Supporting Information

π vs σ-Radical States of One-Electron Oxidized DNA/RNA Bases: A Density Functional Theory Study

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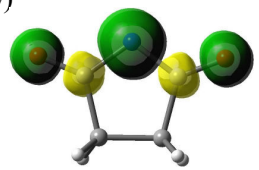
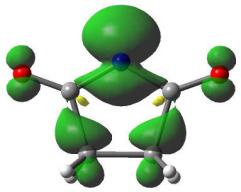
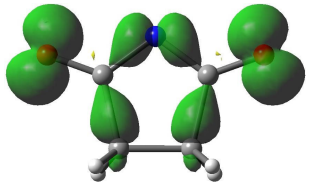
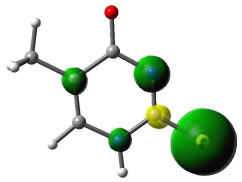
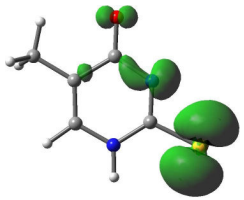
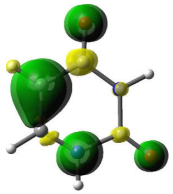
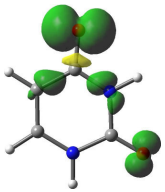
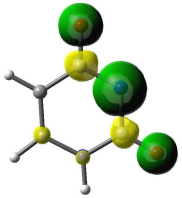
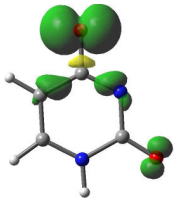
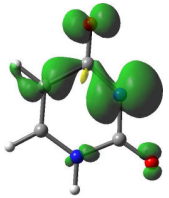
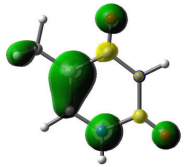
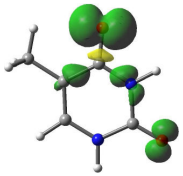
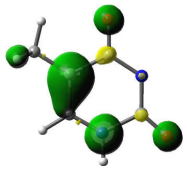
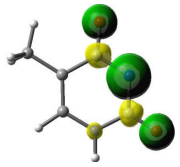
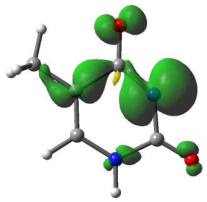
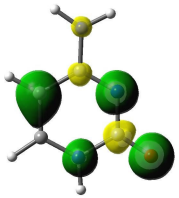
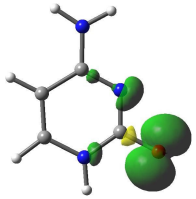
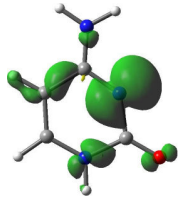
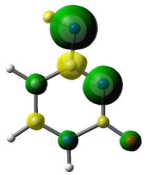
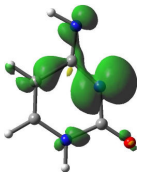
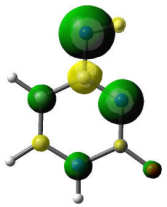
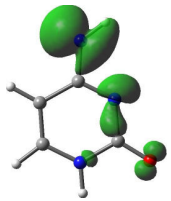
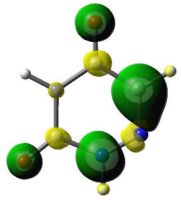
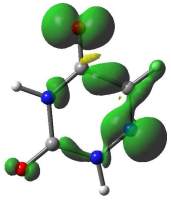
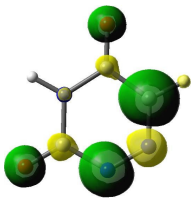
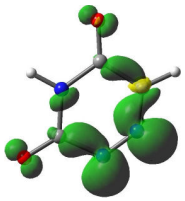
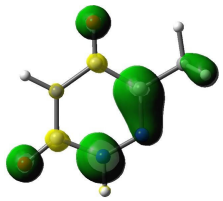
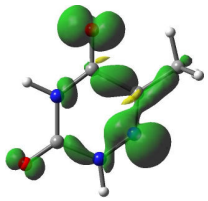
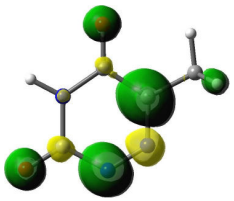
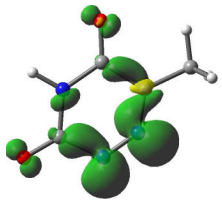
Table S1- B3LYP/6-31++G** calculated hyperfine coupling constants (HFCCs) of all the radicals considered in the present study and their comparison with the available experimental values. The couplings are given for those atoms which have maximum spin density and thus only the large couplings which are experimentally observed are reported. **For all molecules the z-axis points perpendicular to the molecular ring plane.** The couplings are given in Gauss.

