Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

A Theoretical Study of 5,6,7,8-Tetrahydro-6-Hydroxymethylpterin: Insight into Intrinsic Photoreceptor Properties of 6-Substituted Tetrahydropterins

A.A. Buglak[a,*], T.A. Telegina[b]

[a] St. Petersburg State University, St. Peterburg, Russia

[b] Research Center of Biotechnology of the Russian Academy of Sciences, Moscow, Russia

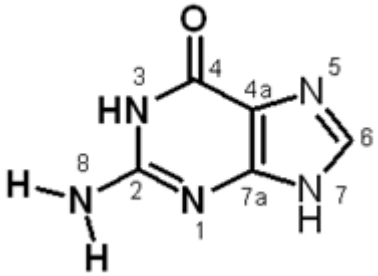
***Corresponding Author:**

E-mail: andreybuglak@gmail.com

Supporting Information

Table S1. Wavelengths (in nm) of the first six transitions in the electronic absorption spectrum of H_4Hmp according to different DFT functionals, oscillator strengths are shown in parentless. In all the calculations we used Pople basis set 6-311G++(2d,2p).

Experiment	**B3LYP**	**CAM-B3LYP**	**PBE**	**PBE0**
-	331 (0.009)	283 (0.062)	380 (0.006)	307 (0.018)
-	303 (0.025)	268 (0.124)	339 (0.020)	287 (0.065)
298	289 (0.129)	258 (0.030)	319 (0.098)	277 (0.099)
-	281 (0.009)	248 (0.004)	311 (0.004)	265 (0.005)
-	266 (0.006)	238 (0.042)	294 (0.006)	252 (0.013)
260	260 (0.040)	235 (0.119)	287 (0.011)	250 (0.107)



Scheme S1. Atom numbering for guanine.

Table S2. Main vertical electron transitions in the absorption spectrum of guanine. Calculation method: B3LYP/6-311++G(2d,2p)//B3LYP/6-31G(d,p) for the gas phase.

State	Dominate transition	Nature of excited state	$E_{calc.}$. eV (nm)	f_{OSC}
S_1	HOMO→ LUMO	Ry	4.54 (273)	0.013
S_2	HOMO→LUMO+1	ππ*	4.93 (252)	0.090
S_3	HOMO→LUMO+3	Ry	5.00 (248)	0.079
S_4	HOMO-1→LUMO+1	nπ*	5.28 (235)	0.022
S_5	HOMO→LUMO+2	ππ*	5.30 (234)	0.253
S_6	HOMO→LUMO+4	Ry	5.54 (224)	0.006

