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Electronic Supplementary Information (ESI)

The reduction potential of the slipped GC base pair in one-electron oxidized duplex DNA

Robert F. Anderson,* Sujata S. Shinde, Andrej Maroz and Jóhannes Reynisson

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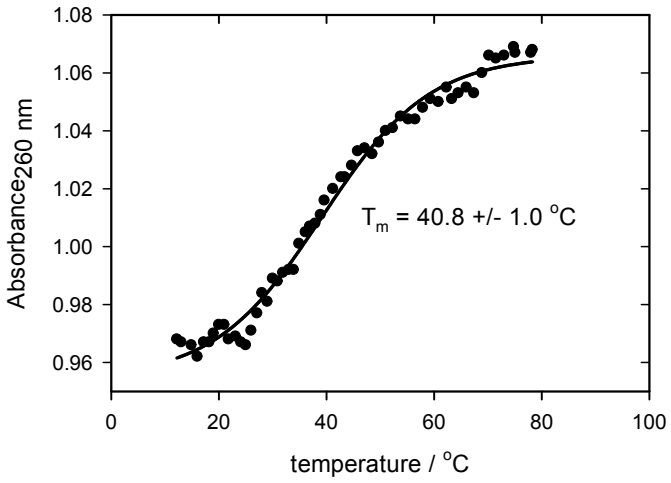


Fig. S1. Melting curve for oligonucleotide duplex 1 under experimental conditions. Temperature dependent absorbance changes of oligonucleotide duplex **1** (83 µM in base pairs) measured at 260 nm in the presence of phosphate buffer (5 mM, pH 7), sodium perchlorate (0.1 M), sodium selenate (25 mM) and 2-methylpropan-2-ol (0.1 M).

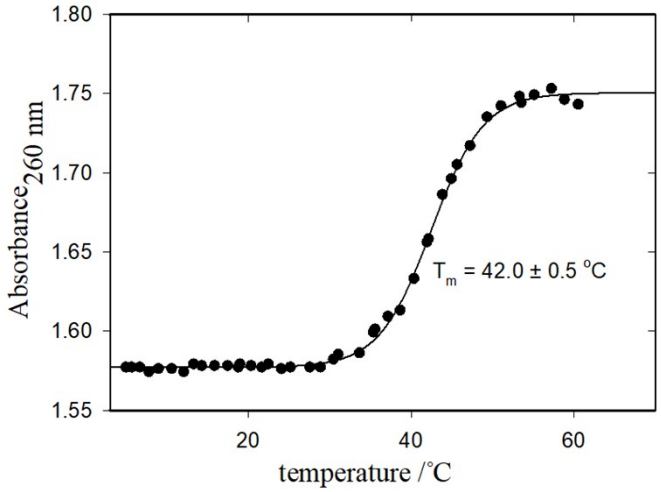


Fig. S2. Melting curve for oligonucleotide duplex 2 under experimental conditions. Temperature dependent absorbance changes of oligonucleotide duplex **2** (130 µM in base pairs) measured at 260 nm in the presence of phosphate buffer (5 mM, pH 7), sodium perchlorate (0.1 M), sodium selenate (25 mM) and 2-methylpropan-2-ol (0.1 M).

