Supporting information

One-Electron Oxidation of Neutral Sugar Radicals of 2'-Deoxyguanosine and 2'-deoxythymidine. A Density Functional Theory (DFT) Study

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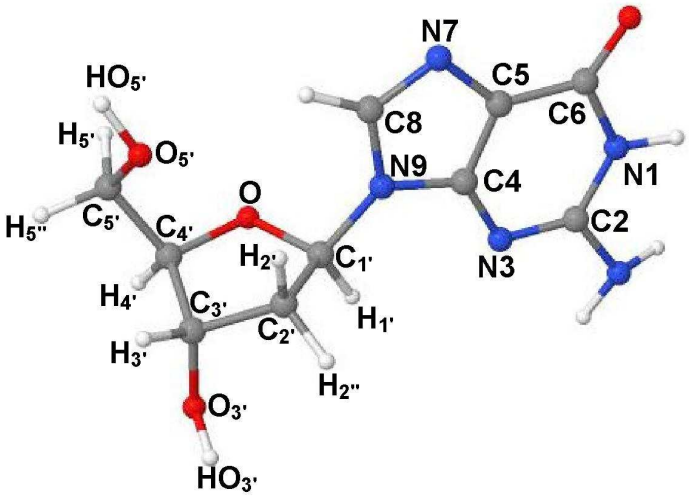
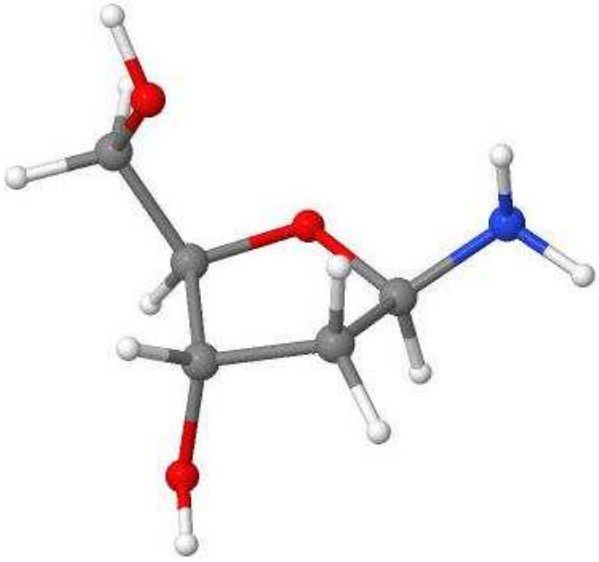
Table T2 B3LYP/6-31++G(D) calculated Mulliken Atomic Spin Densities and isotropic hyperfine couplings for the C1'˙, C2'˙, C3'˙, C4'˙ and C5'˙



2'-deoxyguanosine

Angle	Deg.	Angle	Deg.
N9-$C_{1'}$-O	109.0	$C_{3'}$-$C_{4'}$-O	106.6
O-$C_{1'}$-$C_{2'}$	105.6	O-$C_{4'}$-$C_{5'}$	110.0
$C_{2'}$-$C_{1'}$-N9	114.4	$C_{5'}$-$C_{4'}$-$C_{3'}$	114.7
Sum	329.0	**Sum**	331.3
$C_{1'}$-$C_{2'}$-$C_{3'}$	103.0	$C_{4'}$-$C_{5'}$-$O_{5'}$	109.3
$C_{3'}$-$C_{2'}$-$H_{2''}$	113.1	$O_{5'}$-$C_{5'}$-$H_{5''}$	110.6
$C_{1'}$-$C_{2'}$- $H_{2''}$	112.1	$C_{4'}$-$C_{5'}$-$H_{5''}$	108.7
Sum	328.2	**Sum**	328.6
$C_{2'}$-C3-$C_{4'}$	102.8		
$C_{4'}$-$C_{3'}$-$O_{3'}$	106.6		
$C_{2'}$-$C_{3'}$-$O_{3'}$	112.8		
Sum	322.2		



1'-NH2-furanose

Figure S1- The B3LYP/6-31++G(D) optimized structure of 2'-deoxyguanosine with atom numbering. In the adjacent table the sum of the three angles centering the $C_{1'}$, $C_{2'}$, $C_{3'}$, $C_{4'}$ and $C_{5'}$ atoms in 2'-deoxyguanosine are given in degrees, see discussion in text. Optimized structure of the 1'-NH2-furanose (sugar moiety) (guanine base replaced by NH2 group) used for the calculations, see text.

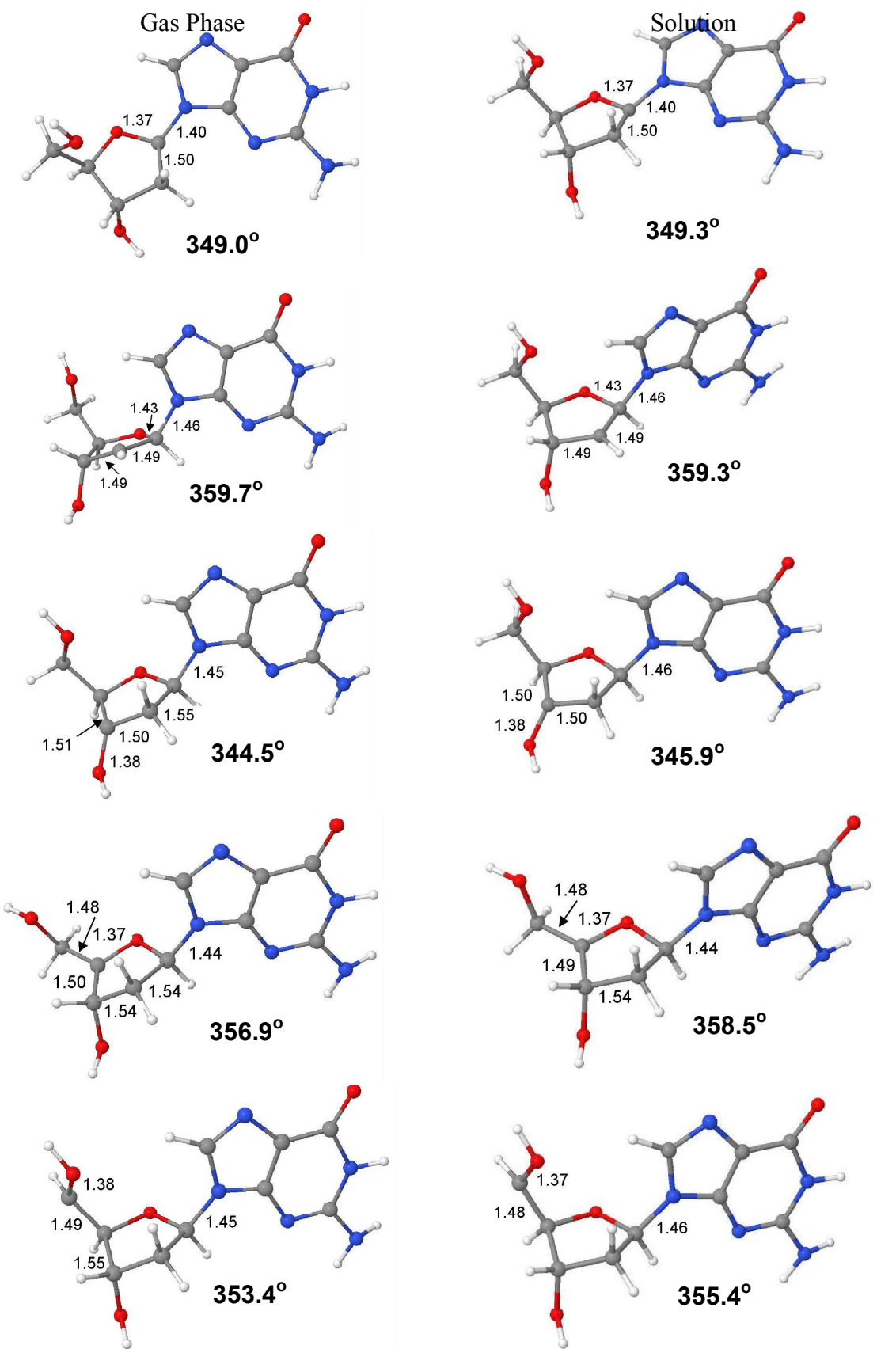


Figure S2- B3LYP/6-31++G(D) optimized structures of C1'•, C2'•, C3'•, C4'• and C5'• radicals in gas phase and in solution. Distances are given in Å. Values in bold are the sum of angles centering the carbon atoms.