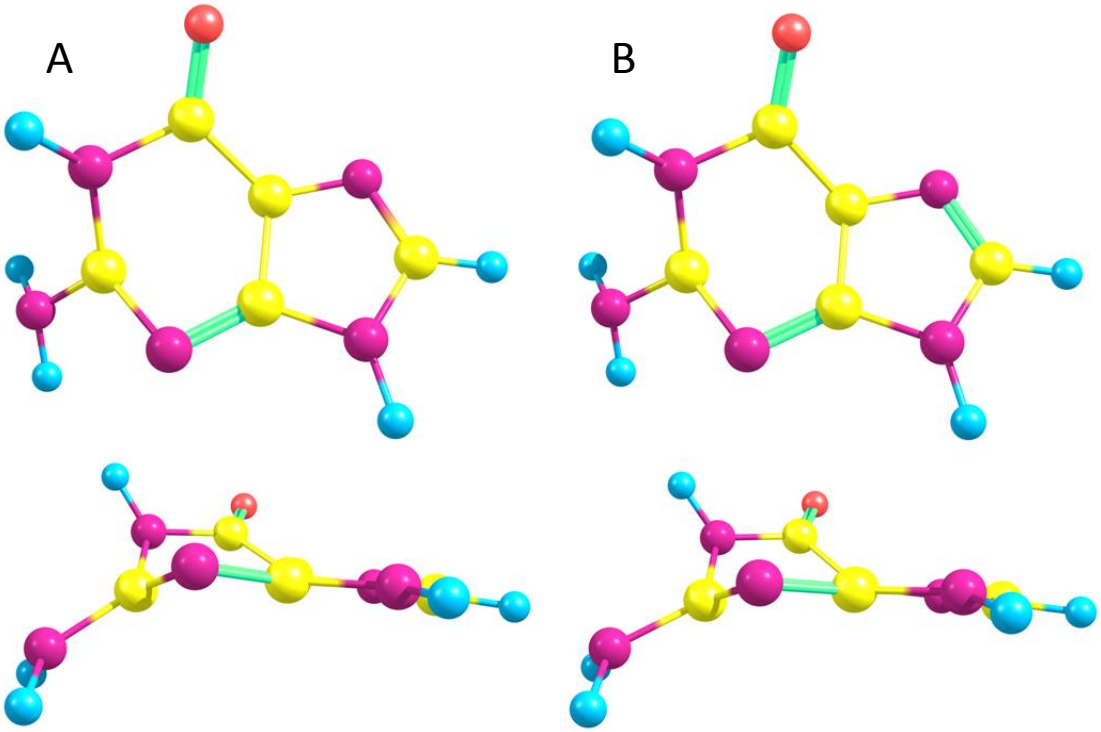


Figure S1. State ^{1}ππ* geometry of the biological tautomer of guanine optimized with B3LYP/6-311G++(d,p) method (A) and CASSCF method (B) (Yamazaki et al., 2008).

Table S3. Geometrical parameters of $^1\pi\pi^*$ state minimum of the biological guanine tautomer obtained with B3LYP/6-311G++(d,p) method are compared with the results of CASSCF method from literature.

Geometrical parameters	Min1		Min2	
	B3LYP/ 6-311G++(d,p)	CASSCF [a]	B3LYP/ 6-311G++(d,p)	CASSCF [a]
N^1 -C^2, Å	1.475	1.459	1.471	1.453
N^1 –C^{7a}, Å	1.280	1.282	1.284	1.286
C^2 –N^8, Å	1.365	1.371	1.371	1.380
C^{7a} –N^1 –C^2 –N^3,°	-68.1	-66.7	-71.1	-67.3
C^{7a} –N^1 –C^2 –N^8,°	138.6	148.5	139.1	149.7
N^1 –C^2 –N^3 –C^4, °	63.8	63.3	76.8	74.9
N^1 –C^2 –N^3 –H, °	-81.6	-83.6	-143.6	-150.1

[a] Yamazaki et al., 2008

We compared the geometries of $^1\pi\pi^*$ excited state and ground state geometry of H_4Hmp. The differences between $^1\pi\pi^*$ state (min(1)) and S_0 state geometries are following:

1. The bond lengths are different within the pyrimidine ring. For example, the N1-C2 bond in the ground state has a length of the double bond (1.302 Å), and in the $^1\pi\pi^*$ state it is a single bond (1.449 Å). In the pyrazine ring only the C4a-N5 bond changes significantly (the bond length is 1.415 Å and 1.368 Å, in S_0 and $^1\pi\pi^*$ state, respectively) (Table S3).
2. Out-of-plane deformation of the pyrimidine ring in the $^1\pi\pi^*$ state occurs. In particular, the geometry of the $^1\pi\pi^*$ state is characterized by a dihedral angle D(N1-C2-N3-C4) = -55.3°, while in the ground state this angle is equal -0.1°.
3. The out-of-plane distortion of the amino group occurs: D(C8a-N1-C2-N9) is equal -86.3 in the excited state while in the ground state it is equal 176.5°.
4. Pyramidization of the C2 atom. It can be seen from Table S3 that the values of all the valence angles formed by the C2 atom in the $^1\pi\pi^*$ state decrease compared to S_0 state: the values of the three valence angles N9-C2-N1, N9-C2-N3, N1-C2-N3 tend to a value of 109.3°, which is a characteristic of a tetrahedron, and not 120°, which is characteristic for a plane triangle.

Table S4. Comparison of structural parameters of states S_0, $^1\pi\pi^*$ and ^{1}Ry minima optimized with B3LYP/6-311G++(d,p) method.

