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An Ab initio and Chemical Shielding Tensors Calculations for Nucleotide 5'-Monophosphates in the Gas Phase

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ABSTRACT

Structural and magnetic properties of purine and pyrimidine nucleotides (CMP, UMP, dTMP, AMP, GMP, IMP) were studied at different levels of ab initio molecular orbital theory.These calculations were performed at the Hartree-Fock level and density functional B3LYP methods. Geometries were fully optimized by following Cs symmetry restrictions.The standard 6-31g* basis set which includes polarization and diffuse functions,was used for all the calculations. The gauge-invariant atomic orbital (GIAO) method and the continuous-set-of-gauge-transformation (CSGT) procedure was employed to calculate atomic shielding tensors of the nucleotides using density functional theory at the B3LYP/6-31g** and HF/6-31g** level. The calculated chemical shifts were used to aid in assigning in the NMR spectra.

Keywords: Ab initio Calculation;, Shielding Tensor; Nucleotide 5'-Monophosphates

INTRODUCTION

Metal complexes of mononucleotides involve phosphate monoesters that carry two negative charges per phosphate group, in the normal protonatio state. Conseguently the role of the phosphate groups either through direct metal binding or through electrostatic interaction with the metal.[5,6]

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 and purine-nucleoside 5′-monophosphate are shown in Figure 1.[1-4]

Properties of Various purine and pyrimidine nucleosides in aqueous solution have been studied extensively by proton magnetic resonance[7,8].Nuclear magnetic resonance(NMR) has played a prominent role in the study of molecular structure in solution.[9]

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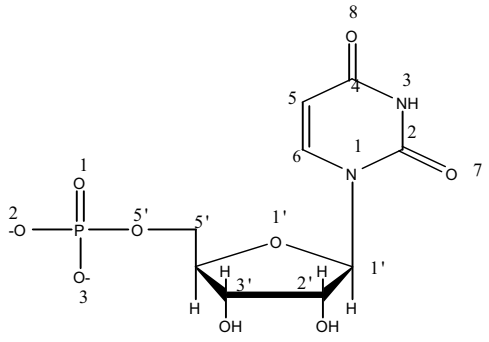
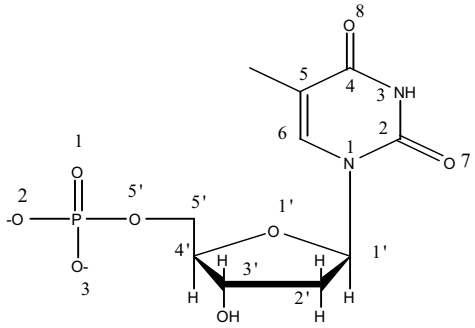
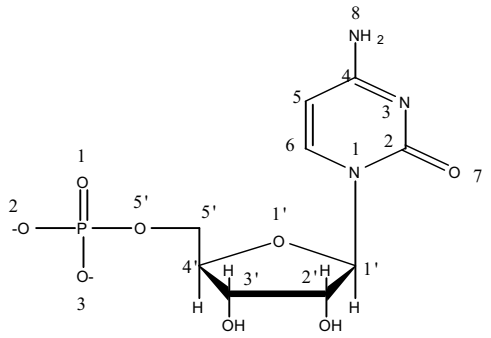


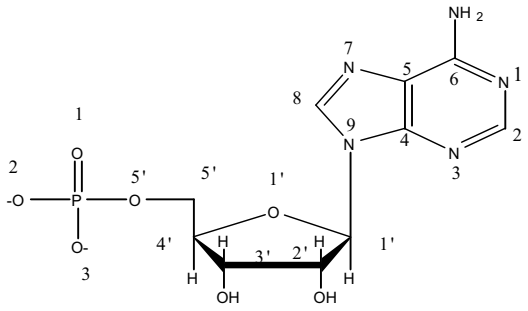
Uridine5'-monophosphates(UMP2-)



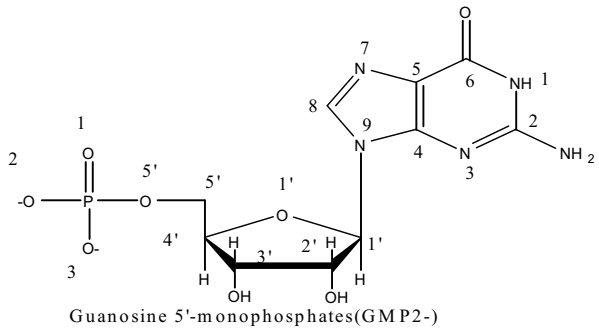
Thymine 5'-monophosphates(dTMP2-)