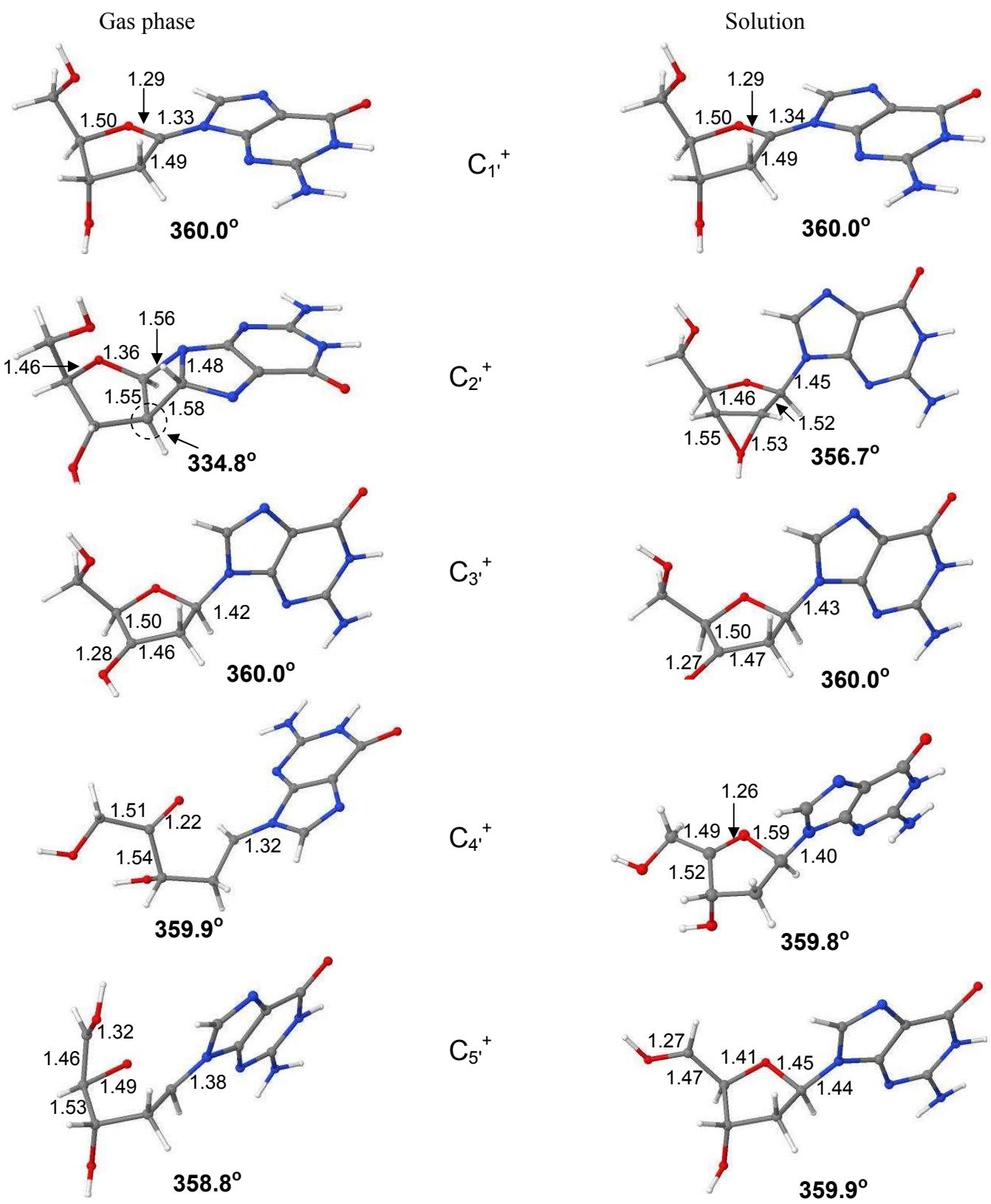


Figure S3- B3LYP/6-31++G(D) optimized structures of sugar radicals in their cation states. Structures were fully optimized in gas phase and in aqueous phase using PCM. Values in bold are the sum of angles centering the carbon atoms.

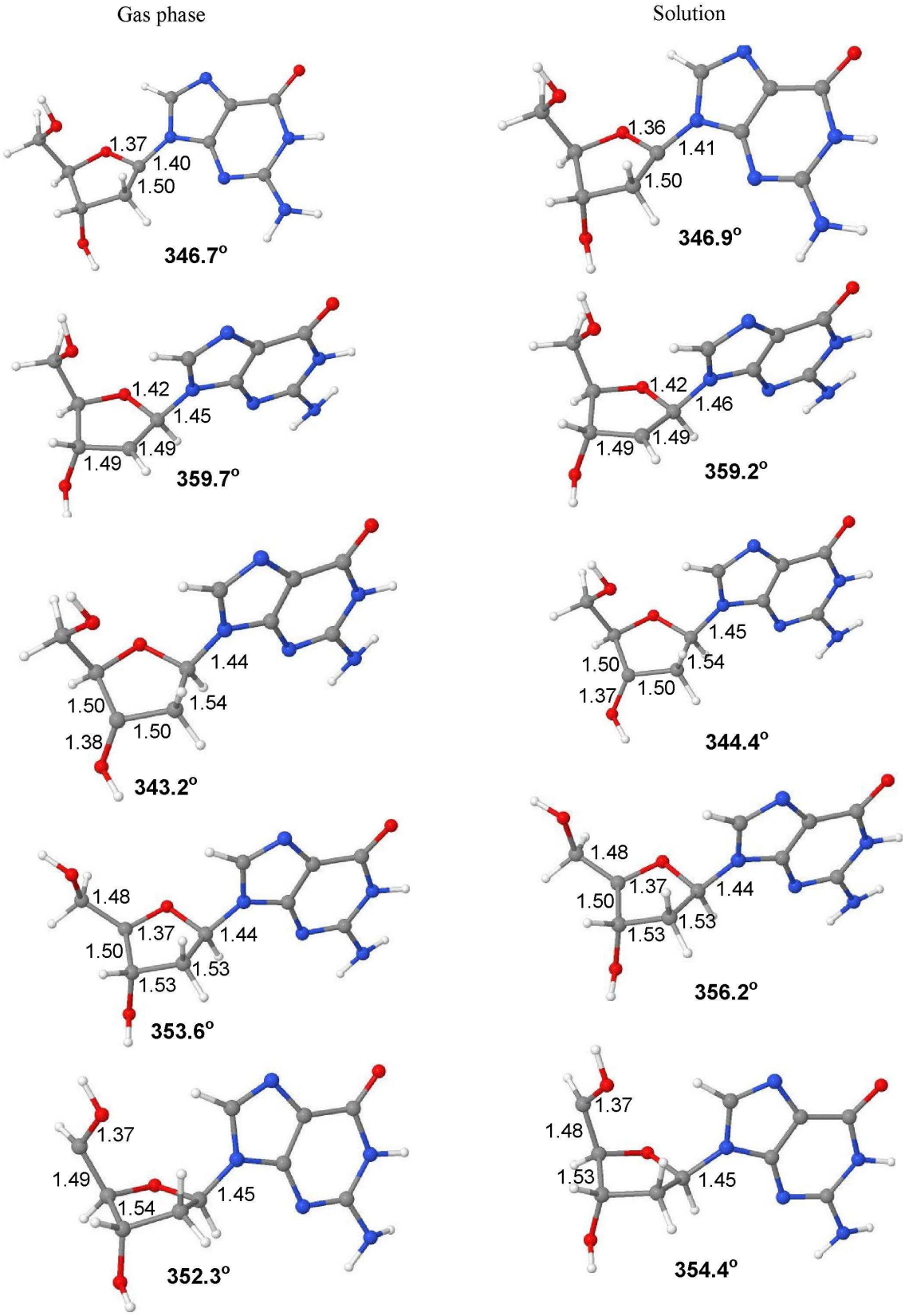


Figure S4- ωB97x/6-31++G(D) optimized structures of C1'•, C2'•, C3'•, C4'• and C5'• radicals in gas phase and in solution. Distances are given in Å. Values in bold are the sum of angles centering the carbon atoms.