Geometrical parameters	**S_0**	**$^1\pi\pi^*$**	**^{1}Ry**
Bond length, Å:			
Pyrimidine ring			
N^1–C^2	1.302	1.449	1.343
N^1–C^{8a}	1.370	1.296	1.329
C^2–N^3	1.363	1.421	1.373
C^{4a} –C^{8a}	1.383	1.461	1.422
N^3–H	1.012	1.010	1.031
C^2 –N^9	1.382	1.392	1.317
N^9–H_a	1.010	1.009	1.018
N^9–H_b	1.010	1.012	1.042
C^{4a}–N^5	1.415	1.368	1.352
Bond angle, °:			
N^9–C^2–N^1	120.0	117.7	119.5
N^9–C^2–N^3	117.1	116.1	117.6
N^1–C^2–N^3	122.9	116.3	122.9
C^2–N^3–C^4	123.4	114.6	123.5
Digedral angle, °:			
N^1–C^2–N^3–C^4	-0.1	-55.3	2.5
N^1–C^2–N^3–H	173.3	109.0	-178.4
N^3–C^2–N^1–C^{8a}	-0.8	58.2	-1.3
N^9–C^2 –N^1–C^{8a}	176.5	-86.3	179.3
N^5–C^6–$C^{1'}$–O’	57.0	64.5	68.1
C^6–C^1 –O’–H’	-45.3	-60.4	-74.5

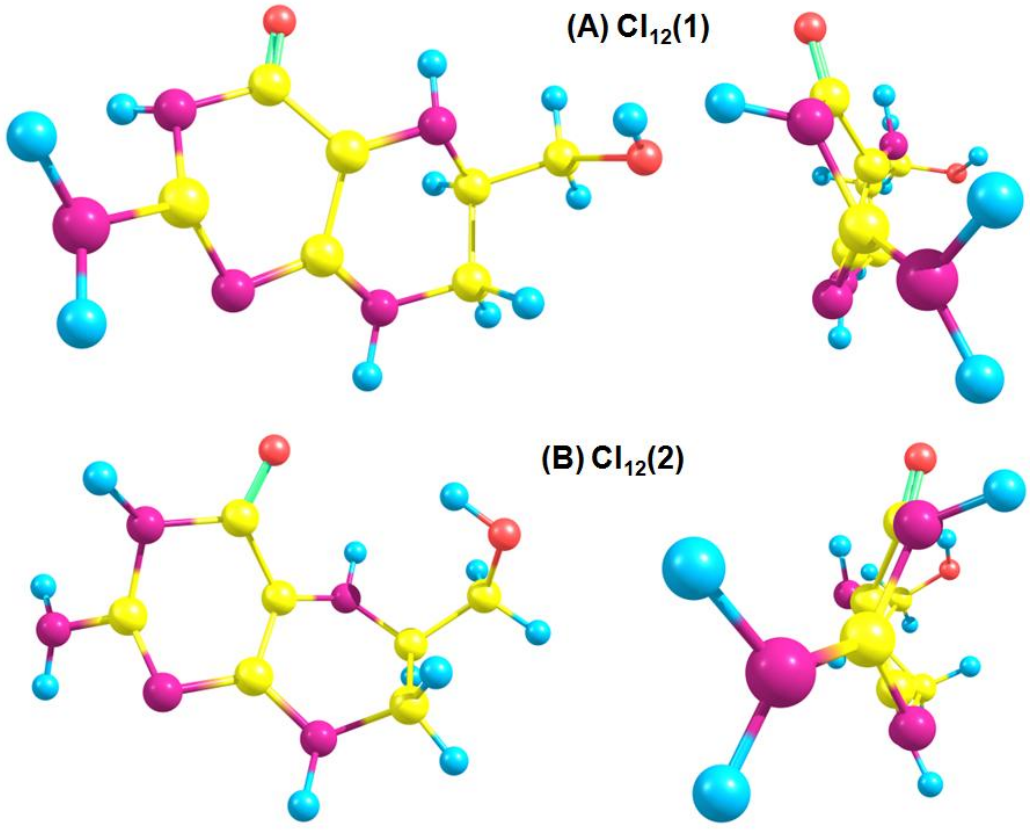


Figure S2. Optimized geometry of conical intersections: (A) CI_{12}(1) and (B) CI_{12}(2).

