

An ab initio study of metalated CMP,UMP& dTMP at HF level: Bond energies and isotropic NMR shielding of atoms

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ABSTRACT:

The interaction of Magnesium hydrate at the phosphate oxygen atom of the pyrimidine nucleotides (CMP,UMP,dTMP) were studied at the Hartree-Fock level Theory. We used LANL2DZ basis set for Mg and 6-31g* basis set for atoms. The basis set superposition error (BSSE) begins to converge for used Method/basis set. The gauge-invariant atomic orbital (GIAO) method and the continuous-set-of-gauge-transformation (CSGT) procedure were employed to calculate isotropic atomic shielding of the nucleotides using density functional theory at the B3LYP/6-31g** . These calculations yield molecular geometries in good agreement with available experimental data.

Keywords: Ab initio Calculation, NMR shielding Tensor, Nucleotide 5'- Monophosphates, Magnesium complexes.

INTRODUCTION:

The interactions of nucleotides in biological systems, particularly ADP², ATP², require a divalent metal ion as a cofactor where by the phosphate moiety of the nucleotide chelates the metal ion. To understand these processes, it is important to know the detailed molecular structure and geometry of metal-nucleotide complexes^{1,2}.

Magnesium, the divalent metal ion usually found in relatively high concentrations in vivo, stabilizes both DNA and RNA against thermal denaturation and in many cases is required for these molecules to function properly^{3,4}.

A nucleotide consists of three main subunits, the nucleobase residue (purine or pyrimidine), the sugar part and the phosphate group(s). The structures of the three common pyrimidine-nucleoside 5'-monophosphates are shown in Fig 1^{7,8,9,10}.

Nucleotide ligands offer a variety of potential binding sites for metal ions. In addition, these ligand molecules can adopt various conformations and thus exhibit complex steric properties. The whole area of metal ion-nucleotide interactions is therefore of interest also from the point of general coordination chemistry. Main-group metal ions apparently bind only to the phosphates groups of nucleotides. whereas transition metal ions bind to the organic base as well^{5,6}, forming achelate complexes. The structurally characterized metal complexes of mononucleotides involve phosphate monoesters that carry two negative charges per phosphate group, in the normal protonation state consequently the role of the phosphate groups either through direct metal binding or through electrostatic interaction with the metal. In solution, structures, of metal-nucleotide complexes have been studied mainly by NMR methods^{1,2}.

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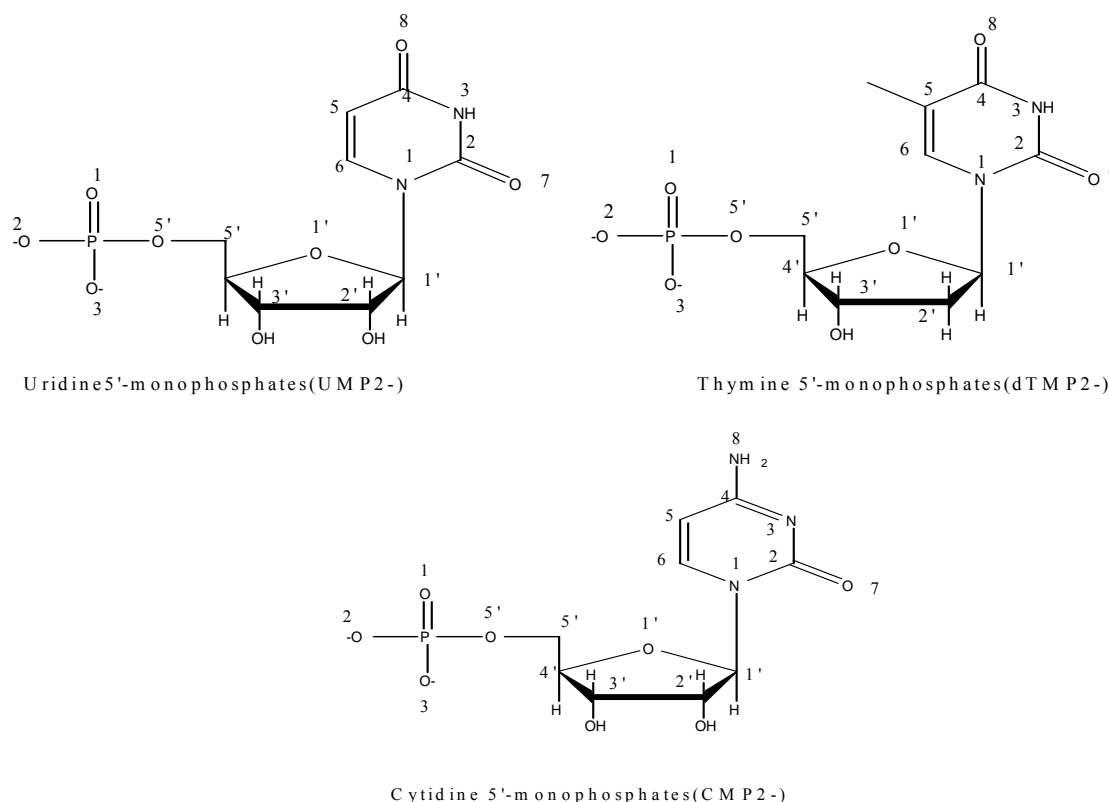