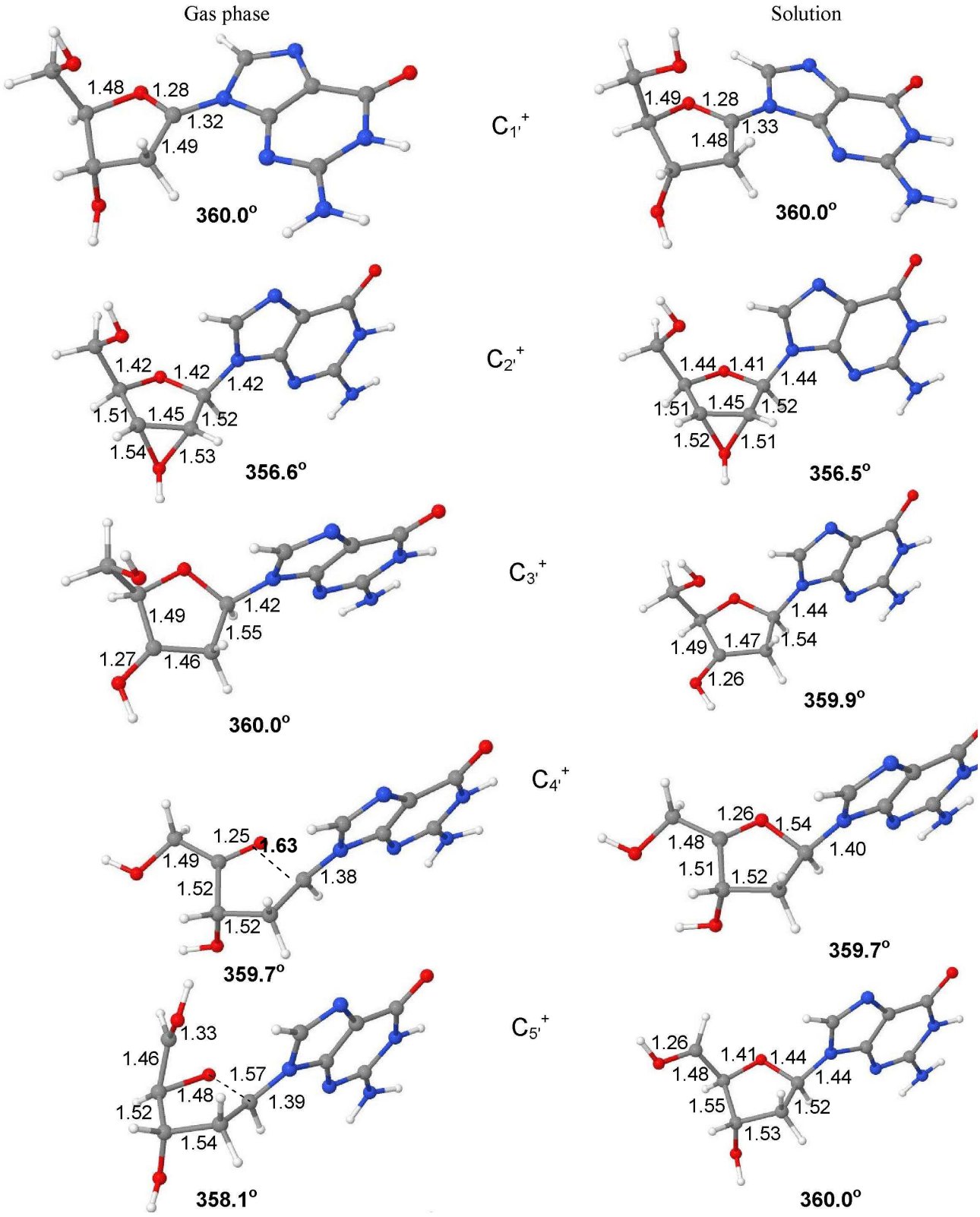


Figure S5- ωB97x/6-31++G(D) optimized structures of sugar radicals in their cation states ($C_{1'}^{+}$, $C_{2'}^{+}$, $C_{3'}^{+}$, $C_{4'}^{+}$, $C_{5'}^{+}$). Structures were fully optimized in gas phase and in aqueous phase using PCM. Values in bold are the sum of angles centering the carbon atoms.

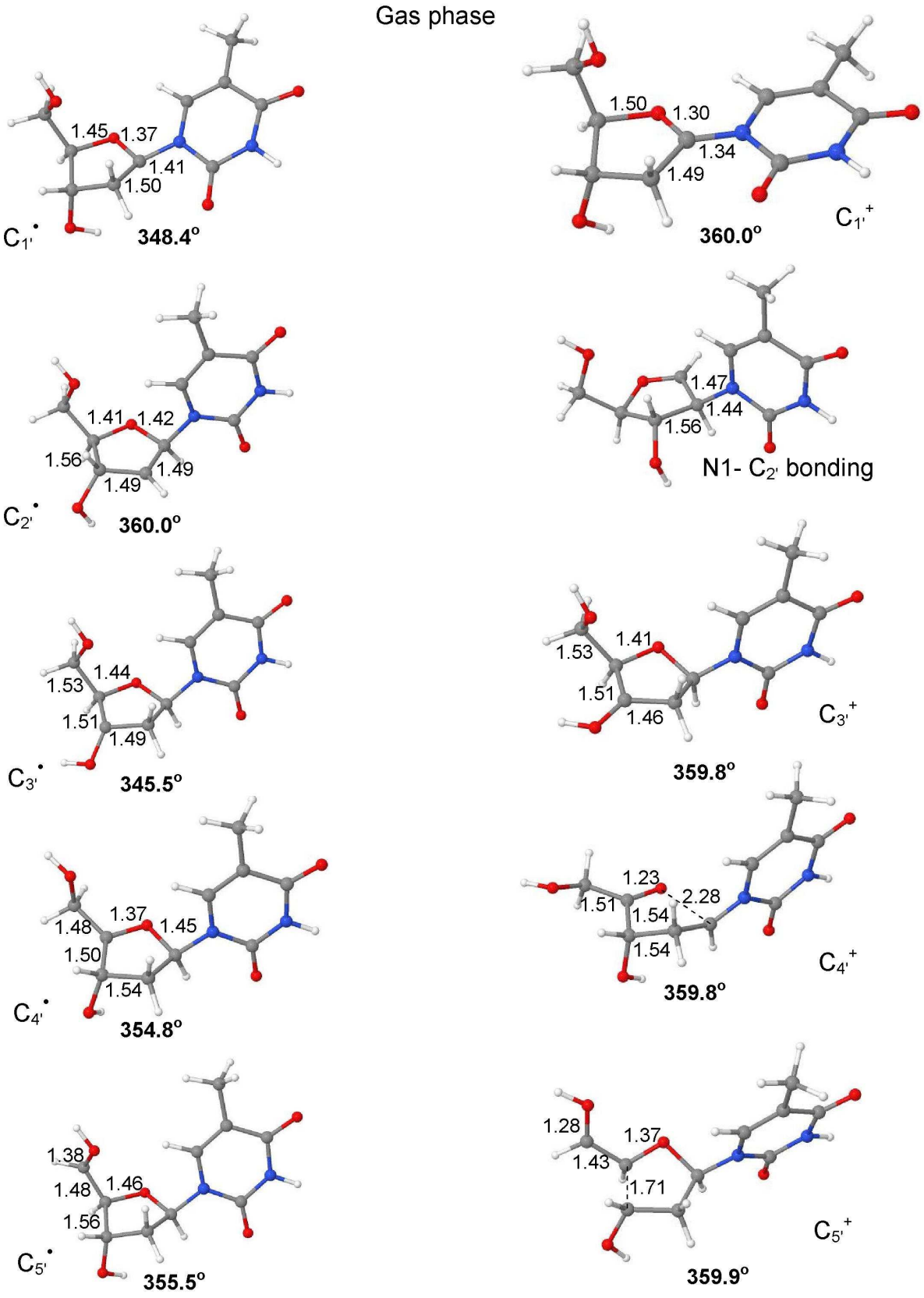


Figure S6- B3LYP/6-31++G(D) optimized structures of C1'•, C2'•, C3'•, C4'• and C5'• radicals of 2'-deoxythymidine and their cations in gas phase. Distances are given in Å. Values in bold are the sum of angles around the respective Cn' site.