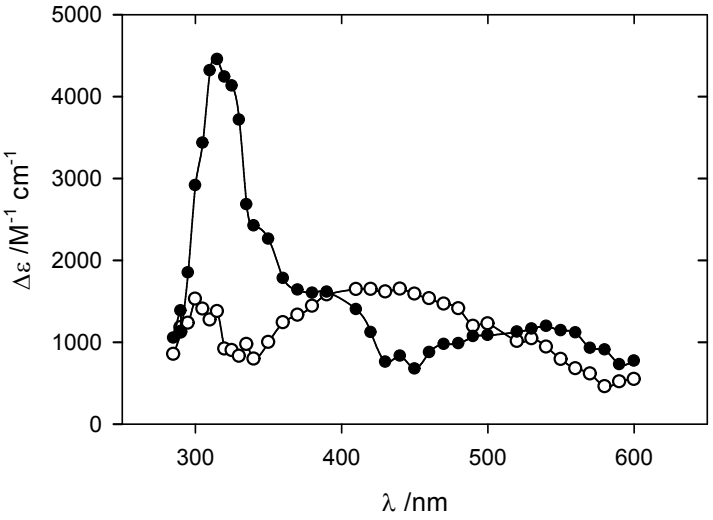


Fig. S3. Absorption difference spectra of radicals observed following pulse radiolysis (arrow) of N_2-saturated aqueous solution of Duplex **1** (2 mM in base pairs) containing Na_2SeO_4 (25 mM), $NaClO_4$ (0.1 M), 2-methyl-2-propanol (0.2 M) and phosphate buffer (5 mM, pH 7.0); ○ 10 μs and ● 400 μs after the pulse.

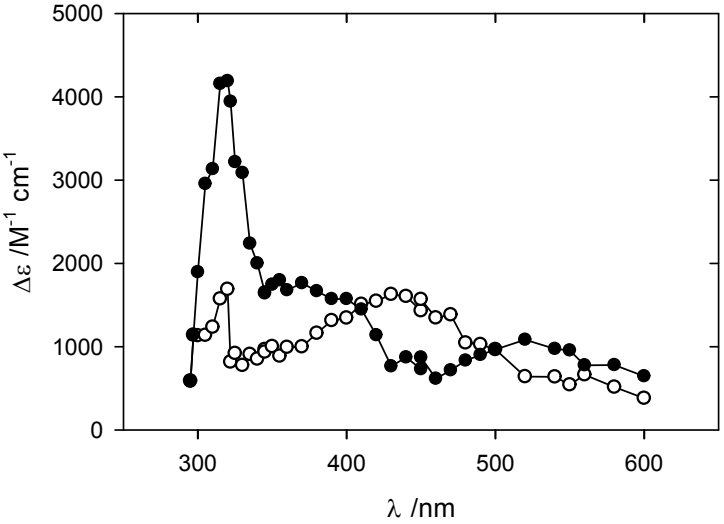


Fig. S4. Absorption difference spectra of radicals observed following pulse radiolysis (arrow) of N_2-saturated aqueous solution of Duplex **2** (2 mM in base pairs) containing Na_2SeO_4 (25 mM), $NaClO_4$ (0.1 M), 2-methyl-2-propanol (0.2 M) and phosphate buffer (5 mM, pH 7.0); ○ 10 μs and ● 400 μs after the pulse.

Computational data

With the pK value of the aniline radical being 7.05 it is clear that roughly half of the concentration is neutral deprotonated form (Ar–HN$^{\bullet}$) and the other half is the positively charged radical (Ar$^{\bullet+}$-NH_2). The question therefore emerged by what mechanism the aniline radical oxidised the G-C base pair, i.e. by hydrogen atom extraction of the amine moieties or by direct removal of an electron. The bond dissociation energies of the N-H bonds in the amino groups were calculated (see Fig. S5) and they are ~100 kcal mol^{-1} for both groups. On the one hand, the anilino neutral radical does not have the energy to extract hydrogen atoms from either of the amine groups on the base pair as its N-H bond dissociation energy is considerably lower at 88.4 kcal mol^{-1} as shown in Fig. S6. On the other hand, the ionization potential of aniline is much higher by ~20 kcal mol^{-1} in vacuum, and roughly the same in water, compared to the ionization potential of the GC base pair as shown in Scheme 2 and Fig. S6.

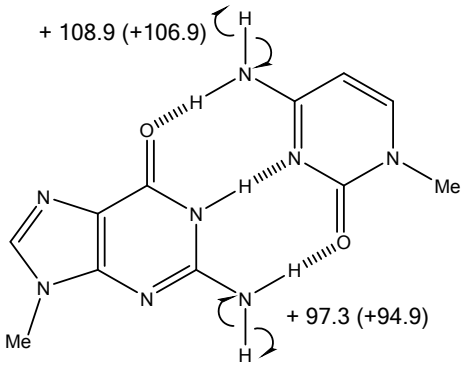


Fig. S5. The bond dissociation energies (BDEs) of the amino functional groups on the G-C base pair. All the values are in kcal mol^{-1} and the numbers in parenthesis include the water simulation.

