	5.02	
A^8	8.18		5.92	2.77	2.87	5.08	7.22
A^9	8.19		6.22	2.60	2.93	5.00	7.75
T^{10}		7.18	5.92	2.09	2.50	4.87	1.33
C^{11}		7.59	6.06	2.23	2.50	4.85	5.65
C^{12}		7.67	6.26	2.28	2.28	4.59	5.77
G^{13}	7.88		5.67	2.56	2.74	4.85	
G^{14}	7.89		5.69	2.74	2.83	5.06	
A^{15}	8.29		6.33	2.74	2.99	5.08	7.89
T^{16}		7.23	6.00	2.03	2.60	4.89	1.33
T^{17}		7.39	6.10	2.13	2.52	4.98	1.56
C^{18}		7.66	6.14	2.36	2.40	4.96	5.77
C^{19}		7.63	6.04	1.91	2.25	4.79	5.79
A^{20}	8.51		6.31	2.81	3.01	5.06	7.54
T^{21}		7.14	5.73	2.07	2.42	4.89	1.42
G^{22}	7.91		5.86	2.64	2.70	4.98	

C^{23}		7.40	5.77	1.93	2.36	4.85	5.43
G^{24}	7.98		6.18	2.38	2.64	4.71	

[a] Values in parts per million. [b]10 mM phosphate buffer in D_2O, 100 mM NaCl, pH 8.6. Etheno protons H7 and H6 observed at 6.54 and 6.21 ppm, respectively.

Table S2. Exchangeable Proton Chemical Shifts[a] of 1,N^2-εdG duplex in H_2O[b] at pH 8.6, 7 °C.

Base Pair	C N^4 H_{nhb}	C N^4 H)$_{hb}$	G N1H	T N3H
C^1•G^{24}	7.14	8.17		
G^2•C^{23}	6.67	8.48	13.1	
C^3•G^{22}	6.60	8.40	12.7	
A^4•T^{21}				13.5
T^5•A^{20}				13.4
X^6•C^{19}	nd	nd	nd	
G^7•C^{18}	6.91	7.97	12.0	
A^8•T^{17}				13.8
A^9•T^{16}				13.7
T^{10}•A^{15}				13.6
C^{11}•G^{14}	6.71	8.40	12.8	
C^{12}•G^{13}	7.17	8.33		

[a] Values in parts per million. [b]10 mM phosphate buffer in H_2O, 100 mM NaCl, pH 8.6. nh and nhb refer to the hydrogen-bonded and non-hydrogen bonded cytidine amino protons, respectively. nd, not detected.

Table S3. Distribution of Experimental NOE Restraints Among Nucleotide Units of the 1,N^2-εdG duplex[a] in D_2O Buffer at pH 8.6.

Nucleotide	Number of Restraints			
	intra-nucleotide	inter-nucleotide[b]	Cross-strand	Total
C^1	20	4	0	24
G^2	7	13	0	20
C^3	9	14	0	24
A^4	9	15	1	25
T^5	12	13	0	25
X^6	11	6	6	23
G^7	7	7	0	14
A^8	10	9	0	19
A^9	9	15	2	26
T^{10}	10	17	0	27
C^{11}	9	13	1	23
C^{12}	8	6	0	14
G^{13}	16	3	0	19
G^{14}	8	7	0	15
A^{15}	11	15	2	28
T^{16}	10	21	0	31
T^{17}	8	16	1	25
C^{18}	6	8	0	14
C^{19}	11	7	2	20
A^{20}	11	16	1	28
T^{21}	9	14	0	23
G^{22}	7	11	0	18

C^{23}	9	13	0	22
G^{24}	9	5	0	14

[a]Nucleotides $C^{1}\rightarrow C^{12}$ and $G^{13}\rightarrow G^{24}$ are in the modified and complimentary strand, respectively. [b]The internucleotide NOEs includes both 3′- and 5′-neighbors.

Figure S1. NOE cross peak intensities between the base protons and the sugar H1′ protons of the attached deoxyribose moieties. **A.** The modified strand. **B.** The complementary strand. Black bars represent intraresidue cross-peaks. Gray bars represent interresidue cross-peaks.