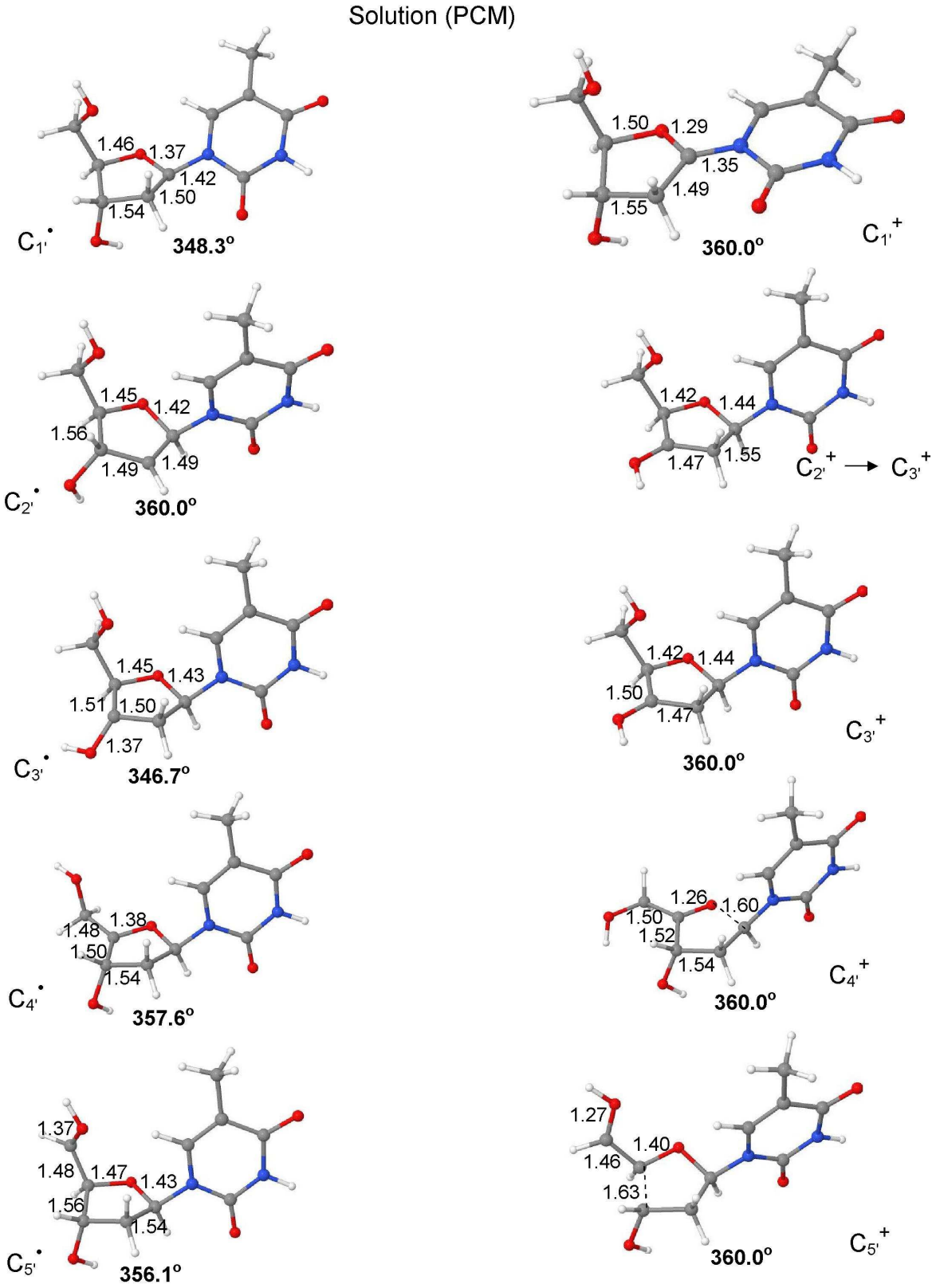
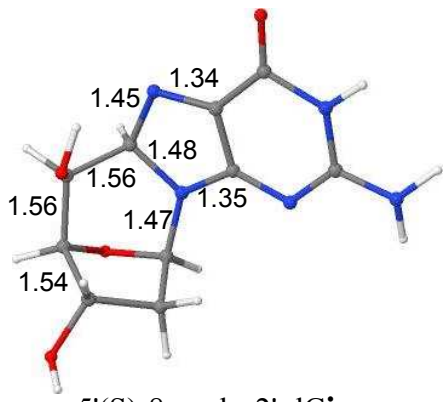
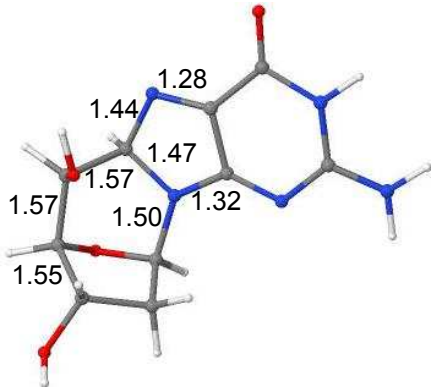


Figure S7- B3LYP/6-31++G(D) optimized structures of C1'•, C2'•, C3'•, C4'• and C5'• radicals of 2'-deoxythymidine and their cations in solution. Distances are given in Å. Values in bold are the sum of angles centering the carbon atoms.

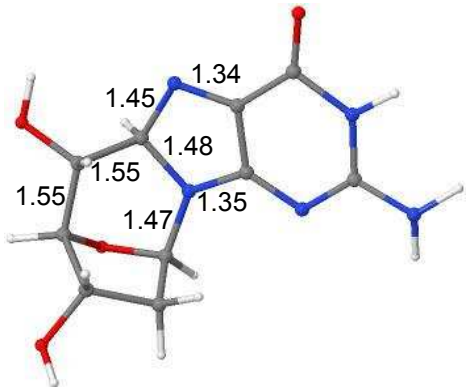
(Radical) (Cation)



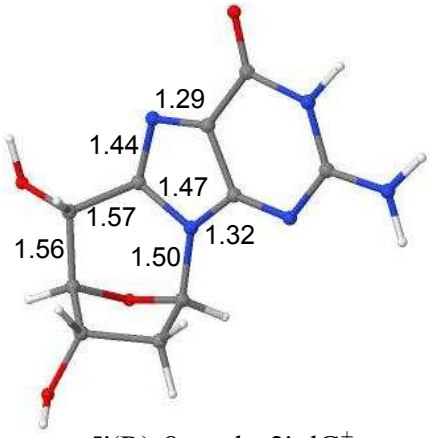
5'(S)-8-cyclo-2'-dG$^{\bullet}$



5'(S)-8-cyclo-2'-dG^{+}



5'(R)-8-cyclo-2'-dG$^{\bullet}$



5'(R)-8-cyclo-2'-dG^{+}

Figure S8- B3LYP/6-31++G(D) optimized two diastereoisomeric forms of 5'-8-cyclo-2'-dG in their radical and cation states. Structures were fully optimized in the gas phase.