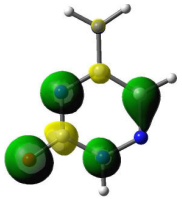
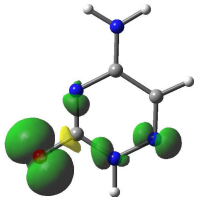
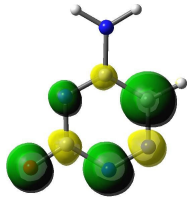
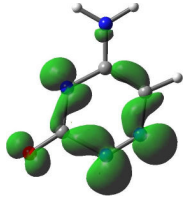
π-radical					σ-radical									
Succinimidyl$^{\bullet}$ (C_{2V}) 					σ(N) 					σ(O) 				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz			xx	yy	zz
N	9.6	-9.5 (0.1)	-9.2 (0.4)	18.7 (28.3)	N	18.8	-10.0 (8.8)	21.4 (40.2)	-11.4 (7.4)	^{17}O	-12.8	19.3 (6.5)	-41.2 (-54.0)	21.8 (9.0)
Exp.[10]				**(31)**										
2-thio-T(N3-H)$^{\bullet}$ (C_s) 					σ(S) 					Left blank				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]							
		xx	yy	zz			xx	yy	zz					
^{33}S	6.6	-25.7 (-19.1)	-25.9 (-19.3)	51.5 (58.1)	^{33}S	8.5	-26.7 (-18.2)	52.2 (60.7)	-25.5 (-17.0)					
N3	1.9	-2.0 (-0.1)	-2.1 (-0.2)	4.1 (6.0)	N3	15.4	-2.0 (13.4)	3.8 (19.2)	-1.8 (13.6)					
					Exp[36] **(^{14}N)**		**(46.6)**	**(55.5)**	**(45.2)**					

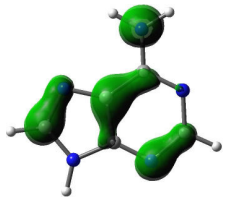
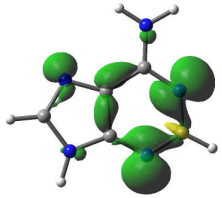
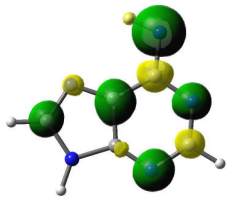
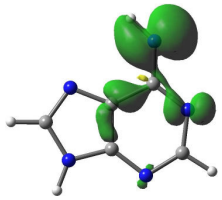
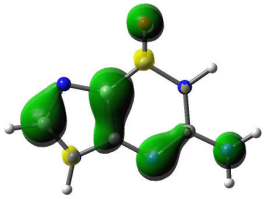
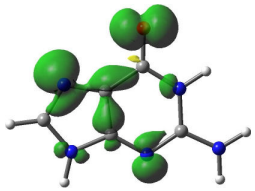
π-radical					σ-radical										
$U^{\bullet+}$ (C_s) 										Left blank					
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]								
		xx	yy	zz			xx	yy	zz						
H5	-15.4	8.7 (6.7)	-7.6 (-23.0)	-1.1 (-16.5)	^{17}O4	-24.0	43.7 (19.7)	-83.2 (-107.2)	39.5 (15.5)						
Exp[10, d]	**15.7**	**-8**	**-24**	**-15**											
U(N3-H)$^{\bullet}$ (C_s) π(N3) 					σ(O4) 					σ(N3) 					
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]			
		xx	yy	zz			xx	yy	zz			xx	yy	zz	
N3	10.0	-9.4 (0.6)	-9.6 (0.4)	19.0 (29.0)	^{17}O4	-26.2	44.8 (18.6)	-86.8 (-113.0)	41.9 (15.7)	N3	20.0	-11.0 (9.0)	20.6 (40.6)	-9.6 (10.4)	
$T^{\bullet+}$ (C_s) π(C5) 					σ(O4) 					Left blank					
Atom	A_{iso}	A_{aniso}			Atom	A_{iso}	A_{aniso} (A_{total})[a]								
		xx	yy	zz			xx	yy	zz						
CH_3 (av.)[b] (H atoms) **Exp.[42]**	23.4 - - **(20.3)**	- - -	- - -	- - -	^{17}O4	-24.0	-82.4 (-106.4)	43.2 (19.2)	39.2 (15.2)						
N1 **Exp.[42]**	5.3 **Ca. 5**	-4.5 (0.8) **<(3)**	-4.3 (1.0) **<(3)**	8.7 (14.0) **(11.9)**											