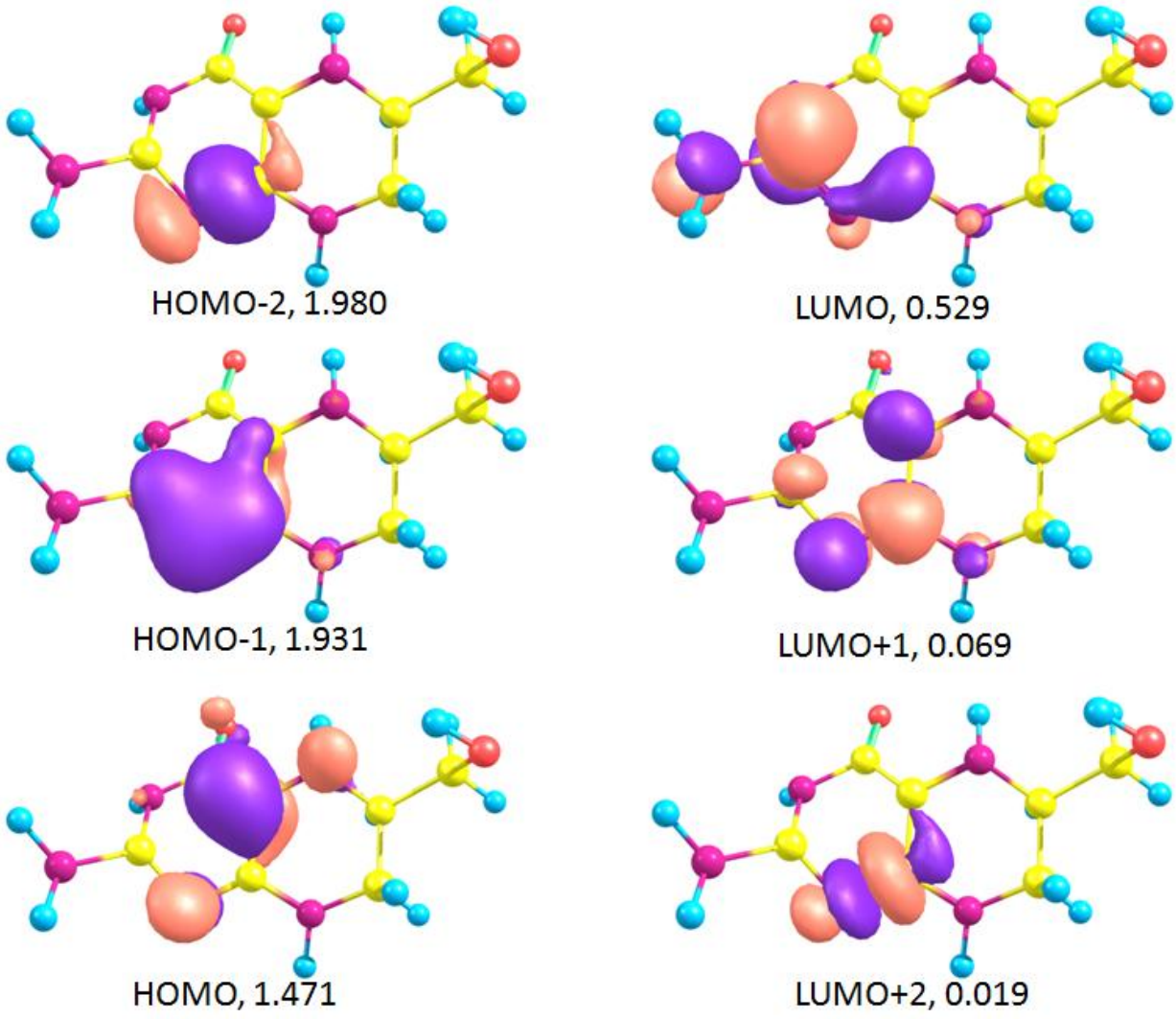


Figure S3. Molecular orbitals (and their occupation numbers) used in the active space during conical intersection optimization.