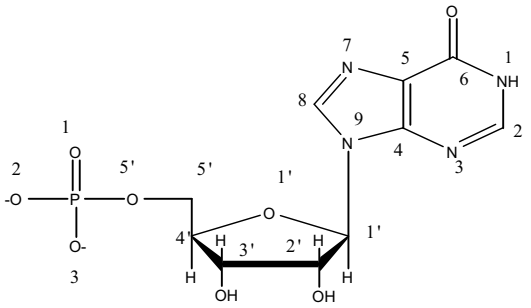
Cytidine 5'-monophosphates(CMP2-)



Adenosine 5'-monophosphates(AMP2-)



Guanosine 5'-monophosphates(GMP2-)



Inosine 5'-monophosphates(IMP2-)

Fig 1. Chemical structures of the pyrimidine-nucleoside 5'-monophosphates (UMP, dTMP, CMP) and purine-nucleoside 5'-monophosphates(AMP,GMP,IMP).

The main NMR spectroscopic parameters are dependent on the second-order molecular property tensors[11] .The NMR shielding tensor σ ,nuclear spin-spin coupling J can be all written as second derivatives of the energy.

(NMR Shilding) $\sigma = (\partial^2 E/\partial B \partial m)_{B-0,m-0}$

(NMR Coupling) $J = (\partial^2 E/\partial n \partial m) n_{-0,m-0}$

Where E is the energy of the molecule, B external magnetic field,E electric intensity ,and n,m nuclear magnetic moments.Scalar parametersJnm and σ observable for an isotropic medium are defined as a 1/3 of the traces of the tensors J and σ, respectively.[10]

In this context ,we report ab initio optimized structure of the six nucleotides using 6-31g* basis set and Hartree-Fock level of theory and the B3LYP hybrid density function method and the structures was supported by comparing the measured ^{1}H-NMR spectra to the results of ab initio gauge-invariant atomic orbital (GIAO)[12]and continuous-set-of-gauge-transformation(CSGT)[13] computations of chemical shifts using density functional theory at the B3LYP/6-31g** and HF/6-31g** level.

METHODS

All geometry optimizations have been performed using 6-31g* basis set [15,16]and the Hartree-Fock and DFT level of theory for nucleotides with charge and multipilicity -2,3 but Ab initio calculation of GMP have been done at UHF level with charge and multipilicity -2,1 .The B3LYP hybrid density functional method, with allows for

electron correlation, has been used as incorporated in the Gaussian 98 program.[14] .

NMR analysis have been performed using 6-31g** basis set and the B3LYPand HF levels.The GIAO[12] and CSGT[13] methods were used to calculate the shielding tensors at the B3LYP/6-31g**and HF/6-31g** level of theory. For the basis sets used here in , density functional methods tend to predict NMR values that are deshielded when compared and to Hartree-Fock methods.

RESULT AND DISCUSSION

Natural nucleotides already offer a number of possibls conformation; the most evident among them are defined by the angle of torsion about the glycosyl bond[17]. Consequently, differences in the interaction of metal ions with polynucleotides may also be related to the influence that the nature and orientation of the base have on the polynucleotide back bone conformation[17]. The structures of nucleotides have been determined experimentally in the solid state[18-20]. These structures are compared with those predicted from an HF/6-31g* and B3LYP/6-31g* level in Table 1.

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 ring[21]. The phase angle, P, and the maximum pucker, τ_m, are calculated with eq 1 and 2 [21].