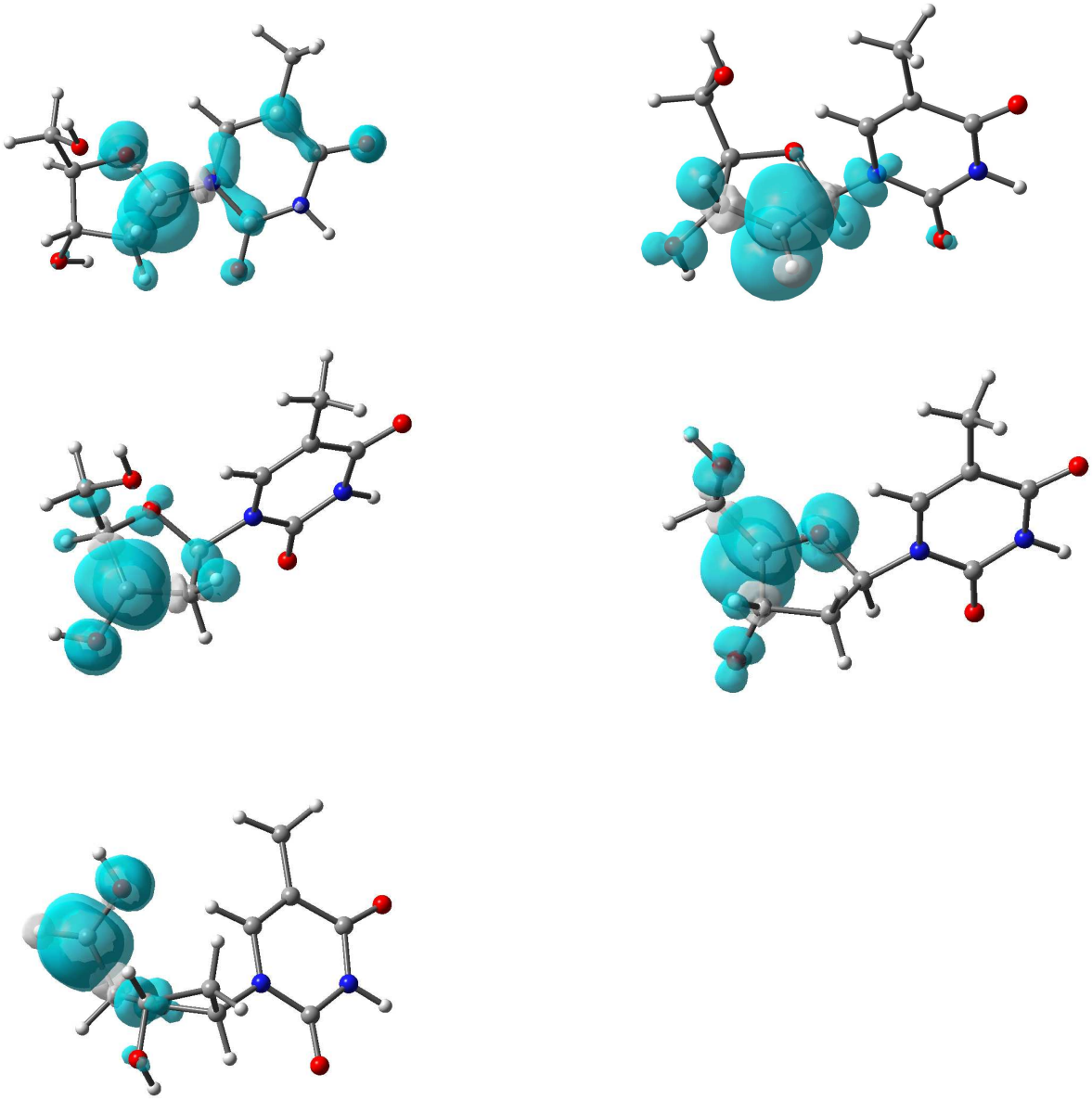


Figure S9- B3LYP/6-31++G(d) calculated Mulliken spin density distribution in sugar radicals (dT(C1'•) – dT(C5'•)). Spin densities were calculated with 0.002 electron/bohr^3.

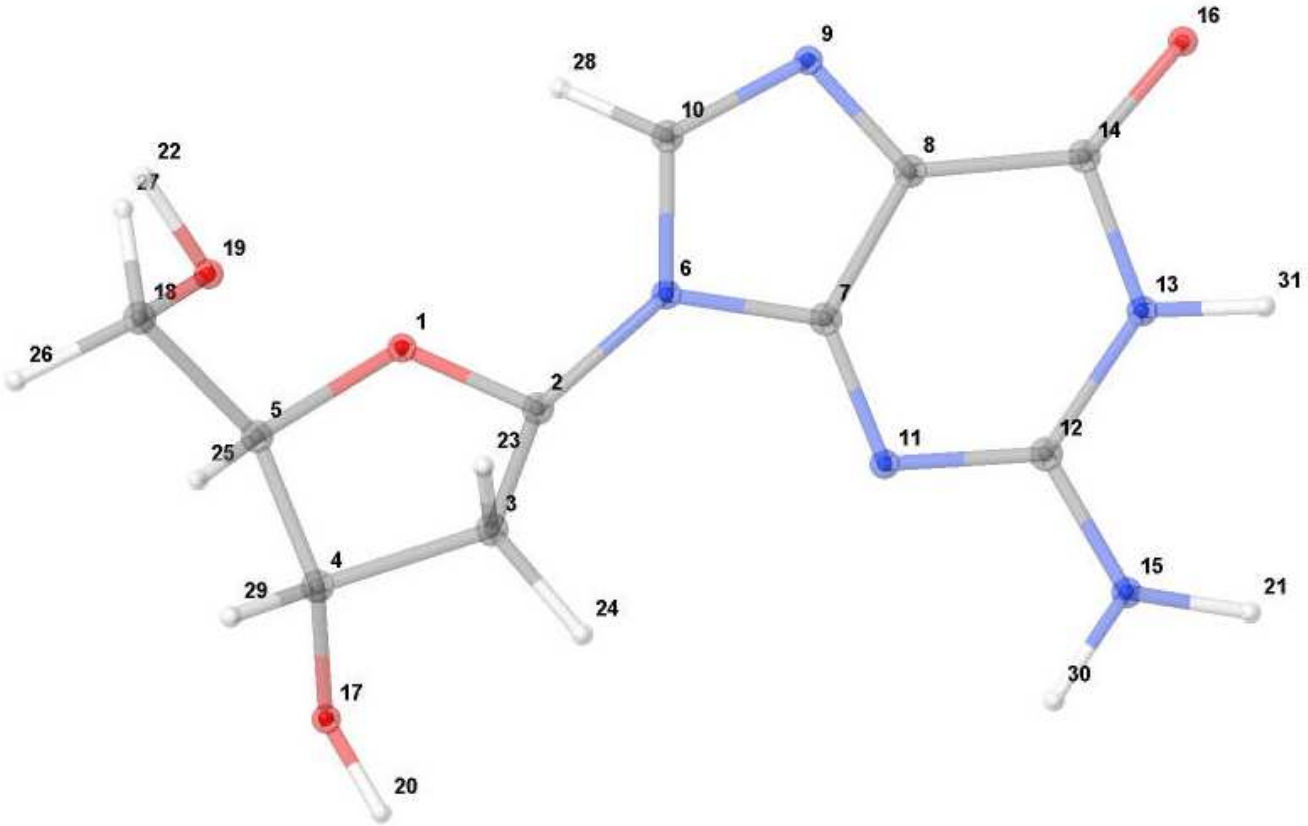
A small delocalization of spin on N9, C4, C8 and N7 atoms of guanine is seen from the spin density distribution maps (Figure 1) of $C_{1'}$ and $C_{2'}$ radicals Therefore, we tested the degree that the guanine base lowers the IP of the sugar radicals by considering a model of deoxyribose (sugar) by replacing the guanine base with NH_2 group connected at the $C_{1'}$ atom of the sugar ring, see Figure S1 in the SI. Using this model of the sugar moiety, we calculated the IPs of $C_{1'}$, $C_{2'}$, $C_{3'}$, $C_{4'}$ and $C_{5'}$ radicals in the gas phase and in solution. The calculated vertical IPs by the B3LYP/6-31++G(D) and ωB97x/6-31++G(D) methods are given in Table S1. The calculated vertical IPs of $C_{1'}^{\bullet}$, $C_{2'}^{\bullet}$, $C_{3'}^{\bullet}$, $C_{4'}^{\bullet}$ and $C_{5'}^{\bullet}$ using this sugar model are slightly lower both in the gas phase and in solution than those calculated for the corresponding sugar radical of 2'-deoxyguanosine and 2'-deoxythymidine. The gas phase IPs of $C_{2'}^{\bullet}$ and $C_{5'}^{\bullet}$ are in close agreement while the IPs of $C_{1'}^{\bullet}$, $C_{3'}^{\bullet}$ and $C_{4'}^{\bullet}$ differ by ca. 0.4 eV, see Tables 2 and S1. In both the models $C_{1'}^{\bullet}$ has the lowest IP while $C_{2'}^{\bullet}$ has the highest IP.

