Electronic Supplementary Information

On the Evolution of One-Electron-Oxidized Deoxyguanosine in Damaged DNA under Physiological Conditions, a DFT and ONIOM Study on Proton Transfer and Equilibrium

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Testing PM6

The quality of the HB description when using PM6 was tested, since this method is used to model the low level region in the ONIOM calculations. It was found that the mean unsigned error (MUE) for the distances relevant to HB obtained from PM6 calculations in vacuum is identical to that arising from M05-2X calculations in conjunction with SMD (see tables below). The MUE is only 0.06 Å, which represent ~2.4% deviation. When PM6 is used in conjunction with SMD the deviations from the experimental values increase, but still remain low. In this case MUE=0.14 Å (~4.7%). Therefore, it can be stated that PM6 properly describes the HB interactions in the base pairs. However it is important to notice that in this work the main purpose of the low level region in the ONIOM calculations (model d) is to impose the necessary constrains to the high level fragment to mimic the DNA environment.

	d(O6-N4)	d(N1-N3)	d(N2-O2)	**MUE**
EXP	2.91	2.95	2.86	
	Absolute error			
M05-2X+SMD	2.97	2.99	2.94	**0.06**
PM6	2.91	2.99	3.01	**0.06**
PM6+SMD	3.06	3.04	3.03	**0.14**
	% error			
M05-2X+SMD	2.1	1.4	2.8	**2.1**
PM6	0.0	1.4	5.2	**2.2**
PM6+SMD	5.2	3.1	5.9	**4.7**

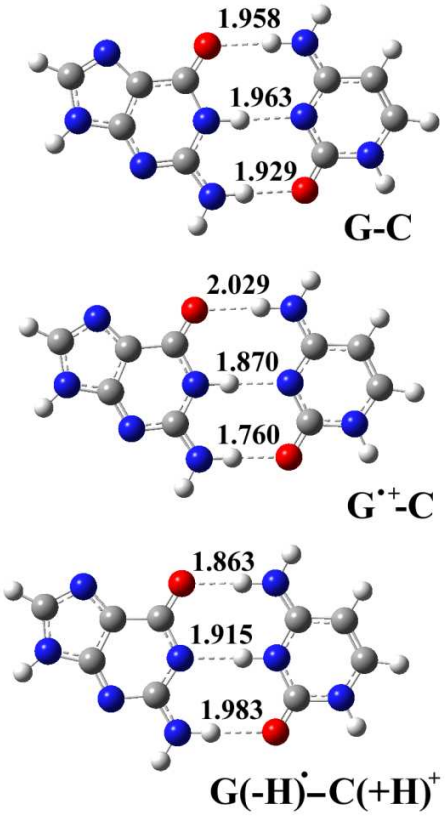

Figure S1. Main geometrical parameters involved in the HB between pairs in the neutral species, the radical cation, and the PT(I) product for model ***b***.

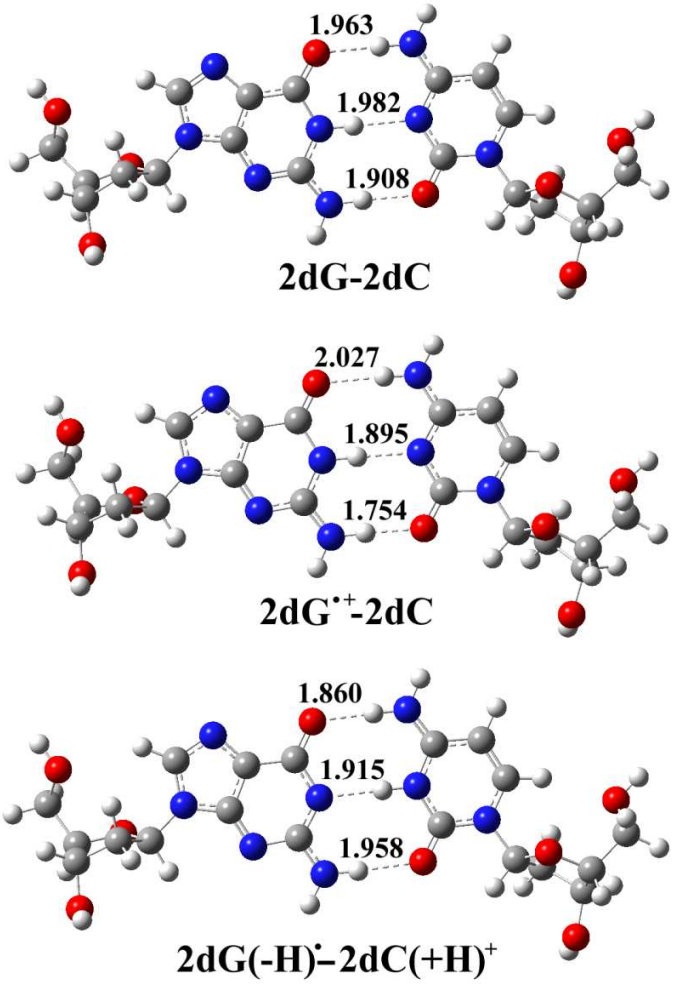

Figure S2. Main geometrical parameters involved in the HB between pairs in the neutral species, the radical cation, and the PT(I) product for model ***c***.

Table 1S. Relative energies including ZPE corrections (kcal/mol) of radicals yield by deprotonation from the purine unit in the radical cation.

	N1	N2(*syn*)	N2(*anty*)
guanine	0.00	4.90	3.52
model ***a***	0.00	3.77	2.40
model ***b***	0.00	1.22	2.50
model ***c***	0.00	0.46	
model ***d***	0.00	0.28	

Table 2S. Relative enthalpy (kcal/mol) of radicals yield by deprotonation from the purine unit in the radical cation.

	N1	N2(*syn*)	N2(*anty*)
guanine	0.00	4.74	3.37
model ***a***	0.00	3.83	2.47
model ***b***	0.00	0.80	2.25
model ***c***	0.00	0.41	
model ***d***	0.00	1.22	

Table 3S. Relative energies including ZPE corrections (kcal/mol) of radicals yield by deprotonation from the sugar unit in the radical cation.

	C1'	C2'	C3'	C4'	C5'
2-deoxyribose	2.11	6.25	2.56	0.00	2.30
model ***a***	0.34	5.45	1.62	0.13	0.00
model ***c***	0.23		1.26	0.00	0.31
model ***d***	3.91		3.65	0.00	2.68

Table 4S. Relative enthalpy (kcal/mol) of radicals yield by deprotonation from the sugar unit in the radical cation.

	C1'	C2'	C3'	C4'	C5'
2-deoxyribose	1.82	6.27	3.37	0.00	2.19
model ***a***	0.16	5.50	1.53	0.18	0.00
model ***c***	0.00		1.28	0.19	0.25
model ***d***	3.30		2.73	0.00	2.45