Supporting Information

Addressing the competitive formation of tandem DNA lesions by a nucleobase peroxyl radical: a DFT-D screening

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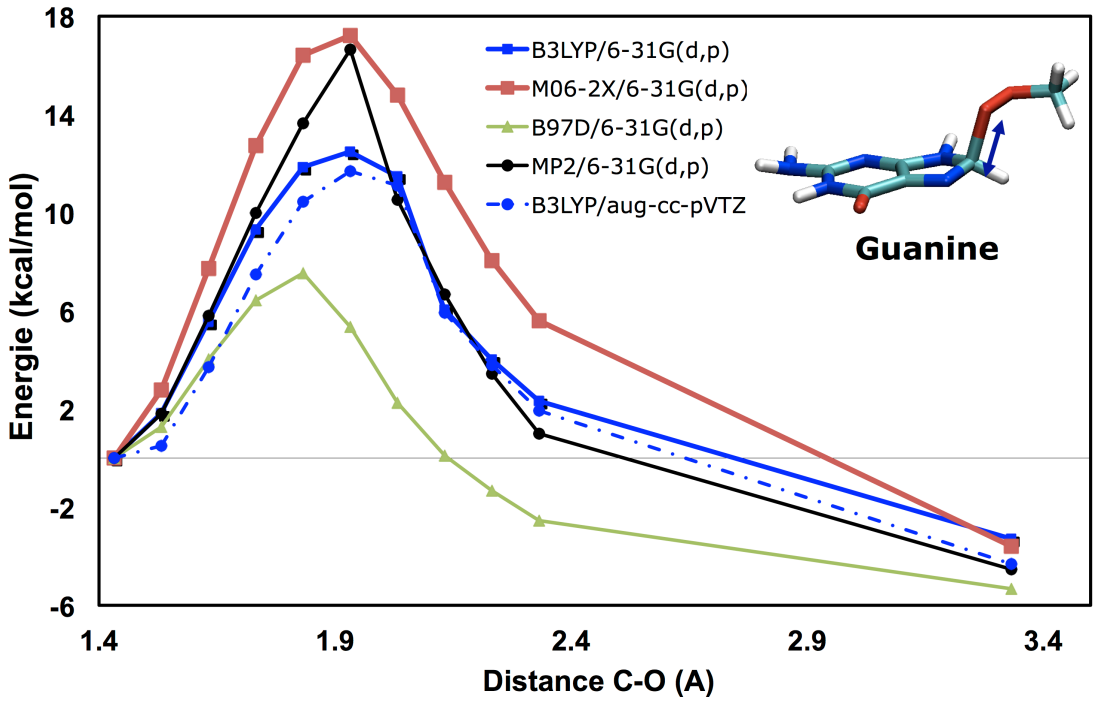
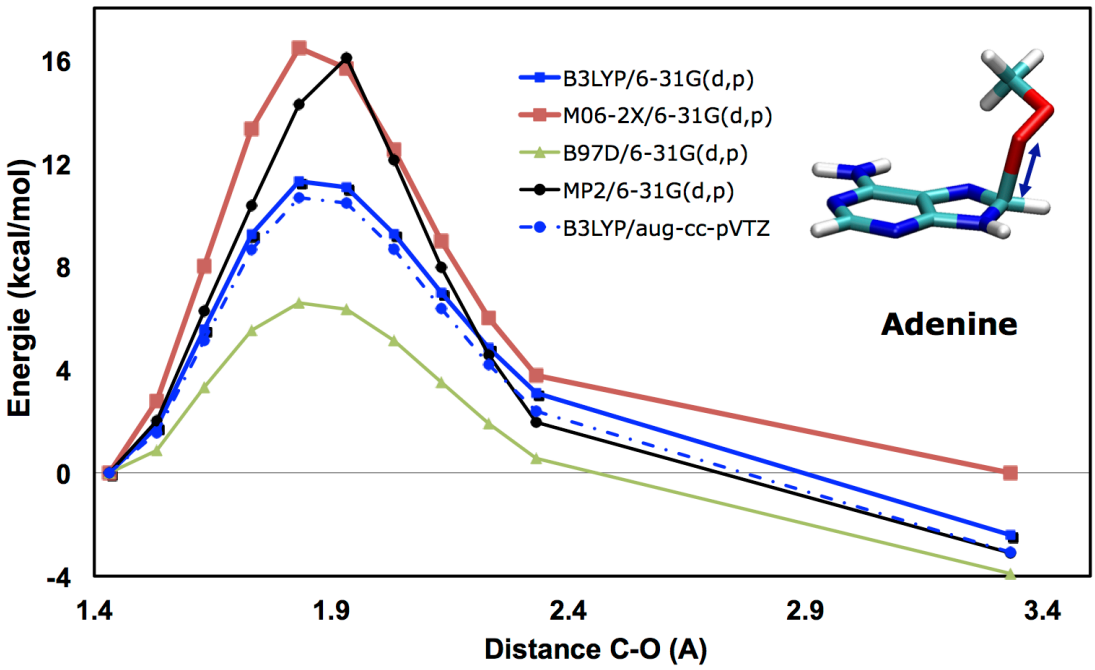
Potential energy relaxed scan for the attack of methyl peroxyl radical onto guanine (up) or adenine (bottom), obtained with B3LYP (blue), M06-2X (red), B97D (green) and MP2 (black). The 6-31G(d,p) basis set is used throughout (solid lines). The blue dashed line curve corresponds to the B3LYP/aug-cc-pVTZ level of theory: the similarity between the two B3LYP curves ascertains a limited basis set dependence. A cartoon representation is given, on which the carbon—oxygen distance chosen as the reaction coordinate is depicted with a double arrow.