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

$\tau_2=\tau_m \cos P$

All the possible conformations are grouped into two categories. Type N(P=0±90º) or 3' endo and type S(P=180±90º) or 2' endo/C1' exo[22]. We have theoretical computed the P values for all nucleotides using B3LYP/6-31g* and HF/6-31g* level on the optimized structures.(Table 2)

Table 1. Dihedral angles CMP,UMP,dTMP ,AMP,GMP,IMP at basis set 6-31g*

Dihedral Angle	CMP		UMP		dTMP		AMP		GMP		IMP	
	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	UHF	B3LYP	HF	B3LYP
O1PO5'C5'	-37.0	56.4	-36.6	56.1	41.2	63.6	-178.3	-78.6	-178.4	178.9	36.6	56.0
PO5'C5'C4'	162.9	158.8	162.2	158.0	65.8	108.8	-139.1	164.8	163.2	-134.1	161.3	164.2
O5'C5'C4'C3'(ψ)	-164.4	-162.9	-1640	-163.8	-89.1	-86.1	177.7	-168.1	-169.8	174.3	-170.7	-170.1
O1'C1'N1C6	-95.3	-145.2	-107.5	-154.0	-71.9	-101.6						
O1'C1'N1C2	77.6	66.8	75.2	59.0	80.9	79.2						
O5'C5'C4'O1'	79.2	76.3	79.8	75.4	151.6	156.5	60.0	72.6	70.7	56.7	70.6	70.5
O1'C1'N9C4							-161.4	-99.0	176.3	-154.8	176.7	175.9
O1'C1'N9C8							164.4	118.3	-17.1	21.9	16.3	20.0
C3'C4'O1'C1'(τ_4)	41.0	32.8	41.2	28.8	24.2	39.5	-13.6	23.4	-7.7	23.1	23.6	23.2
C3'C2'C1'O1'(τ_1)	-2.1	40.6	-1.5	42.5	44.1	0.7	28.7	48.9	33.6	41.6	40.2	41.6
O1'C4'C3'C2'(τ_3)	-40.2	-6.6	-39.7	-1.6	4.1	-37.0	30.8	7.9	28.4	4.0	3.2	4.0
C4'O1'C1'C2'(τ_0)	-24.4	-46.3	-25.1	-45.0	-43.6	-25.1	-9.7	-45.0	-16.6	-41.1	-40.7	-41.2
C4'C3'C2'C1'(τ_2)	-25.3	-19.5	24.5	-23.4	-27.4	21.4	-35.3	-33.5	-36.6	-26.5	-25.4	-26.5

Table 2. P Angles CMP,UMP,dTMP, AMP,GMP,IMP at basis set 6-31g*

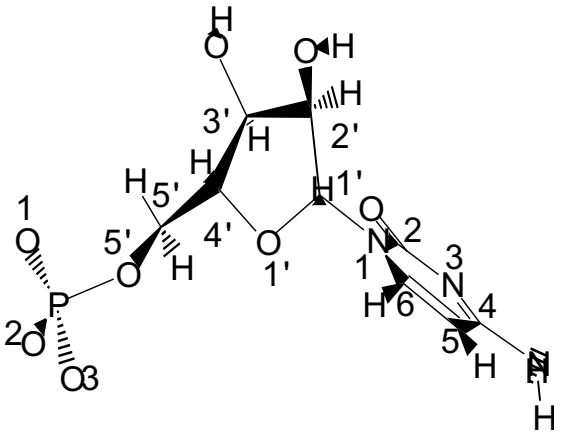
Nucleotides	P	
	HF	B3LYP
CMP	-53.7	-65.2
UMP	-54.9	59.2
dTMP	-19.2	57.9
AMP	-3.2	-47.4
GMP	-7.3	-52.1
IMP	-53.1	-52.1

The ribofuranose rings of nucleosides and nucleotides are puckered, usually into one of two preferred conformations, described as C3'-endo C2'-endo[23]. 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 purine 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 angle [24-26,17].

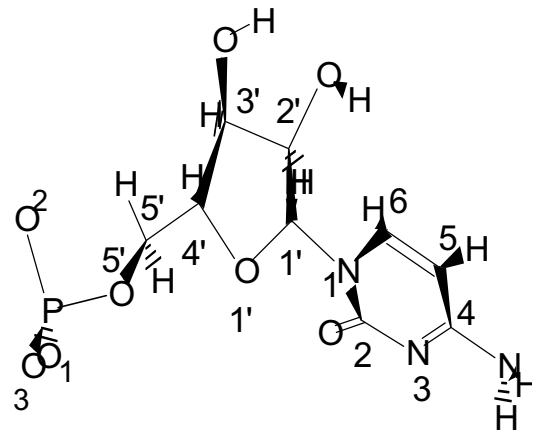
Rotations about the C4'-C5' bond are designated gauche-gauche(gg), gauche-trans(gt) or trans-guche (tg) depending on whether the angles φ_{oo}(O5'C5'C4'O1') φ_{OC}(O5'C5'C4'C3') will be near 60 and 60, 60 and 180 or 180 and 60, respectively [30,31,32].