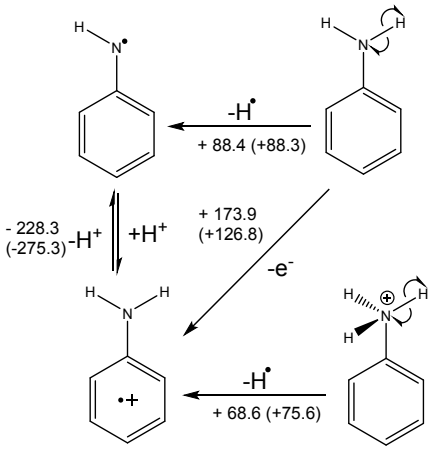


Fig. S6. The bond dissociation energies (BDEs) and proton affinities of the amino functional groups on aniline and its protonated counterpart. Also the ionisation potential is given for aniline. All the values are in kcal mol^{-1} and the numbers in parenthesis include the water simulation.

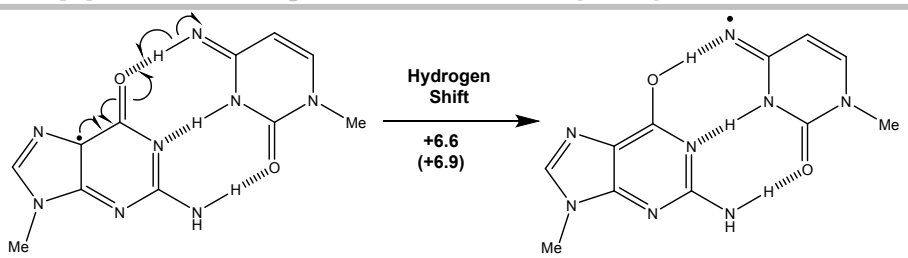


Fig. S7. The thermochemical step for the formation of an iminyl radical base pair. All the values are in kcal mol^{-1} and the number in parenthesis includes the water simulation.

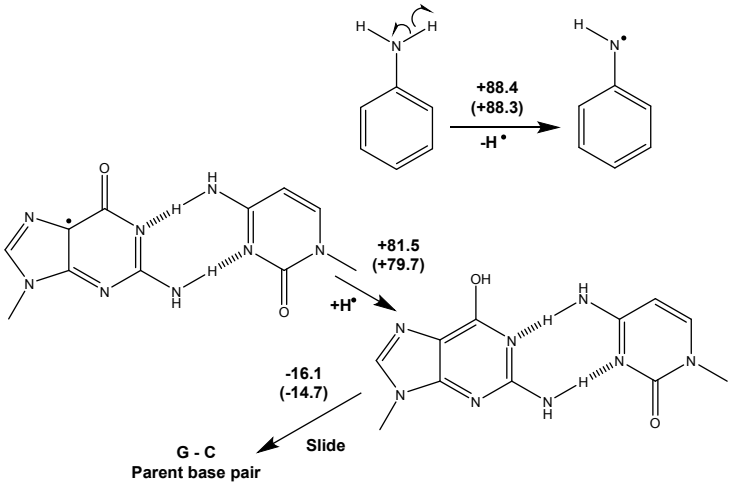


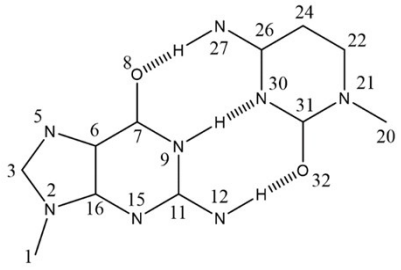
Fig. S8. The thermochemical steps for the abstraction of an H-atom from aniline by the slipped base pair forming a hydroxyl tautomer of the parent G – C based pair. All the values are in kcal mol^{-1} and the number in parenthesis includes the water simulation.