Fig1.Chemical structures of the pyrimidine-nucleoside 5'-monophosphates (UMP, dTMP, CMP).

Nuclear magnetic resonance techniques applied to poly- or mononucleotides can be directly used to detect the effects caused by the binding of a metal ion on these molecules in aqueous solutions. The magnetic resonance of protons has been most widely used. Depending on the nature of the metal in the complex, it will be convenient to measure one or another NMR parameter. Selective line broadenings observed in the ligand's spectrum may provide useful indications about the proximity of a paramagnetic metal ion to the nuclear species whose characteristic line happens to be broadened. Also, measurements of chemical shift variations, induced on the NMR signals of the ligand by modifications of the chemical environment, represent a handy method for determining the proximity of a metal ion to a particular chemical group of the ligand¹⁴. Moreover, the main NMR spectroscopic parameters are dependent on the second-order molecular property tensors¹⁵. The NMR shielding tensor σ can be all written as second derivatives of the energy $\sigma = (\partial^2 E / \partial B \partial m)_{B=0, m=0}$. Where E is the energy of the molecule, B external magnetic field, E electric intensity, and n, m nuclear magnetic moments. Scalar parameter and σ observable for an isotropic medium are defined as a 1/3 of the traces of the tensors J and σ , respectively.¹⁶

All of the optimized structure were carried out at the HF/6-31g* level. In this report, we describe in detail the structures of Magnesium hydrate complexes of pyrimidine nucleotide 5'-monophosphate using ab initio quantum-chemical calculation made at the Hartree-Fock (HF) theoretical level with 6-31g* basis set predicted

polarization effects of the Magnesium hydrate on the phosphate coordination. LANL2DZ for Mg and pyrimidine nucleotide 5'-monophosphates have been carried out: hydrogen bonding will be discussed in term of observable properties such as geometry and interaction energy. The structures was supported by comparing the measured ¹H-NMR spectra to the results of ab initio gauge-invariant atomic orbital (GIAO)¹¹ and continuous-set-of-gauge-transformation (CSGT)¹² computations of chemical shifts. Ab initio calculations were compared using the experimental geometry, based on the structures derived from x-ray diffraction data for nucleotide 5'-monophosphates. The basis set superposition error (BSSE) was computed, through the counterpoise method¹³ implemented in the Gaussian 98 code, for the most stable complexes.

METHOD

The structures of all the systems were optimized using the analytical gradient method in the framework of the Hartree-Fock and LANL2DZ basis set for Magnesium and 6-31g* basis set^{17,18} for other atoms.

Finally, All NMR analysis have been performed using 6-31g** basis set and the B3LYP level. The GIAO²² and CSGT²³ methods were used to calculate the isotropic NMR shielding at the B3LYP/6-31g** of theory. Electron correlation was included in the NMR calculations by use of density functional theory (DFT) because of its reported accuracy and its availability for GIAO and CSGT calculations in the Gaussian 98 suite of programs. For the basis sets used here in, density functional methods tend to

predict NMR values that are deshielded. The model chemistry used for calculations is based on the B3LYP method²⁴. This corresponds to the approximation method that makes use of Becke-Style parameters density functional theory^{19,25} with the Lee-Yang-Parr correlation functional^{20,21,26}.