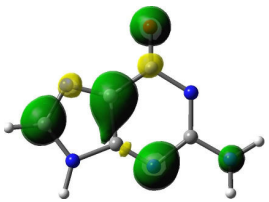
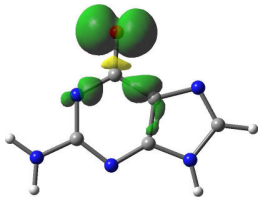
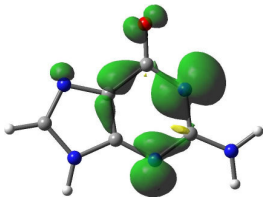
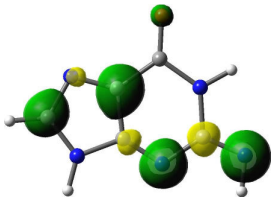
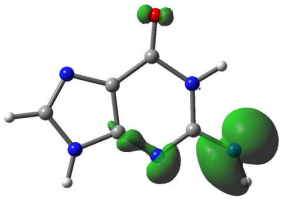
π-radical										σ-radical				
T(N3-H)$^{\bullet}$ (C_s)  π(C5)					 π(N3)					 σ(N3)				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz			xx	yy	zz
CH_3 (av.)[b]	17.7	-	-	-	N3	10.0	-9.6	-9.4	19.1	N3	22.9	21.9	-11.7	-10.2
Exp[20, c]	**21**	-	-	-			(0.4)	(0.6)	(29.1)			(44.8)	(11.2)	(12.7)
N1	6.6	-5.2	-5.1	10.3										
		(1.4)	(1.5)	(16.9)										
Exp.[20, c]	**5.0**	**(1)**	**(1)**	**(13.2)**										
π-radical					**σ-radical**									
$C^{\bullet+}$ (C_s) 					 σ(O2)					 σ(N3)				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz			xx	yy	zz
H5	-8.2	5.0	-4.5	-0.5	$^{17}O2$	-26.7	47.2	-91.7	44.5	N3	30.7	-13.1	24.2	-11.2
		(-3.2)	(-12.7)	(-8.7)			(20.5)	(-118.4)	(17.8)			(17.6)	(54.9)	(19.5)
Exp[10, d]		**(-5)**	**(-16)**	**(-13.5)**										
C(N4-H')$^{\bullet}$ (C_s)  π(N4)					σ(N3) 					Left blank				
Atom	A_{iso}	A_{aniso}			Atom	A_{iso}	A_{aniso} (A_{total})[a]							
		xx	yy	zz			xx	yy	zz					
N4	10.4	-10.4	-10.7	21.1	N3	29.0	-12.2	22.7	-10.5					
		(0)	(-0.3)	(31.5)			(16.8)	(51.7)	(18.5)					

π-radical					σ-radical				
C(N4-H")$^{\bullet}$ (C_s)  π(N4)					 σ(N4)				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz
N4	11.0	-10.8 (0.2)	-10.7 (0.3)	21.5 (32.5)	N4	30.4	22.3 (52.7)	-12.0 (18.4)	-10.3 (20.1)
6-azaU$^{\bullet+}$ (C_s) 									
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz
H5	-13.0	7.3 (-5.7)	-6.1 (-19.1)	-1.2 (-14.2)	N6	15.7	-5.7 (10.0)	10.5 (26.2)	-4.8 (10.9)
6-azaU(N1-H)$^{\bullet}$ (C_s) 					σ(N) 				
Atom	A_{iso}	A_{aniso}			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz
N1	8.9	-8.0 (0.9)	-7.8 (1.1)	15.8 (24.7)	N1	44.5	-5.5 (39.0)	9.7 (54.2)	-4.2 (40.3)
H5	-13.6	7.5 (-6.1)	-6.8 (-20.4)	-0.7 (-14.3)	N6	40.5	-7.0 (33.5)	12.7 (53.2)	-5.7 (34.8)
					Exp[13] (N1,N6)	**(30.2)**	**(26.0)**	**(38.5)**	**(26.0)**

π-radical					σ-radical				
6-azaT$^{\bullet+}$ (C_s) 									
Atom	A_{iso}	A_{aniso}			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz
CH_3 (av.)[b] (H atoms)	22.0	- - -	- - -	- - -	N6	20.8	-7.0 (13.8)	12.5 (33.3)	-5.5 (15.3)
6-azaT(N1-H)$^{\bullet}$ (C_s) 					σ(N) 				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz
CH_3 (av.)	15.8	-	-	-	CH_3 (av.)[b]	-1.5	-	-	-
N1	8.2	-7.4 (0.8)	-7.2 (1.0)	14.6 (22.8)	N1	44.9	-5.5 (39.4)	9.5 (54.4)	-4.0 (40.9)
N6	-2.6	1.4 (-1.2)	2.1 (0.5)	-3.5 (-6.1)	N6	40.0	-7.2 (32.8)	12.9 (52.9)	-5.7 (34.3)
Exp.[13] (CH_3)	**14.7**	-	-	-					
Exp[13] (N1)	**8 – 10**	**< 3**	**< 3**	**23.0**					
Exp[13] (N6)	**< 4**	**< 4**	**< 4**	**< 4**					

