Supporting Information

Base-Displaced Intercalated Conformation of the 2-Amino-3-methylimidazo[4,5-*f*]quinolone N^2-dG DNA Adduct Positioned at the non-Reiterated G^1 in the NarI Restriction Site

Kallie M. Stavros, Edward K. Hawkins, Carmelo J. Rizzo, and Michael P. Stone*

[1] Department of Chemistry, Center in Molecular Toxicology, Vanderbilt-Ingram Cancer Center, and Vanderbilt Institute of Chemical Biology, Vanderbilt University, Nashville, Tennessee, 37235-1822, United States of America

[2] Deceased

*To whom correspondence should be addressed

Telephone 615-322-2589

e-mail: Kallie M. Stavros, kallie.m.stavros@vanderbilt.edu; Carmelo J. Rizzo, c.rizzo@vanderbilt.edu; Michael P. Stone, michael.p.stone@vanderbilt.edu

Table S1. Comparative Thermal Melting Temperatures (T_m) of IQ, AF, and AAF-Modified Oligodeoxynucleotides.

	Oligodeoxynucleotide [a]	T_m (ΔT_m)[b]			
		C8-IQ [c, d]	C8-AF [d]	C8-AAF [e]	N^2-IQ [f]
a	5'–CTC **G**GC GCC ATC–3' *Nar*I-G_1 3'–GAG CCG CGG TAG–5'	58° (-7°)	57° (-8°)		62° (-1°)
b	5'–CTC G**G**C GCC ATC–3' *Nar*I-G_2 3'–GAG CCG CGG TAG–5'	60° (-5°)	56° (-9°)		64° (+1°)
c	5'–CTC GGC **G**CC ATC–3' *Nar*I-G_3 3'–GAG CCG CGG TAG–5'	61° (-4°)	52° (-13°)		63° (0°)
d	5'–ACC **G**GC GCC ACA–3' *Nar*I-G_1 3'–TGG CCG CGG TGT–5'			51° (-10°)	
e	5'–ACC G**G**C GCC ACA–3' *Nar*I-G_2 3'–TGG CCG CGG TGT–5'			48° (-13°)	
f	5'–ACC GGC **G**CC ACA–3' *Nar*I-G_3 3'–TGG CCG CGG TGT–5'			48° (-13°)	
g	5'–ACC GGC **G**CC ACA–3' *Nar*I-G_3 3'–TGG CC– –GG TGT–5'			49° (+15°)	
h	5'–CTC GGC **G**CC ATC–3' *Nar*I-G_3 3'–GAG CC– –GG TAG–5'	48° (+10°)	44° (+6°)		54° (+16°)
i	5'–CTC GGC **G**CC ATC–3' *Nar*I-G_3 3'–GAG CCG –GG TAG–5'	55° (+4°)			

[a] **G** is the modified dG.

[b] ΔT_m= T_m (modified) - T_m (unmodified). The T_m's for our (entries **a**-**c**, 12-mer), and Fuchs' unmodified *Nar*I (entries **d**-**f**, 12mer) oligonucleotides were 60, 65 and 61 °C, respectively. The T_m's for our (entry **h**) and Fuch's unmodified *Nar*I (entry **g**) oligonucleotide opposite a two-base deletion was 38 and 34 °C, respectively. The T_m's for our unmodified *Nar*I (entry **i**) oligonucleotide opposite a one-base deletion was 51 °C.

[c] Reference 1; [d] Reference 2; [e] References 3-5; [f] References 6,7 and this work.

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(3) Koehl, P., Valladier, P., Lefevre, J.-F. and Fuchs, R. P. P. (1989) Strong structural effect of the position of a single acetylaminofluorene adduct within a mutation hot spot. *Nucleic Acids Res. 17*, 9531-9541.

(4) Milhe, C., Fuchs, R. P. P. and Lefevre, J.-F. (1996) NMR data shows that the carcinogen N-2-acetylaminofluorene stablises an intermediate of -2 frameshifts mutagenesis in a region of high mutation frequency. *Eur. J. Biochem. 235*, 120-127.