The interaction energies of the counterparts estimated as the energy difference between the complex and the isolated components and were corrected for the basis set superposition error (BSSE). The Boys-Bernardi counterpoise method²⁷, applied at the Magnesium hydrate nucleotide complexes geometry, is used to account for BSSE. According to this method:

$$E_{\text{Corr.}} = E_{\text{Interaction}} + \Delta E_{\text{BSSE}}$$

Where $E_{\text{Corr.}}$ is corrected-interaction energies. And:

$$\Delta E_{\text{BSSE}} = [E^*_{\text{Magnesium Hydrate}} - E_{\text{Magnesium Hydrate}}(\text{Complex})] + [E^*_{\text{Pyrimidine nucleotide}} - E_{\text{Pyrimidine nucleotide}}(\text{Complex})]$$

Where E^* indicates that the energy of components at complex geometry calculated of Methods/Basis set of complex geometry.

RESULTS

Theoretical results of the calculated optimized geometries for structures of pyrimidine nucleotide complexes are given in Table 1 and optimized structures obtained in the HF/6-31g*:LANL2DZ is shown in Figure 2: In HF-SCF study, it was found that the Magnesium ion forms a coordination with water and phosphate oxygens at distances ranging from 2.11Å and 1.952Å that were in agreement with the available experimental results (2.02Å and 2.11Å).

Hard Lewis acids, including alkali, alkaline earth, and rare earth metal ions, display almost equal affinities to all the nucleoside monophosphates studied, suggesting that coordination takes place at

the phosphate dianion without involvement of the base moiety.

The latter kind of structure was also described for the Mg(II)-hydrate complexes of the 5'-monophosphates interaction with the phosphate group was suggested to be either a direct one or mediated through water of molecule, depending on the conditions in which the complexes were prepared.^{29,30}

Sigel²⁸ have shown by comparing the stabilities of metal ion complexes of nucleoside monophosphates and simple phosphate monoesters that the base moiety does not play any role in complexing of CMP, UMP, dTMP. In other words, the complex stabilities are solely determined by the basicity of the phosphate group and the metal ion affinity of the phosphate group.

The conformation of the sugar ring in nucleotides and nucleosides can be examined by using a concept of pseudorotation, which utilizes a quantitative description of puckering and conformation in terms of the maximum torsion angle (τ_m) and the "Phase angle" of pseudorotation (P), which is a function of the interrelationship between the five torsion angles (τ_0 - τ_4) in the nonplanar five-membered ring³¹. The phase angle, P, and the maximum pucker, τ_m , are calculated with eq 1 and 2

$$\tan P = (\tau_4 + \tau_1) - (\tau_3 + \tau_0) / 2\tau_2 (\sin 36^\circ + \sin 72^\circ) \quad (1)$$

$$\tau_2 = \tau_m \cos P \quad (2)$$

All the possible conformations are grouped into two categories. Type N ($P=0^\circ$ or 90°) or 3' endo or type S ($P=180^\circ$ or 90°) or 2' endo/C1' exo (Figure 3). A majority of the ribose and deoxyribose P values fall in the ranges 0-36° and 144-180°³². We have theoretically computed the P values for all nucleotides using HF/6-31g* level on the optimized structures. (Table 2)

Table 1: Optimized bond length (Å) of pyrimidine nucleotide complexes in the 6-31g*:LANL2DZ basis set

Bond Length	Mg(H2O)4CMP	Mg(H2O)5UMP	Mg(H2O)5dTMP
Mg-O(H2O)	2.105, 2.112, 2.068, 2.099	2.138, 2.170, 2.141, 2.149, 2.096	2.161, 2.122, 2.126, 2.120, 2.155
Mg-O(PO4)	1.923	1.942	1.952
O(PO4)---H(H2O)	1.643	1.677, 1.722	1.632
O1'---H(H2O)	1.952	1.981, 2.592	
O7---H(H2O)	1.926		
N3---H(H2O)	2.129		
P-O1	1.530	1.526	1.476
P-O3	1.462	1.462	1.526
P-O2	1.559	1.557	1.565