Table S5. Vertical ionization potentials (in eV) calculated for guanine and H_4Hmp in the gas phase with different methods.

Guanine	**VIP**
B3LYP/6-31G(d,p)	7.57
B3LYP/6-311++G(2d,2p)	7.90
MP2/6-31G(d,p)	8.46
MP2/6-311++G(2d,2p)	8.93
CCSD/6-31G(d,p)	8.01
H4Hmp	
MP2/6-31G(d,p)	6.86
CCSD/6-31G(d,p)	7.34

Cartesian coordinates for the optimized geometry of the ground state of H_4Hmp calculated at B3LYP/6-311G++(d,p) level of theory; energy: -697.4225574 Hartree.

O	0.948319000	3.969475000	2.109379000
N	-1.247402000	1.722554000	-0.493179000
N	2.206027000	1.718260000	0.881802000
N	0.607982000	0.422346000	-1.022672000
N	-1.024329000	3.480588000	1.036895000
N	-3.054708000	3.122951000	-0.073901000
C	0.073882000	1.433858000	-0.271886000
C	0.866927000	2.106437000	0.639372000
C	-1.749262000	2.733487000	0.156556000
C	0.340633000	3.232922000	1.332817000
C	2.859557000	0.991934000	-0.211326000
C	1.919335000	-0.124896000	-0.695512000
C	4.182912000	0.425519000	0.316638000
H	-1.407607000	4.319340000	1.453140000
H	1.854735000	-0.899515000	0.076691000
H	-3.569618000	3.492684000	0.712578000
H	-3.573857000	2.449293000	-0.619203000
H	4.669496000	-0.180179000	-0.452717000
H	4.856591000	1.262149000	0.555822000
O	3.999956000	-0.411552000	1.448404000
H	3.385716000	0.053774000	2.033979000
H	2.741851000	2.510871000	1.225179000
H	-0.051297000	-0.144225000	-1.534265000
H	2.343182000	-0.577533000	-1.596107000
H	3.078517000	1.651387000	-1.066446000

Cartesian coordinates for the optimized geometry of the $^1\pi\pi^*$ excited singlet state of H_4Hmp calculated at TDDFT B3LYP/6-311G++(d,p) level of theory; energy: -697.3145991 Hartree.

O	0.015527000	-0.059890000	-0.080632000
N	4.115292000	-0.001887000	0.017684000
N	1.328883000	2.340249000	-0.049383000
N	4.061455000	2.273466000	-0.526920000
N	2.007652000	-1.181812000	0.330703000
N	3.456370000	-0.847515000	2.197150000
C	3.470317000	1.118637000	-0.077361000
C	2.023404000	1.172901000	0.115280000
C	3.315019000	-0.905222000	0.813960000
C	1.228661000	-0.065409000	0.114684000
C	1.949307000	3.519495000	-0.653952000
C	3.429902000	3.563575000	-0.265470000
C	1.190630000	4.780515000	-0.223456000
H	1.727781000	-2.070287000	-0.060032000
H	3.518997000	3.856071000	0.787577000
H	2.633191000	-0.826625000	2.786179000
H	4.265642000	-0.357577000	2.547411000
H	1.625796000	5.650972000	-0.719029000
H	0.146045000	4.699617000	-0.555732000

O	1.264393000	5.037609000	1.169768000
H	0.877890000	4.287610000	1.637414000
H	0.343455000	2.173755000	-0.247485000
H	5.071077000	2.239291000	-0.555590000
H	3.926043000	4.326018000	-0.868440000
H	1.876573000	3.437285000	-1.749462000

Cartesian coordinates for the optimized geometry of ^{1}Ry singlet state of H_4Hmp calculated at TDDFT B3LYP/6-311G++(d,p) level of theory; energy: -697.3054974 Hartree.