(5) Zhou, Y. and Romano, L. J. (1993) Solid-phase synthesis of oligonucleotides containing site-specific N-(2'-deoxyguanosin-8-yl)-2-(acetylamino)fluorene adducts using 9-fluorenylmethoxycarbonyl as the base-protecting group. *Biochemistry 32*, 14043-14052.

(6) Stavros, K.M., Hawkins, E.K., Rizzo, C.J., & Stone, M.P. (2014) Base-Displaced Intercalation of the N2-2-Amino-3-methylimidazo[4,5-f]quinoline-dG Adduct in the NarI Recognition Sequence. *Nucleic Acids Res. 42*, 3450-3463.

(7) Stover, J. S. and Rizzo, C. J. (2007) Synthesis of oligonucleotides containing the N^2-deoxyguanosine adduct of the dietary carcinogen 2-amino-3-methylimidazo[4,5-*f*]quinoline (IQ). *Chem. Res. Toxicol. 20*, 1972-1979.

Table S2. Chemical Shift Assignments (ppm) for the Non-exchangeable DNA Protons of the *N*^{2}-dG-IQ Modified Duplex at the G^1 Position of the NarI Sequence. The temperature was 15 °C.

	H1'	H2'	H2''	H3'	H6/H8	H2/H5
C^1	5.90	2.32	2.63	4.70	7.93	6.01
T^2	6.18	2.28	2.61	4.94	7.71	1.76
C^3	6.10	1.76	2.39	4.94	7.39	5.63
G^4	6.26	2.91	2.77	5.12	8.30	
G^5	5.81	2.562	2.72	5.03	7.98	
C^6	5.62	2.01	2.38	4.98	7.22	5.17
G^7	5.87	2.64	2.72	5.00	7.86	
C^8	5.93	2.08	2.46	4.82	7.35	5.32
C^9	5.44	2.17	2.43	4.94	7.52	5.62
A^{10}	6.32	2.74	2.97	5.05	8.38	7.78
T^{11}	6.04	2.07	2.48	5.04	7.25	1.53
C^{12}	6.30	2.28	2.29	4.60	7.65	5.80
G^{13}	5.69	2.61	2.78		7.95	
A^{14}	6.34	2.78	2.99	5.08	8.37	8.00
T^{15}	5.73	1.97	2.36	5.08	7.14	1.39
G^{16}	5.64	2.65	2.73	5.00	7.81	
G^{17}	5.85	2.68	2.68	2.54	7.72	
C^{18}	5.65	1.95	2.37	4.83	7.22	5.20
G^{19}	5.89	2.63	2.74	5.02	7.86	
C^{20}	6.02	2.17	2.50	5.00	7.10	5.36
C^{21}	6.61	2.43	2.71	5.11	8.17	6.31
G^{22}	5.22	2.05	2.44	4.93	7.52	
A^{23}	6.02	2.65	2.89	5.01	8.05	7.82
G^{24}	6.01	2.27	2.40	4.63	7.63	

Table S3. Chemical Shift Assignments (ppm) for the Exchangeable DNA Protons of the N^2-dG-IQ Modified Duplex at the G^1 Position of the NarI Sequence. The temperature was 5 °C.

	N1H/N3H	N^4 H_a	N^4 H_b
C^1:G^{24}	13.4	7.24	7.76
T^2:A^{23}	14.1		
C^3:G^{22}	12.4	7.23	8.65
X^4:C^{21}	11.8		
G^5:C^{20}	11.5	6.55	7.93
C^6:G^{19}	12.7	6.32	8.18
G^7:C^{18}	11.6	6.31	7.71
C^8:G^{17}	12.9	6.32	8.14
C^9:G^{16}	12.8	6.83	8.50
A^{10}:T^{15}	13.6		
T^{11}:A^{14}	13.8		
C^{12}:G^{13}	12.6	7.14	8.22

Table S4. Chemical Shift Assignments for the IQ Protons of the N^2-dG-IQ Modified Duplex at the G^1 Position of the NarI Sequence. The temperature was 15 °C.

IQ Proton	δ (ppm)
H4a	8.57
H7a	8.11
H8a	6.88
H9a	7.74
CH_3	3.23