π-radical					σ-radical				
6-azaC$^{\bullet+}$ (C_s) 					σ(O2) 				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz
^{17}O2	-15.9	30.4 (14.5)	30.1 (14.2)	-60.5 (-76.4)	^{17}O2	-25.2	45.3 (20.1)	-87.2 (-112.4)	42.0 (16.8)
N3	3.9	-3.9 (0)	-4.0 (-0.1)	7.9 (11.8)					
6-azaC(N1-H)$^{\bullet}$ (C_s) 					σ(N) 				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	xx	yy
N1	7.1	-6.7 (0.4)	-6.5 (0.6)	13.1 (20.2)	N1	22.6	-6.9 (15.7)	12.3 (34.9)	-5.5 (17.1)
H5	-11.7	6.7 (-5.0)	-6.3 (-18.0)	-0.4 (-12.1)	N6	32.1	-4.3 (27.8)	8.4 (40.5)	-4.1 (28)
					N3	-0.1	-2.8 (-2.9)	5.5 (5.4)	-2.7 (-2.8)
					Exp[13] (N1, N6)	**31**	**27**	**39**	**27**
					Exp[13] (N3)	**< 5**	**< 5**	**< 5**	**< 5**

π-radical					σ-radical								
$A^{\bullet+}$ (C_s) 					σ(N) 								
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]						
		xx	yy	zz			xx	yy	zz				
H8	-6.0	3.8 (-2.2)	-3.1 (-9.1)	-0.7 (-6.7)	N1	11.8	12.8 (24.6)	-7.0 (4.8)	-5.8 (6.0)				
					N3	13.6	14.2 (27.8)	-7.8 (5.8)	-6.4 (7.2)				
A(N6-H)$^{\bullet}$ (C_s) 					σ(N6) 								
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]						
		xx	yy	zz			xx	xx	yy				
H6	-14.0	-11.2 (-25.2)	13.6 (-0.4)	-2.4 (-16.4)	N6	31.7	21.7 (53.4)	-11.7 (20.0)	-10.0 (21.7)				
$G^{\bullet+}$ (C_s) 													
Atom	A_{iso}	A_{aniso}			Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]	
		xx	yy	zz			xx	yy	zz			xx	yy	zz
H8	-8.9	5.1 (-3.8)	-4.5 (-13.4)	-0.6 (-9.5)	N7	25.8	8.3 (34.1)	-4.7 (21.1)	-3.6 (22.2)	O6	-13.2	23.5 (10.3)	-43.8 (-57)	20.3 (7.1)
Exp[22]		**(-3.5)**	**(-10.5)**	**(-7.5)**										

π-radical					σ-radical									
G(N1-H)$^{\bullet}$ (C_s) 					σ(O6) 					σ(N) **PCM** 				
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]		
		xx	yy	zz			xx	yy	zz			xx	yy	zz
N2	0.9	-1.0 (-0.1)	-0.8 (0.1)	1.8 (2.7)	O6	-26.4	45.0 (18.6)	-87.2 (113.6)	42.2 (15.8)	N1	13.8	17.6 (31.4)	-9.4 (4.4)	-8.2 (5.6)
N3	5.8	-4.8 (1.0)	-4.8 (1.0)	9.6 (15.4)										
Exp[22](N2)		**0**	**0**	**8**										
(N3)		**0**	**0**	**12**										
G(N2-H)$^{\bullet}$ (C_s) 					σ(N2) 									
Atom	A_{iso}	A_{aniso} (A_{total})[a]			Atom	A_{iso}	A_{aniso} (A_{total})[a]							
		xx	yy	zz			xx	yy	zz					
N2	6.0	-5.7 (0.3)	-5.6 (0.4)	11.3 (17.3)	N2	35.7	24.0 (59.7)	-12.7 (23.0)	-11.3 (24.4)					
N3	6.3	-5.2 (1.1)	-5.3 (1.0)	10.5 (16.8)										
Exp[22] (N3)		**(0)**	**(0)**	**(8)**										
(N2)		**(0)**	**(0)**	**(12)**										

[a] $A_{total} = (A_{iso} + A_{aniso})$; A_{iso} = isotropic and A_{aniso} = anisotropic coupling.

[b] Methyl hydrogens couplings are the average of the three A_{iso} couplings (assumes rapid rotation as found by experiment). The calculated A_{aniso} couplings are very small and are not given.

[c] Experimental values in Ref. 20 are for thymidine.

[d] Experimental values for N1 deprotonated U and C.