These structures are compared with those predicted from an HF/6-31g* and B3LYP/6-31g* basis in Table 1-2. The optimized geometries obtained for nucleotides are given in Figure 2.

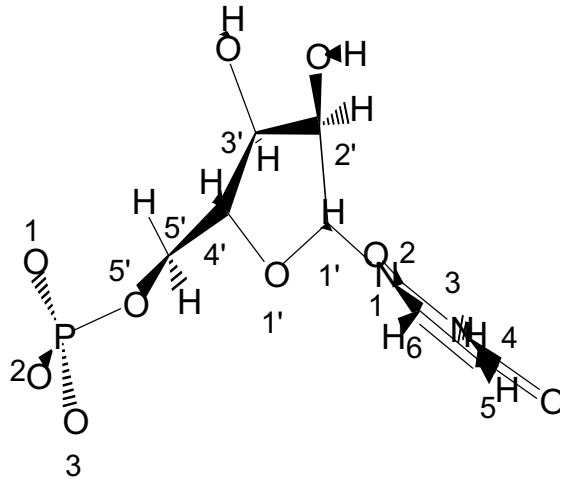
The results of these calculations showed that the orientation of the base with respect to the glycosidic C1'-N9 bond of the purine bases were anti ,but the torsional angle for AMP corresponds to syn conformation at B3LYP/6-31g* level and C1'-N1 bond of the pyrimidine bases were syn, and the puckering of the ribose ring is C3'-endo and the conformation about the C4'-C5' bond in the GMP,IMP,UMP,CMP are guche-trans (gt) and the dTMP is trans-gauche.