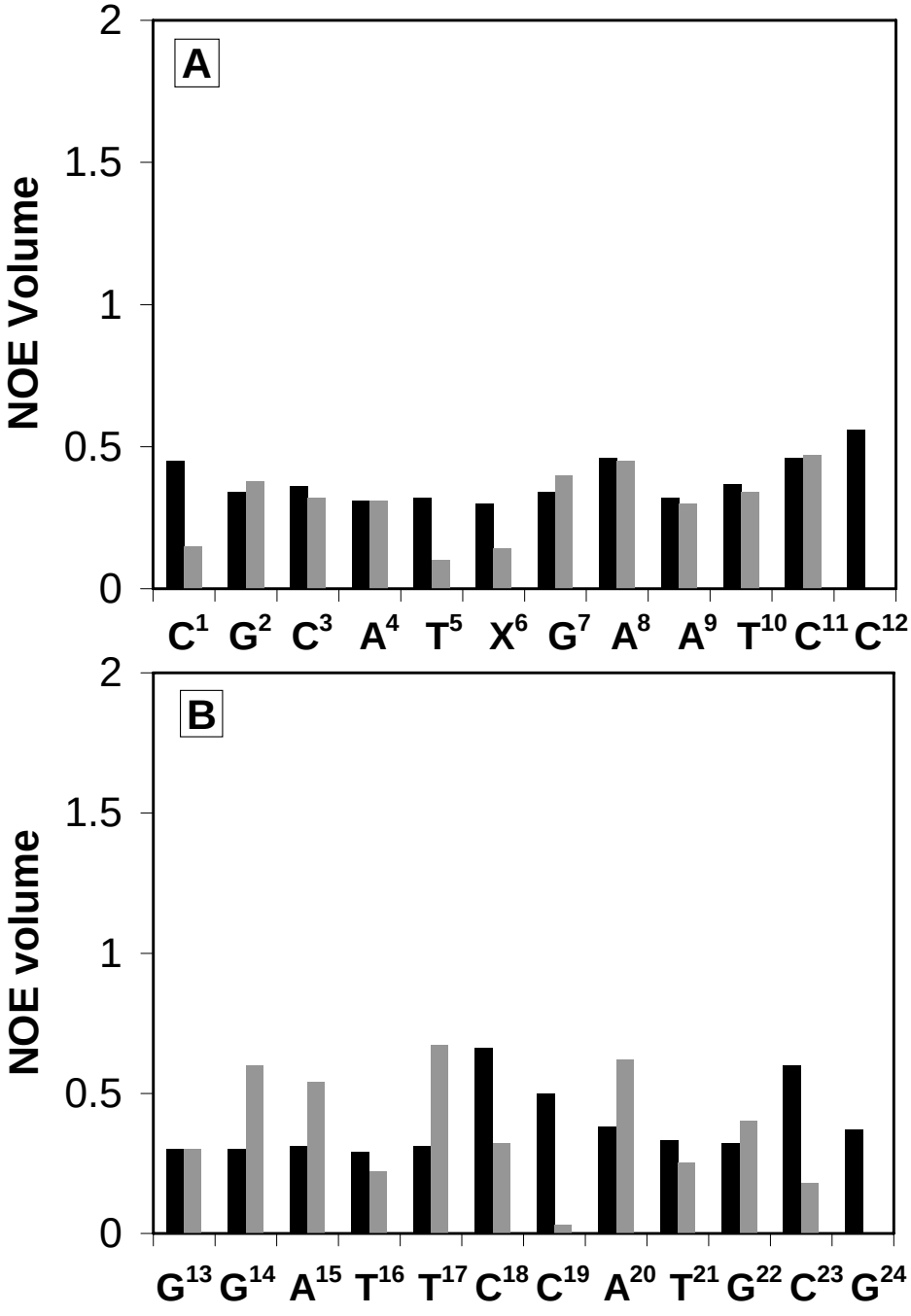

Figure S2. The partial charges assigned to the 1,N^2-εdG adduct, calculated using the RESP protocol in the program GAUSSIAN98.