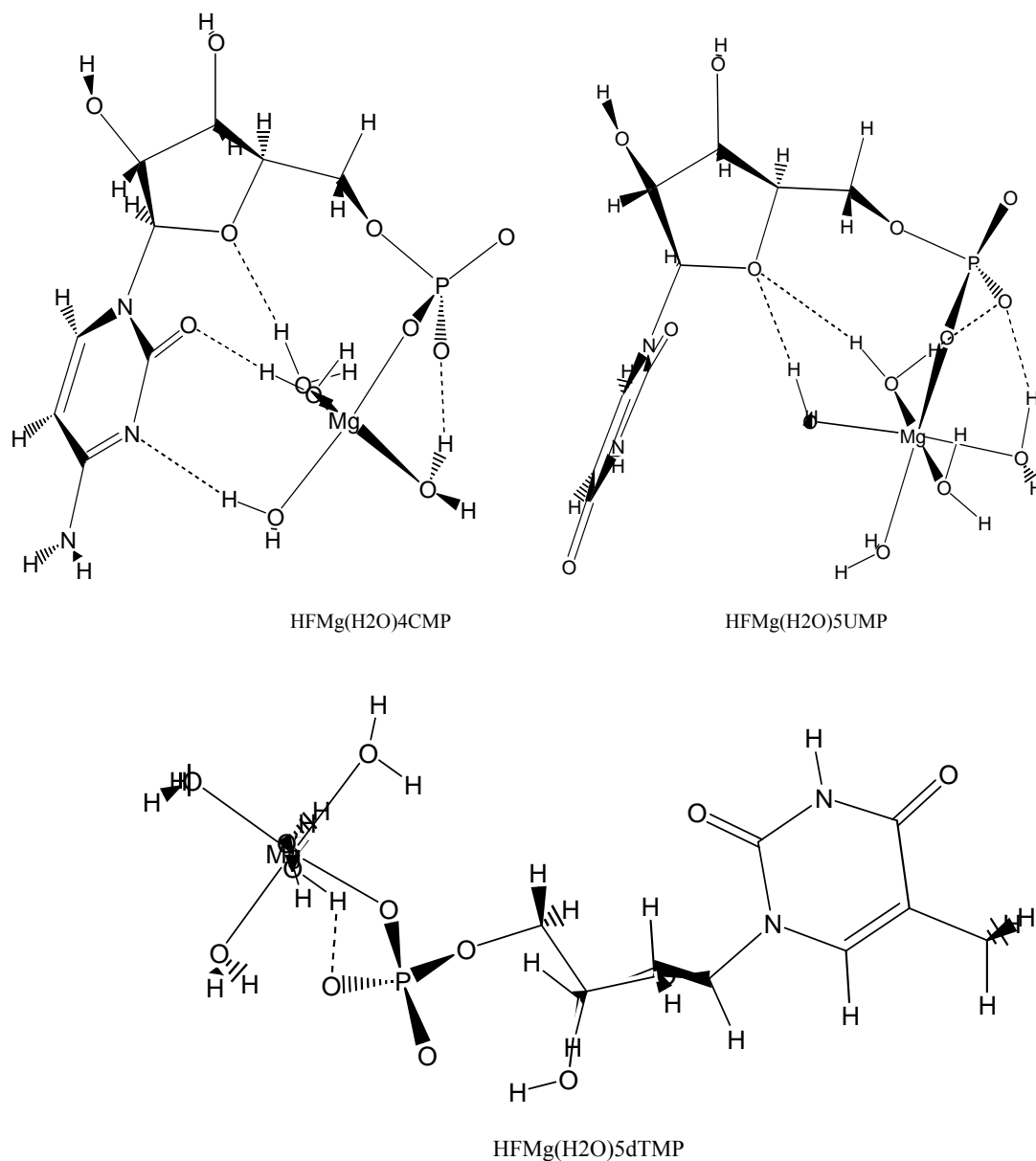


Fig 2: Optimized structures of Mg-nucleotide complexes in the HF/6-31g*:LANL2DZ Indirect (outer-sphere) phosphate coordination probably occur between atoms oxygen phosphate and water molecules of Mg-coordination.