Table S1. The single point and corrected zero point vibrational energies (ZPE) of the optimized complexes and aniline derivatives in hartrees (a.u.). The molecular structures are shown in Scheme 2 and Fig. S5, S6, S7 and S8.

Systems	Energy/a.u.	ZPE/a.u. [a]
G – C	-1016.501026	0.267577631
G$^{\bullet+}$ - C	-1016.254027	0.267629592
G$^{\bullet}$ - C(+H)$^{+}$	-1016.252316	0.26794332
G$^{\bullet}$ - C-N$_4$(-H)	-1015.821987	0.254588311
G - C$^{\bullet}$	-1015.812935	0.253071632
G$^{\bullet}$ - C (slipped)	-1015.831949	0.2539236
G - C-N4(-H)$^{\bullet}$	-1015.812937	0.253072613
G-N$_2$(-H)$^{\bullet}$ - C	-1015.832666	0.254255956
G - C$^{\bullet}$ (N4) iminly	-1015.81108739	0.25426674
G (O$_6$H)- C (slipped)	-1016.47457307	0.26673253
Aniline	-287.7028695	0.114637192
Aniline$^{\bullet+}$	-287.4264389	0.115291118
Aniline-N$^{\bullet}$	-287.0489195	0.101637088
Aniline-NH$_3^{+}$	-288.0492797	0.128843188
Water simulation		
G – C	-1016.528123	0.267162922
G$^{\bullet+}$ - C	-1016.324658	0.267487434
G$^{\bullet}$ - C(+H)$^{+}$	-1016.325452	0.26804038
G$^{\bullet}$ - C-N$_4$(-H)	-1015.854263	0.254748116
G - C$^{\bullet}$	-1015.843824	0.253247124
G$^{\bullet}$ - C (slipped)	-1015.864561	0.254009875
G - C-N$_4$(-H)$^{\bullet}$	-1015.843823	0.253247124
G-N$_2$(-H)$^{\bullet}$ - C	-1015.864226	0.254484389
G - C$^{\bullet}$ (N4) iminly	-1015.84115046	0.25259516
G (O$_6$H)- C (slipped)	-1016.50398	0.26649821
Aniline	-287.7095843	0.114677388
Aniline$^{\bullet+}$	-287.5078183	0.114949939
Aniline-N$^{\bullet}$	-287.0558693	0.101724343
Aniline-NH$_3^{+}$	-288.143072	0.129660841

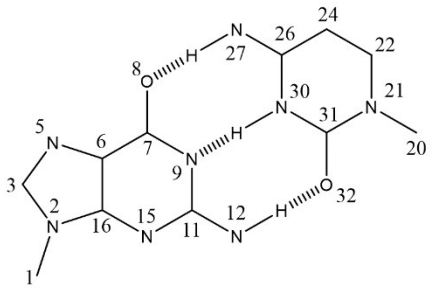
[a] Corrected values (Wong).

Scheme S1. Spin charge distributions as calculated by Mulliken and NBO methods of the $G^{\bullet+}$ - C base pair.