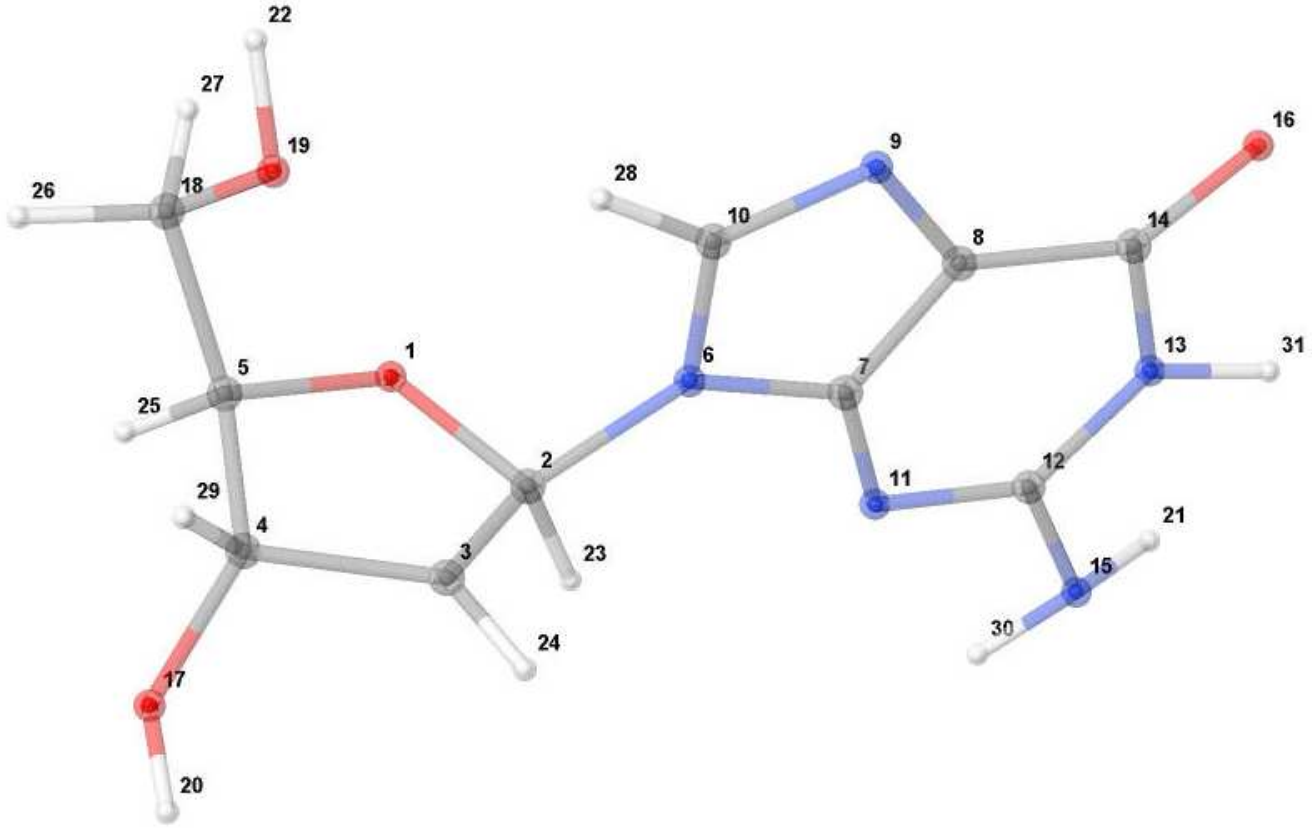
Table T1- B3LYP/6-31++G(D) and ωB97x/6-31++G(D) calculated vertical ionization potentials (IPs) in eV of neutral sugar radicals in gas phase and in aqueous solution using the 1'-NH2-furanose model system. See Figure S1 in the SI.

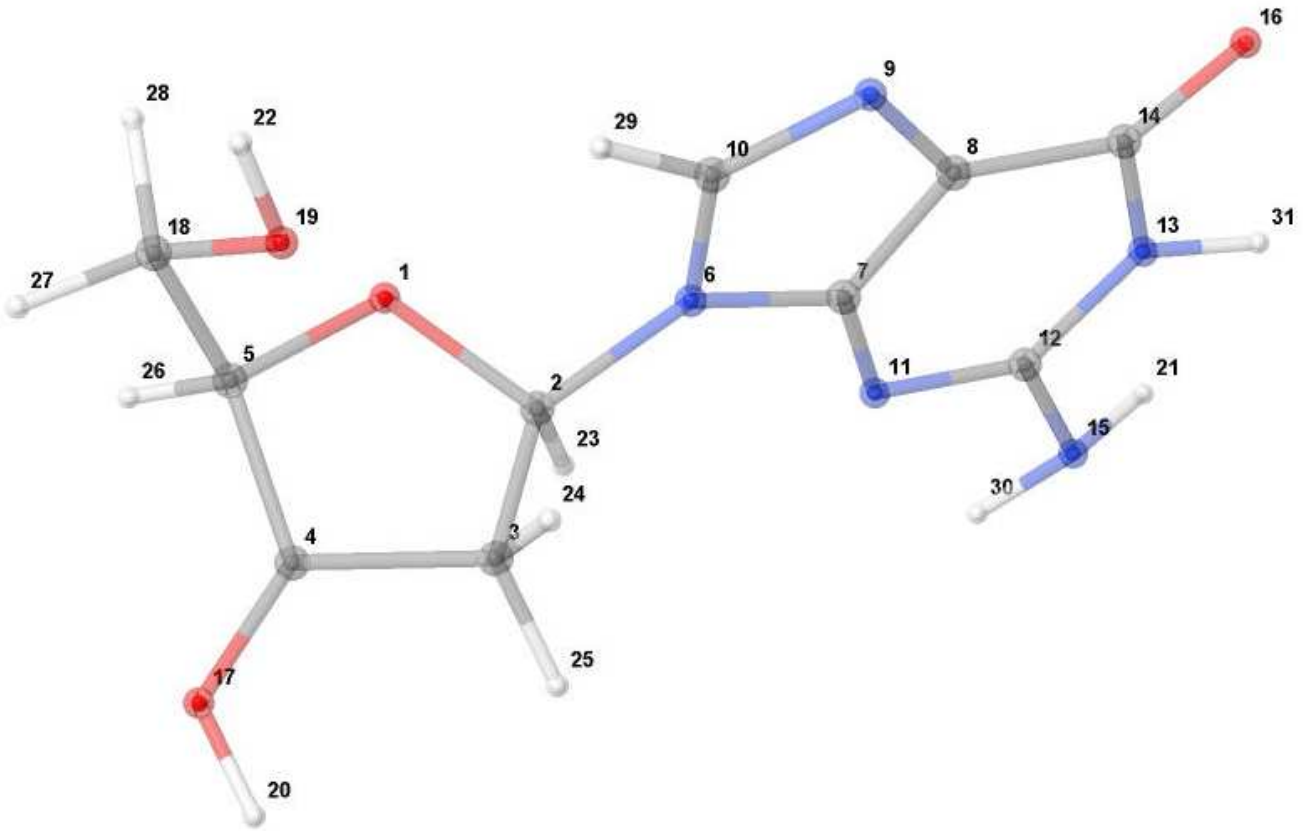
Sugar radical	B3LYP/6-31++G(d)		ωB97x/6-31++G(d)	
	Gas phase	Aqueous phase[a]	Gas phase	Aqueous phase[a]
	IP^{vert}	IP^{vert}	IP^{vert}	IP^{vert}
$C_{1'}^{\bullet}$	5.99	4.13	6.19	4.41
$C_{2'}^{\bullet}$	8.01	6.00	8.24	6.16
$C_{3'}^{\bullet}$	6.92	4.90	7.22	4.99
$C_{4'}^{\bullet}$	6.76	4.95	6.87	5.05
$C_{5'}^{\bullet}$	7.55	5.30	7.69	5.34