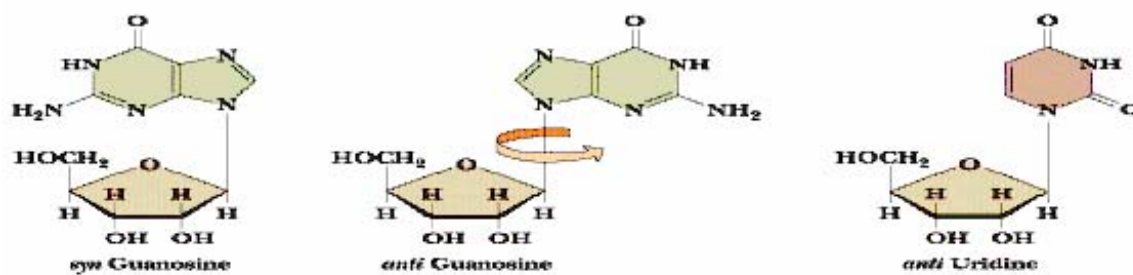


Fig 3-Two familiar conformations about the glycosyl bond,(a) anti and (b) syn, illustrated by the guanine and uracyl base. The projections down to the glycosyl bond are also shown ³³.

The ribofuranose rings of nucleosides and nucleotides are puckered, usually into one of two preferred conformations, described as C3'-endo or C2'-endo³⁴. A more precise description of the ribofuranose conformation is given by the torsion angles about each bond. The orientation of the ribose rings relative to the pyrimidine base is given by torsion angle χ_{CN} about the glycosidic bond for the sequence of atoms C4-N9-C1'-O1' and pyrimidine base χ_{CN} is defined as the C2-N1-C1'-O1' torsion angle³⁵⁻³⁸(Figure 4).

These structures are compared with those predicted from an HF/6-31g* basis in Table 1-3. The

agreement between the theoretical structures predicted in both level and the experimental geometry is very good for Magnesium-nucleotides. The results of these calculations showed that Metal-nucleotide sugar conformations fall into categories, C3' endo, syn.

The computed energies of the complexes for non metalated and metalated pyrimidine nucleotides are compared by HF/6-31g* method (Table 4). Their relative stabilities are markedly influenced by the metalation. On the other hand metalation of pyrimidine nucleotides have been found more stable than in nonmetalated molecule.

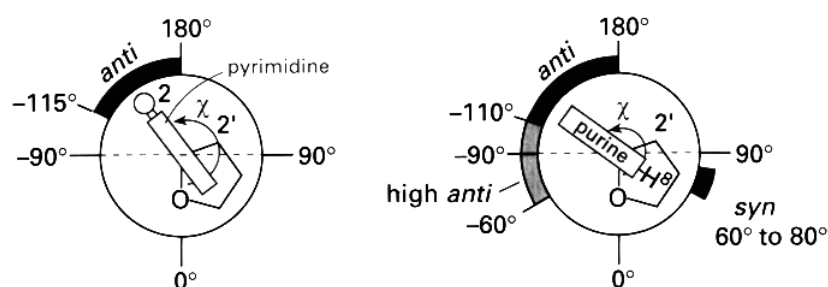


Fig. 4 :Glycosidic Bond in the purine and pyrimidine⁴².

Table 2: Dihedral Angles complexes at 6-31g* basis set.

Dihedral Angles	Mg(H2O)4CMP	Mg(H2O)5UMP	Mg(H2O)dTMP
MgOPO5'	83.0	76.7	110.1
PO5'C5'C4	-155.7	-162.6	60.5
O5'C5'C4'C3'(ψ)	164.7	179.1	-88.4
O1'C1'N1C6	-117.0	-110.0	-109.8
O1'C1'N1C2	56.2	66.3	61.4
O5'C5'C4'O1'	48.5	62.6	152.7
C3'C4'O1'C1'(τ ₄)	32.2	38.7	70.0
C3'C21'C1'O1'(τ ₁)	8.6	2.4	28.1
O1'C4'C3'C2'(τ ₃)	24.7	-35.0	11.0
C4'O1'C1'C2'(τ ₀)	-26.2	-25.9	-22.4
C4'C3'C2'C1'(τ ₂)	10.0	19.8	-23.0

Table 3: P Angles complexes in HF/6-31g* level.