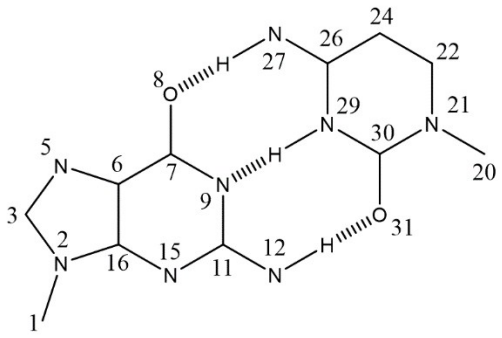
		NBO		Mulliken	
Atom	No	Charge	Spin	Charge	Spin
C	1	-0.35339	0.00041	-0.36492	-0.00164
N	2	-0.41659	-0.01079	0.130698	-0.0274
C	3	0.34942	0.23651	0.149901	0.251566
N	5	-0.44592	0.0233	-0.28862	0.016263
C	6	0.17994	0.25828	0.282375	0.264665
C	7	0.64214	-0.01002	0.236795	-0.02304
O	8	-0.56714	0.0982	-0.37568	0.109607
N	9	-0.65379	-0.01676	-0.37069	-0.01956
C	11	0.66964	0.00027	0.522553	0.009471
N	12	-0.6707	0.15188	-0.66692	0.159883
N	15	-0.48284	0.23302	-0.42835	0.242914
C	16	0.38402	0.0486	0.008072	0.041212
C	20	-0.34604	-0.00027	-0.28144	-6.50E-05
N	21	-0.44768	0.00239	0.134947	0.000805
C	22	0.13286	-0.00075	-0.01323	-0.00014
C	24	-0.34068	0.0019	-0.62328	0.001453
C	26	0.48455	-0.00173	0.739736	-0.00054
N	27	-0.74003	-0.00093	-0.60907	0.000954
N	30	-0.67343	0.00217	-0.52213	-0.00005
C	31	0.84061	-0.00345	0.354023	-0.00039
O	32	-0.71718	0.00309	-0.58773	0.000748

Scheme S2. Spin charge distributions as calculated by Mulliken and NBO methods of the G$^{\bullet}$ - C(+H)$^{+}$ base pair.



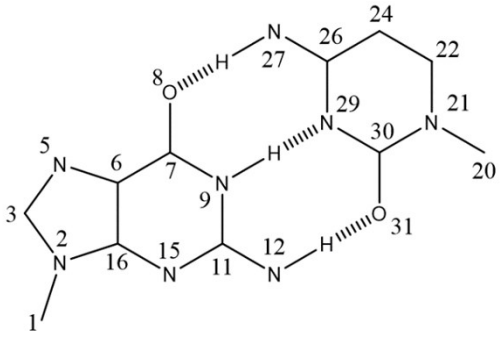
		NBO		Mulliken	
Atom	No	Charge	Spin	Charge	Spin
C	1	-0.35272	0.00068	-0.362776	-0.002084
N	2	-0.42182	-0.01045	0.128913	-0.023064
C	3	0.3381	0.2473	0.148593	0.2507
N	5	-0.4381	0.00056	-0.310996	0.006865
C	6	0.109	0.28394	0.308149	0.280275
C	7	0.65701	-0.01281	0.185672	-0.015824
O	8	-0.63334	0.11003	-0.461641	0.10976
N	9	-0.70235	-0.02089	-0.48477	-0.02147
C	11	0.64591	0.00763	0.534681	0.022559
N	12	-0.70197	0.13	-0.60484	0.1347
N	15	-0.4924	0.25308	-0.437628	0.255931
C	16	0.39826	0.02854	-0.000023	0.026469
C	20	-0.34822	-2E-05	-0.279319	-0.000017
N	21	-0.44765	0.00025	0.106001	0.000236
C	22	0.14861	2E-05	-0.004136	0.000054
C	24	-0.33922	0.00016	-0.441422	0.000434
C	26	0.5085	6E-05	0.587021	-0.000292
N	27	-0.7084	-0.00041	-0.641438	0.000752
N	30	-0.62436	-8E-05	-0.410757	0.0001
C	31	0.85754	2E-05	0.328047	-0.000103
O	32	-0.64927	-7E-05	-0.463382	0.000012

Scheme S3. Spin distributions as calculated by Mulliken and NBO methods of the G• - C-N_4(-H) base pair.



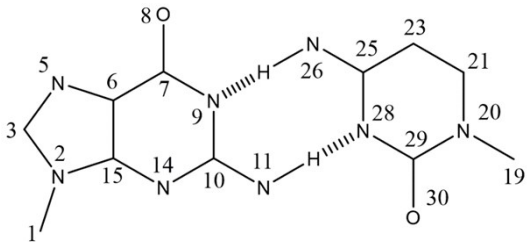
		NBO	Mulliken
Atom	No	Spin	Spin
C	1	0.00045	-0.00271
N	2	-0.0065	-0.020136
C	3	0.25055	0.254864
N	5	-0.03294	-0.02714
C	6	0.31484	0.311773
C	7	-0.03949	-0.037986
O	8	0.14659	0.145527
N	9	-0.01385	-0.014876
C	11	-0.00959	0.006883
N	12	0.10397	0.107724
N	15	0.29863	0.300974
C	16	0.00248	-0.002237
C	20	-2E-05	-0.000022
N	21	0.00046	0.000463
C	22	-2E-05	0.000038
C	24	0.00035	0.000566
C	26	1E-05	-0.000734
N	27	5E-05	0.001284
N	29	-0.00014	0.000321
C	30	-5E-05	-0.00017
O	31	4E-05	0.000132