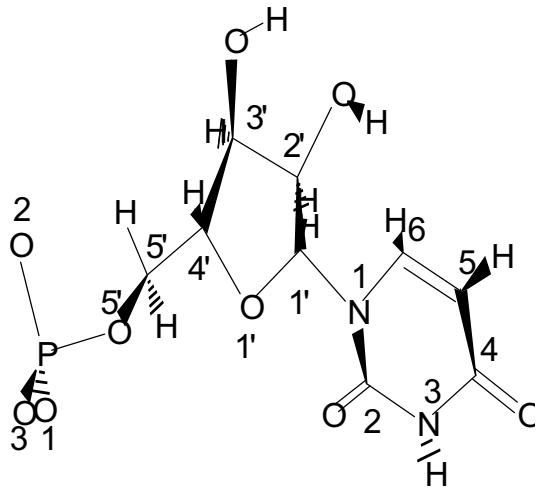
HFCMP



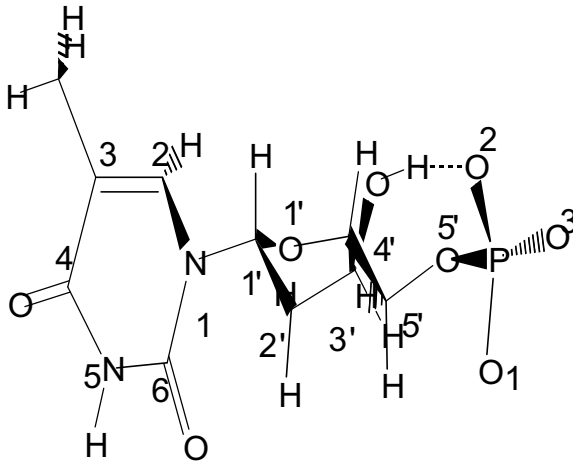
B3LYPCMP



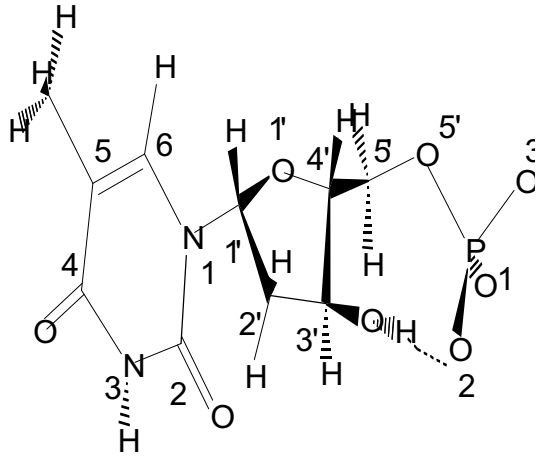
HFUMP



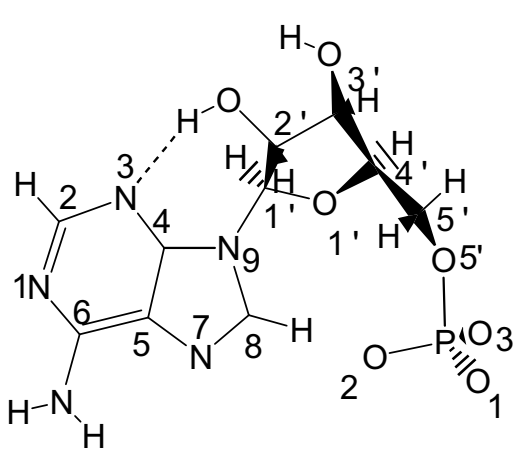
B3LYPUMP



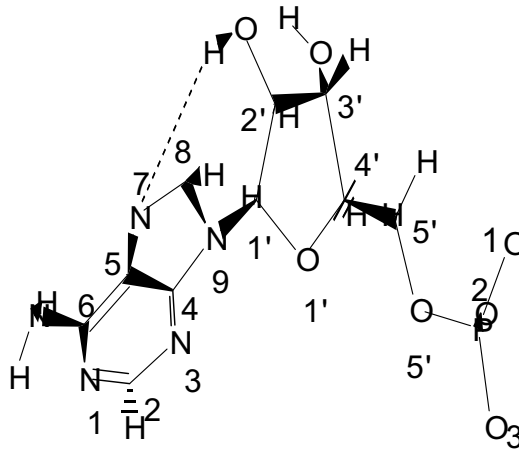
HF dTMP



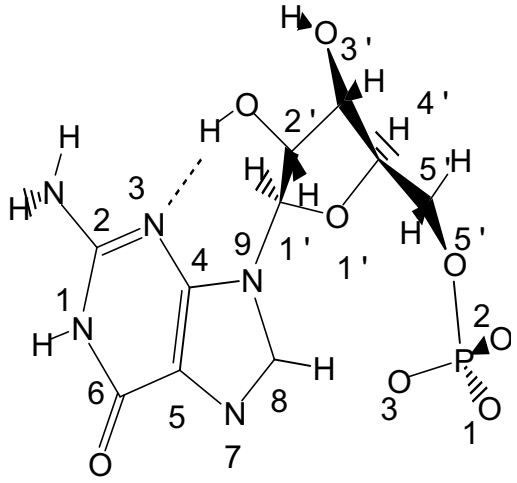
B3LYPdTMP



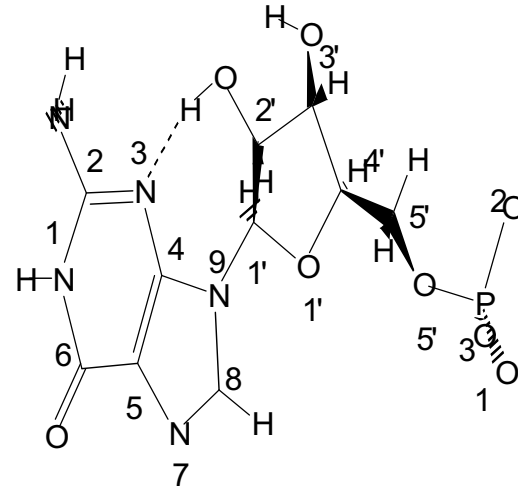
HFAMP



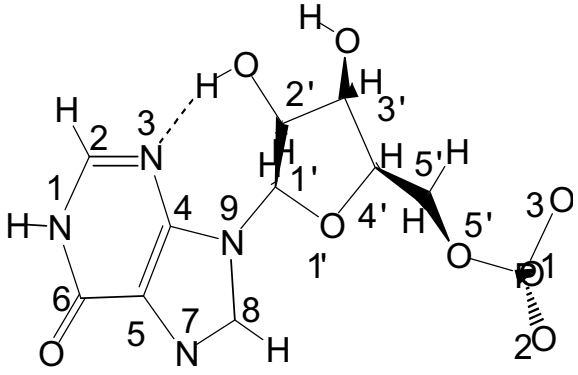
B3LYPAMP



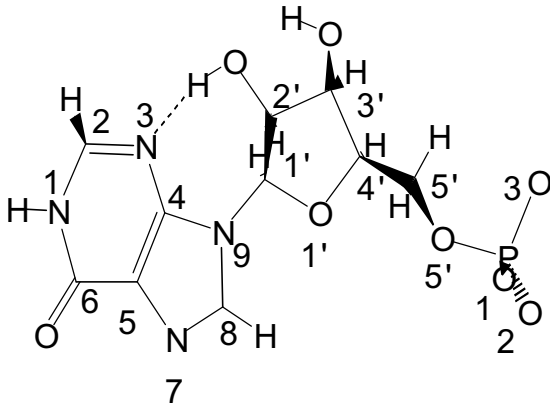
UHFGMP



B3LYPGMP



HFIMP



B3LYPIMP

Fig. 2. Optimized structure of the nucleotides as computed at the HF/6-31g* and B3LYP/6-31g* level.

A bout intramlecular hydrogen bonding of the 2'−OH group of the ribose to the N-3 of purine or to the 2-keto of the pyrimidines [27-28]. ,table 3 show the Hydrogen-bonds in the nucleotides calculated by the HF and DFT methods.

Table 3. Hydrogen bonding nucleotides in HF/6-31g* and B3LYP/6-31g* level

Hydrogen Bonding	dTMP		AMP		GMP		IMP	
	HF	B3LYP	HF	B3LYP	UHF	B3LYP	HF	B3LYP
O3'H------O2(PO4)	1.655	1.765						
O2'H------N3			2.204		2.298	1.685	1.817	1.678
O2'H------N7				3.147				

NMR CHEMICAL SHIFT ASSIGNMENTS

We first optimized the geometry of nucleotides with the B3LYP and HF level and 6-31g* basis set. Then, we calculate nuclear magnetic isotropic spectroscopic shielding [21] for all atoms in nucleotides using density functional theory at the B3LYP/6-31g** level and HF theory. In this letter, we use both the GIAO method and CSGT procedure,which is implemented in the GAUSSIAN 98 program [29].