Complexes	P Angle
Mg(H2O)4CMP	3.0
Mg(H2O)5UMP	1.7
Mg(H2O)5dTMP	-1.5

Table 4: Relative energies(Hartree) for Mg-Pyrimidine nucleotide complexes in gas phase with HF/6-31g* level.

Complexes	HF/6-31g*
CMP	-1450.764
UMP	-1470.623
dTMP	-1434.751
Mg(H2O)4CMP	-1954.752
Mg(H2O)5UMP	-2050.633
Mg(H2O)5dTMP	-2014.823

Table 5 shows the interaction energies of metalated pyrimidine nucleotides. The interaction energies of the metalated pyrimidine nucleotides increase. The increase is due to Hydrogen bonding in metalated pyrimidine nucleotides (Table 1). Table 5 shows the value of BSSE and E_{I+BSSE} for the structures. Clearly for the all complexes, values of BSSE are rather small. Therefore, for these cases BSSE is negligible.

NMR CHEMICAL SHIFT ASSIGNMENTS

With using the GAUSSIAN 98 program³⁹, we first optimized the geometry of nucleotides with the B3LYP and HF level and 6-31g* basis set. Then, we calculated isotropic spectroscopic shielding for all atoms in nucleotides using density functional theory at the B3LYP/6-31g** level. In this letter, we use both the GIAO method and CSGT

procedure, which is implemented in the GASSIAN 98 program.

The isotropic part σ_{iso} of σ is measured by taking the average of σ with respect to the orientation to the magnetic field, i.e., $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$. The results calculated are summarized in (Table 6,7).

The anisotropy is $\zeta = |\sigma_{33} - \sigma_{iso}|$, and the asymmetry is $\eta = (\sigma_{22} - \sigma_{11})/\zeta$ ⁴¹.

Ab initio calculations yield the data in Table 10,11 show that the values for the shielding isotropics O2, P,O1,O3 atoms in metalated CMP,UMP,dTMP are more but the isotropic C6 atoms is less than in nonmetalated CMP, UMP,dTMP. It was found that the isotropic O8 atom in metalated UMP,dTMP is less than in nonmetalated CMP, UMP,dTMP, but isotropic O7 atoms in metalated CMP was increased.

Table 5: E_I (Interaction energies), BSSE and E_{I+BSSE} (Hartree) for complexes in HF/6-31g* level

Complexes	E_I	BSSE	E_{I+BSSE}
Mg(H2O)4CMP	-0.36075	-0.0188594	-0.3796106
Mg(H2O)5UMP	-0.36299	0.0282317	-0.3347583
Mg(H2O)5dTMP	-0.37151	-0.0111472	-0.3826603

Table 6: B3LYP/6-31g** calculations of the σ_{iso} in ppm, of the nuclear magnetic shielding tensor σ for atoms in CMP, UMP, dTMP

Atom	Method	CMP Σ_{iso}	UMP σ_{iso}	dTMP σ_{iso}
O2	GIAO	514.377	-513.054	-4.045
	CSGT	-511.822	-510.512	-0.191
P	GIAO	366.270	366.430	364.199
	CSGT	293.750	293.830	293.171
O1	GIAO	-590.547	-587.577	-720.907
	CSGT	-587.459	-584.394	-722.233
O3	GIAO	15.549	12.750	-535.578
	CSGT	30.802	27.915	-535.555
O5'	GIAO	233.758	233.621	232.857
	CSGT	239.415	239.024	239.501
C5'	GIAO	125.119	125.018	125.844
	CSGT	125.060	24.949	125.870
C4'	GIAO	100.531	100.355	106.892
	CSGT	102.262	102.007	108.008
C3'	GIAO	121.570	120.574	117.132
	CSGT	120.227	119.796	116.344
C2'	GIAO	121.687	119.711	152.480
	CSGT	119.163	117.391	154.051
C1'	GIAO	95.157	97.597	99.964
	CSGT	94.854	97.351	100.223
O1'	GIAO	240.337	245.012	230.663
	CSGT	232.827	237.335	224.565
N1	GIAO	132.145	136.789	129.684
	CSGT	128.985	134.306	126.702
C2	GIAO	39.967	45.671	45.894
	CSGT	34.829	39.151	39.933
O7	GIAO	14.392	40.103	62.373
	CSGT	8.989	39.776	60.832
N3	GIAO	67.916	113.296	118.075
	CSGT	60.573	106.764	110.546
C4	GIAO	48.816	45.055	49.081
	CSGT	44.068	39.291	42.648
C5	GIAO	109.669	110.685	109.099
	CSGT	104.844	105.688	105.477
C6	GIAO	94.626	98.240	99.180
	CSGT	92.096	96.433	93.751
O8	GIAO		46.484	79.939
	CSGT		41.625	71.410