O	0.975107000	3.894617000	2.107142000
N	-1.250525000	1.696542000	-0.525823000
N	2.189409000	1.869376000	0.675013000
N	0.601005000	0.416654000	-1.051747000
N	-1.044427000	3.434451000	1.094985000
N	-3.040809000	3.028156000	0.026442000
C	0.036356000	1.418164000	-0.343958000
C	0.871789000	2.143580000	0.549289000
C	-1.772748000	2.708634000	0.185587000
C	0.309360000	3.228871000	1.331157000
C	2.872358000	0.988488000	-0.271779000
C	1.906923000	-0.130918000	-0.686222000
C	4.162129000	0.435869000	0.350198000
H	-1.530531000	4.179331000	1.616308000
H	1.811021000	-0.848450000	0.134639000
H	-3.480329000	3.779193000	0.598939000
H	-3.614909000	2.477877000	-0.608645000
H	4.705166000	-0.125033000	-0.413549000
H	4.801109000	1.275081000	0.655331000
O	3.937498000	-0.464231000	1.420425000
H	3.660899000	0.021380000	2.205062000
H	2.714666000	2.547311000	1.220626000
H	-0.031197000	-0.135201000	-1.615845000
H	2.318927000	-0.652181000	-1.551331000
H	3.149291000	1.574370000	-1.160205000

Optimized geometry of the conical intersection CI_{12}(1) calculated at CASSCF(6,6)/6-31G(d)+ level of theory; energy: -693.4126917 Hartree.

O	2.381953277	2.665778667	4.002902973
N	0.239165864	5.935520608	5.063418233
N	0.975511063	4.086996274	1.998148796
N	0.689221242	6.733847884	2.901150591
N	1.145435840	3.730413196	5.608801177
N	-0.872374961	4.481279985	6.536298154
C	0.564262297	5.725627029	3.804379626
C	0.862806065	4.358014501	3.364708001
C	0.071213426	4.638426399	5.579500716
C	1.573011926	3.499800680	4.306117927
C	1.391408221	5.196542973	1.141284970
C	0.564727640	6.429818439	1.482848843
C	1.218392540	4.776417003	-0.314585906

H	1.850114059	3.797090250	6.322463083
H	-0.470486518	6.270294770	1.199800225
H	-1.099578990	3.542693119	6.785666289
H	-1.641998161	5.114666955	6.501696735
H	1.518508690	5.583107432	-0.971473124
H	1.870174133	3.928625847	-0.518194194
O	-0.105485430	4.465790971	-0.636101532
H	-0.438357824	3.845927067	0.002129343
H	1.551263652	3.277174625	1.864637057
H	0.296141164	7.599565242	3.203937759
H	0.941077374	7.277093243	0.923972523
H	2.442998891	5.436369361	1.305721642

Optimized geometry of the conical intersection $CI_{12}(2)$ calculated at CASSCF(6,6)/6-31G(d)+ level of theory; energy:-693.4066042 Hartree.

O	0.464950135	0.492710684	1.055084607
N	4.449996802	0.233383458	0.349924146
N	1.667629628	2.199714392	-0.899016249
N	4.303055152	2.513144008	-0.258430957
N	2.336255206	-0.832342079	0.966757512
N	3.997811967	-2.007682940	-0.195035426
C	3.757536134	1.286729586	-0.034762075
C	2.318566909	1.167811908	-0.244905890
C	3.522156449	-0.813551552	0.208780668
C	1.585674037	0.302243818	0.657706627
C	2.165856712	3.571097148	-0.846612858
C	3.437768207	3.656901696	0.002788018
C	1.080435729	4.503731330	-0.308013862
H	2.359860665	-1.115687015	1.931565050
H	3.177301830	3.718361372	1.054147981
H	3.326766173	-2.708211785	-0.425866319
H	4.825623737	-1.992764525	-0.750851820
H	1.438369778	5.526298664	-0.318818027
H	0.214131033	4.456833437	-0.965766435
O	0.716137880	4.228504171	1.013557237
H	0.385405703	3.341246268	1.098919560
H	0.676706818	2.094767209	-0.930275753
H	5.254431714	2.597146764	0.032051530
H	3.977018424	4.556796135	-0.262486827
H	2.408022185	3.892871850	-1.856688436