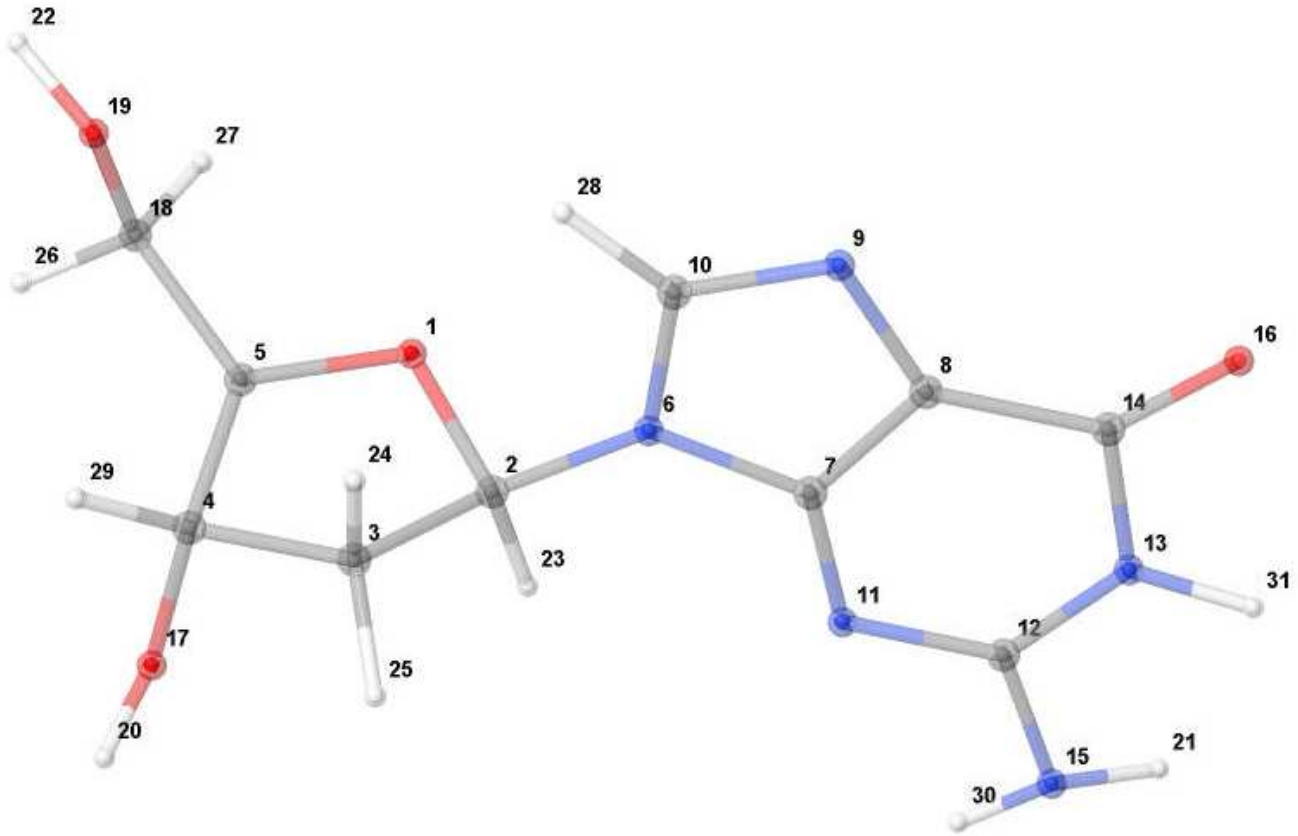
[a]Calculated using IEFPCM model with ε = 78.38.

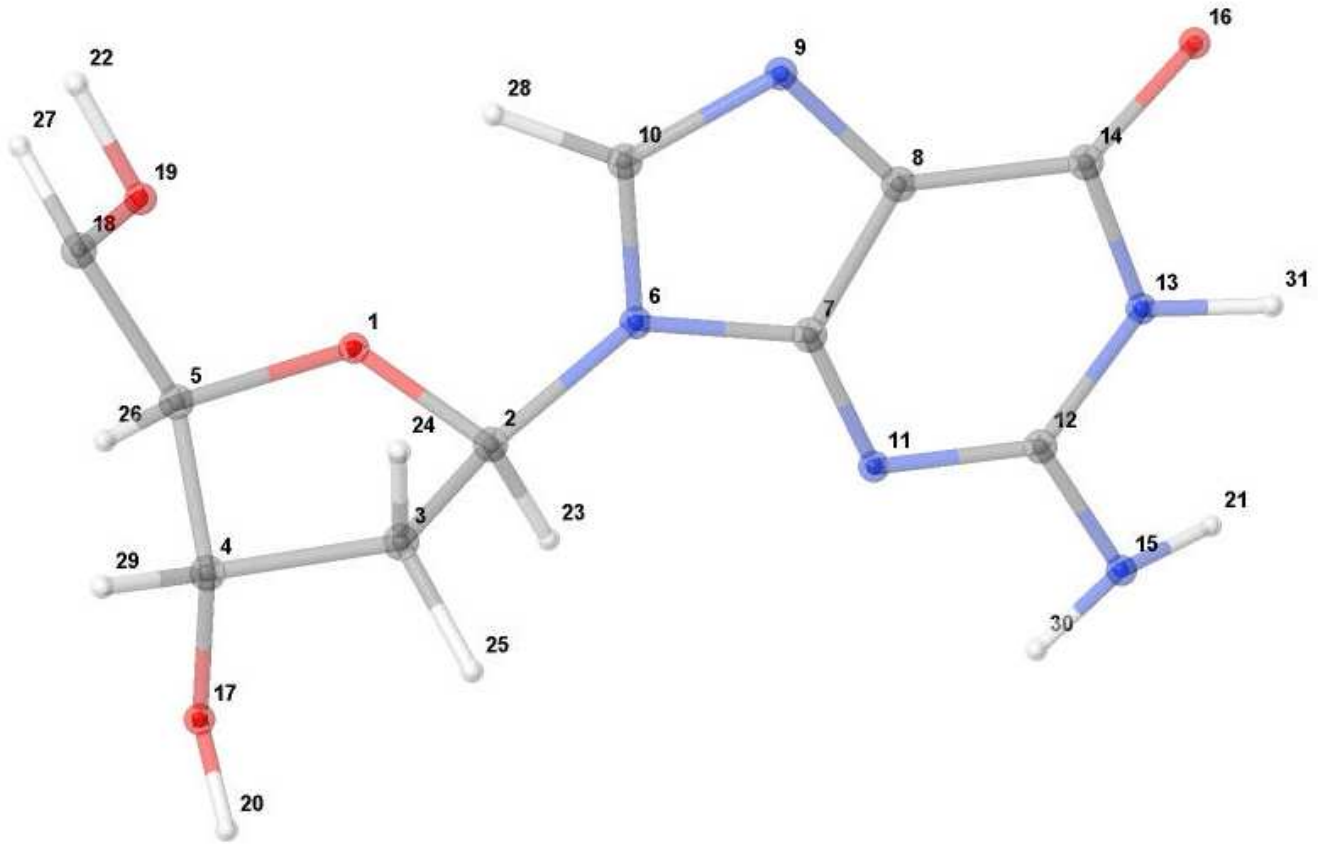
Table T2- B3LYP/6-31++G(D) calculated Mulliken Atomic Spin Densities and Isotropic Hyperfine Couplings for the C1'•, C2'•, C3'•, C4'• and C5'• sugar radicals of 2'deoxyguanosine (dG)