Table 7: B3LYP/6-31g** calculations of the σ_{iso} in ppm, of the nuclear magnetic shielding tensor σ for atoms in Mg-nucleotides of CMP, UMP, dTMP

Atom	Method	Mg(H ₂ O)4CMP		Mg(H ₂ O)5UMP		Mg(H ₂ O)5 dTMP	
		σ_{iso}	η	σ_{iso}	η	σ_{iso}	η
O2	GIAO	226.559	-46.964	224.104	3.543	218.702	4.339
	CSGT	245.753	-2.994	244.728	3.629	236.752	11.230
P	GIAO	386.637	-0.563	385.663	19.280	382.408	3.286
	CSGT	325.640	-0.570	325.363	-2115.929	327.684	3.911
O1	GIAO	197.356	2.022	197.006	-0.101	215.069	4.025
	CSGT	210.913	4.791	212.197	0.029	227.250	1.252
O3	GIAO	215.519	-2.650	219.603	2.207	196.018	-115.399
	CSGT	232.816	0.624	236.211	1.273	211.673	-13.160
O5'	GIAO	244.214	-3.598	240.129	-8.576	245.875	1.197
	CSGT	245.090	-2.320	242.061	-5.269	250.443	0.529
C5'	GIAO	130.488	-17.566	131.773	-7.280	128.093	-2.385
	CSGT	129.008	11.208	130.387	-11.738	127.957	-2.278
C4'	GIAO	108.513	1.641	108.315	1.148	103.166	-26.084
	CSGT	108.789	1.464	108.146	1.127	104.399	69.019
C3'	GIAO	120.071	0.883	123.246	0.957	118.032	2.285
	CSGT	117.975	0.796	120.937	0.830	117.520	2.138
C2'	GIAO	119.906	-41.147	119.693	0.958	156.901	-5.977
	CSGT	117.973	-0.003	117.739	1.135	157.920	-5.004
C1'	GIAO	92.332	-1.403	94.810	-1.221	97.755	-6.201
	CSGT	91.621	-1.289	94.495	-1.059	97.181	-5.156
O1'	GIAO	256.488	0.469	250.821	0.240	246.404	-1.415
	CSGT	250.049	0.471	245.86	0.242	239.893	-1.292
N1	GIAO	101.095	54.200	117.202	-6.065	117.049	0.682
	CSGT	97.856	-54.937	113.191	-5.033	113.560	5.344
C2	GIAO	49.092	70.709	53.739	-2.822	57.748	-1.750
	CSGT	42.842	-111.105	47.646	2.893	48.587	-1.763
O7	GIAO	32.239	-8.898	38.359	1.677	40.062	0.261
	CSGT	26.821	-8.598	36.159	1.607	36.534	0.191
N3	GIAO	59.025	-8.710	108.105	0.354	107.123	-29.852
	CSGT	52.003	10.635	101.876	0.322	101.081	-3.557
C4	GIAO	38.783	-2.875	44.933	0.464	43.129	0.434
	CSGT	33.887	-0.185	39.242	0.368	37.503	0.391
C5	GIAO	106.173	0.042	94.670	0.796	86.876	0.092
	CSGT	100.428	-0.093	88.674	-0.813	81.992	0.123
C6	GIAO	51.699	-0.807	56.145	-0.431	58.317	-1.081
	CSGT	47.519	-0.860	51.811	-0.423	53.335	-1.616
O8	GIAO			-53.366	-5.241	-35.200	0.214
	CSGT			-58.633	2.104	-40.690	0.200

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