Activation energies $\Delta E^{\dagger}$ and $\Delta E_{R\rightarrow P}$ (in kcal/mol) for the addition of C5-peroxyl thymine on both guanine and adenine, with B3LYP-D, B97D and M06-2X functionals. The 6-31G(d,p) basis set is used throughout.

			Orientation 5'⟵3'					
			$\Delta E^{\dagger}$			$\Delta E_{R\rightarrow P}$		
			B3LYP-D	B97D	M06-2X	B3LYP-D	B97D	M06-2X
			Guanine					
Peroxyl-T	C5	*syn*	4.6	1.8	7.9	-6.0	-3.7	-8.4
	C5	*anti*	16.8	14.4	18.8	8.1	9.6	5.7
			Adenine					
Peroxyl-T	C5	*syn*	6.5	9.5	15.2	2.7	4.9	1.5
	C5	*anti*	11.6	11.7	22.3	7.9	1.9	3.7

Spin densities calculated for the two structures displayed in Figure 2 of the main text, on a geometry optimized at the B3LYP-D/6-31G(d,p) level of theory. O17 corresponds to the terminal oxygen. DZP++ is a double-ζ plus polarization quality basis set, including additional diffuse s- and p-type functions as described in *Proc. Natl. Acad. Sc.*, 2005, 102:6698.

		DFT				Post Hartree-Fock		
		BLYP 6-31G(d.p)	B3LYP 6-31G(d,p)	B3LYP DZP++	B3LYP aug-cc-pVTZ	MP4(SDQ) 6-31G(d.p)	MP4(SDQ) DZP++	MP4(SDQ) aug-cc-pVTZ
6-OH-5-	O16	0.28	0.26	0.26	0.25	0.23	0.22	0.21
peroxyl-C	O17	0.66	0.72	0.71	0.72	0.78	0.77	0.76
6-OH-5-	O16	0.29	0.27	0.27	0.25	0.22	0.23	0.22
peroxyl-T	O17	0.67	0.72	0.71	0.73	0.77	0.76	0.76

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