Scheme S4. Spin charge distributions as calculated by Mulliken and NBO methods of the G - C• base pair.



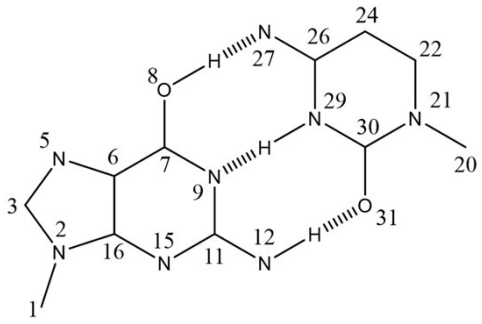
		NBO	Mulliken
Atom	No	Spin	Spin
C	1	3E-05	-3.8E-05
N	2	-0.00074	-0.00106
C	3	0.00757	0.007736
N	5	-0.00102	-0.0009
C	6	0.00998	0.009284
C	7	-0.00338	-0.00342
O	8	0.00888	0.008386
N	9	0.0003	0.003264
C	11	-0.00108	-0.0005
N	12	0.00195	0.002091
N	15	0.00935	0.009416
C	16	0.00114	0.00097
C	20	-0.00451	-0.00645
N	21	0.11943	0.110923
C	22	-0.02139	-0.01648
C	24	0.11807	0.11305
C	26	-0.11763	-0.09233
N	27	0.71277	0.700582
N	29	0.20601	0.203466
C	30	-0.03144	-0.02519
O	31	-0.00718	-0.00785

Scheme S5. Spin distributions as calculated by Mulliken and NBO methods of the G• - C (slipped) base pair.



		NBO	Mulliken
Atom	No	Spin	Spin
C	1	0.00038	-0.00263
N	2	-0.0049	-0.01834
C	3	0.24925	0.251618
N	5	-0.0359	-0.03049
C	6	0.31754	0.300918
C	7	-0.04003	-0.01909
O	8	0.14054	0.137439
N	9	-0.01539	-0.01654
C	10	-0.01322	0.003703
N	11	0.11469	0.117916
N	14	0.30649	0.308752
C	15	-0.00338	-0.01032
C	19	-1E-05	-1E-06
N	20	-4E-05	-6.9E-05
C	21	8E-05	0.000133
C	23	-6E-05	0.000132
C	25	6E-05	-0.00036
N	26	3E-05	0.000473
N	28	-0.00018	-0.00019
C	29	6E-05	0.000126
O	30	7E-05	0.00005

Scheme S6 Spin distributions as calculated by Mulliken and NBO methods of the G - C• (N4) iminly base pair.



		NBO	Mulliken
Atom	No	Spin	Spin
C	1	2E-05	0.000004
N	2	0.00046	0.000215
C	3	0.00129	0.001461
N	5	-0.0013	-0.0014
C	6	0.00367	0.005339
C	7	-0.00274	-0.00912
O	8	0.02002	0.031442
N	9	0.00733	0.008529
C	11	-0.00186	-0.00069
N	12	0	0.000218
N	15	0.0026	0.002972
C	16	-0.00177	-0.00338
C	20	0.00046	-0.00013
N	21	-0.00917	-0.00833
C	22	-0.01696	-0.01823
C	24	0.05672	0.041819
C	26	-0.07536	-0.04055
N	27	0.97527	0.94846
N	29	0.03878	0.041881
C	30	0.00207	0.004219
O	31	0.00529	0.005831