dG(C1'•)	atom	Spin (1)	Isotropic Gauss
	1 O(17)	.095790	-10.36925
	2 C(13)	1.004808	78.66118
	3 C(13)	-.184000	.18772
	4 C(13)	.011642	.18643
	5 C(13)	-.053298	-.52089
	6 N(14)	-.070142	.08451
	7 C(13)	-.016806	2.73380
	8 C(13)	.033301	-.26014
	9 N(14)	.037717	.75494
	10 C(13)	.037819	2.11742
	11 N(14)	.003980	-.02145
	12 C(13)	.011525	.38513
	13 N(14)	.006482	.14033
	14 C(13)	.011772	-.39325
	15 N(14)	.002957	.15483
	16 O(17)	-.001236	.04958
	17 O(17)	.002884	-.48232
	18 C(13)	.007748	1.57890
	19 O(17)	-.000779	-.20398
	20 H(1)	.003388	.16708
	21 H(1)	.000246	.25424
	22 H(1)	-.001532	.00318
	23 H(1)	.067436	29.61253
	24 H(1)	-.001088	13.88135
	25 H(1)	-.003632	1.03004
	26 H(1)	.006958	.71034
	27 H(1)	-.003137	.22174
	28 H(1)	-.002618	-1.54099
	29 H(1)	-.008330	-.56903
	30 H(1)	.000189	-.02556
	31 H(1)	-.000046	-.20444

dG(C2'•)	atom	Spin (1)	Isotropic Gauss
	1 O(17)	.003557	-1.95062
	2 C(13)	-.039321	-8.46080
	3 C(13)	1.034888	43.43506
	4 C(13)	-.047842	-6.95101
	5 C(13)	-.035507	.31864
	6 N(14)	.010460	5.53764
	7 C(13)	.031608	-.02738
	8 C(13)	-.000228	1.09475
	9 N(14)	.000141	.09414
	10 C(13)	-.024543	.10857
	11 N(14)	.006452	.48546
	12 C(13)	.001660	.26972
	13 N(14)	-.000020	.05273
	14 C(13)	-.005611	.08964
	15 N(14)	-.000373	-.00864
	16 O(17)	.000961	-.04356
	17 O(17)	.046506	-9.22707
	18 C(13)	.013046	-.09621
	19 O(17)	.000087	-.81983
	20 H(1)	-.003452	-2.12156
	21 H(1)	-.000023	-.01034
	22 H(1)	.000737	.21185
	23 H(1)	.048640	33.27585
	24 H(1)	-.055442	-23.18284
	25 H(1)	-.000932	.24098
	26 H(1)	-.001016	.15335
	27 H(1)	.000121	.14086
	28 H(1)	-.006848	.61945
	29 H(1)	.022276	13.14030
	30 H(1)	-.000012	.00108
	31 H(1)	.000031	.04250

dG(C3'•)	atom	Spin (1)	Isotropic Gauss
	1 O(17)	.017746	-2.46813
	2 C(13)	.014308	12.76649
	3 C(13)	-.108405	1.24025
	4 C(13)	1.058274	82.78717
	5 C(13)	-.133865	.30793
	6 N(14)	.001821	.05727
	7 C(13)	.004610	.25614
	8 C(13)	.004436	-.02308
	9 N(14)	.002999	.05855
	10 C(13)	.000033	-.00087
	11 N(14)	-.000078	-.00542
	12 C(13)	.001426	.01089
	13 N(14)	.000267	.00185
	14 C(13)	-.000080	.00333
	15 N(14)	.000194	.00528
	16 O(17)	-.000084	.00149
	17 O(17)	.094805	-7.77108
	18 C(13)	-.006549	8.99870
	19 O(17)	-.001580	-.35128
	20 H(1)	-.002608	-2.23934
	21 H(1)	.000010	.00567
	22 H(1)	-.000710	-.09814
	23 H(1)	-.000688	-.83642
	24 H(1)	.030804	23.01797
	25 H(1)	.006888	2.59371
	26 H(1)	.018392	7.29619
	27 H(1)	-.002698	-.15367
	28 H(1)	.000711	1.08164
	29 H(1)	-.000401	.06472
	30 H(1)	.000027	-.00093
	31 H(1)	-.000003	-.00540

dG(C4'•)	atom	Spin (1)	Isotropic Gauss
	1 O(17)	.116901	-9.83518
	2 C(13)	.030216	-1.23324
	3 C(13)	-.011565	.46338
	4 C(13)	-.023744	-8.20723
	5 C(13)	.839962	48.45674
	6 N(14)	.003231	.18773
	7 C(13)	.011952	.06931
	8 C(13)	.000664	.02797
	9 N(14)	-.000644	-.00455
	10 C(13)	.004782	.02060
	11 N(14)	-.000443	.04499
	12 C(13)	-.000374	.03787
	13 N(14)	.000047	.00509
	14 C(13)	-.000472	.00865
	15 N(14)	-.000022	-.00120
	16 O(17)	.000110	-.00500
	17 O(17)	.002423	-23.10410
	18 C(13)	-.064173	-.03757
	19 O(17)	.015352	-24.90018
	20 H(1)	.016433	4.53084
	21 H(1)	-.000008	-.00170
	22 H(1)	.022498	5.89289
	23 H(1)	.000583	3.83510
	24 H(1)	.000621	.36624
	25 H(1)	.001256	.91097
	26 H(1)	.008118	7.11666
	27 H(1)	.004040	2.14668
	28 H(1)	-.000109	.03522
	29 H(1)	.022291	9.41355
	30 H(1)	.000059	.00055
	31 H(1)	.000017	.00217

dG(C5'•)	atom	Spin (1)	Isotropic Gauss
	1 O(17)	.028166	-17.72113
	2 C(13)	.009646	.50800
	3 C(13)	.013820	-.11022
	4 C(13)	-.017880	4.74279
	5 C(13)	-.035726	1.55080
	6 N(14)	.003641	.07573
	7 C(13)	-.006912	.07515
	8 C(13)	.012552	-.01276
	9 N(14)	.000204	.03398
	10 C(13)	-.008817	.09186
	11 N(14)	.000124	.00442
	12 C(13)	-.000067	-.00270
	13 N(14)	.000055	.00095
	14 C(13)	.001515	-.00491
	15 N(14)	.000002	.00003
	16 O(17)	-.000007	.00034
	17 O(17)	-.000019	.02298
	18 C(13)	.953522	58.32471
	19 O(17)	.096312	-8.29907
	20 H(1)	.000413	.27229
	21 H(1)	.000000	-.00020
	22 H(1)	-.005553	-3.53749
	23 H(1)	.002073	1.52325
	24 H(1)	-.000177	-.01212
	25 H(1)	.001286	.52654
	26 H(1)	.003327	.50050
	27 H(1)	-.042098	-12.97841
	28 H(1)	.000081	-.04932
	29 H(1)	-.009475	.50200
	30 H(1)	-.000009	-.00034
	31 H(1)	-.000001	.00168