In high-resolution NMR, the isotropic part σiso of σ is measured by taking the average of σ with respect to the orientation to the magnetic field,i.e.,$\sigma iso=(\sigma_{11}+\sigma_{22}+\sigma_{33})/3$,where σ_{11},σ_{22} and σ_{33} are the principlal axis values of σ.The results calculated are summarized in Table 4,5,6,7.

Ab initio calculation yield in Table 4 show that isotropic shielding of C6 and H6 atoms of anionic pyrimidine nucleotides (CMP, UMP,dTMP) and C8,H8 atoms of AMP,GMP and C2,H2 atoms of IMP nucleotides have been decreased at the single multipilicity at the HF/6-31g** level.

It was found that isotropic shielding tensor of C2 atom of the CMP, UMP and C4,H6 atoms of dTMP and C4≈C8, H8 atoms of AMP and C6≈C8, H8 atoms of GMP and C4, H8 atoms of IMP have been decreased at triplate multipilicity (Table5)

The result calculated by using B3LYP/6-31g** level at GIAO and CSGT to predict the NMR shielding tensor σiso nucleotides in Table 6,7 show that the isotropic shielding of C2,H6 atoms of CMP,dTMP and C2,C4,H6 atoms of UMP and C4, H2 atoms of AMP and C6,H8 atoms of GMP have been decreased.

This finding indicates the influence of the multipilicity and structural in isotropic shielding tensor of mononucleotides.

The gauge-invariant atomic orbital (GIAO) method was employed to calculate atomic shielding tensors of the nucleotides at HF and B3LYP level in good agreement with available experimental data.

Ab initio calculation yield show a deshilding of the H6 proton of pyrimidine nucleotides and the H8 proton of purine nucleotides by the effect of the anisotropy of the phosphoryl group, but torsional angle for AMP corresponds to syn conformation at B3LYP/6-31g* level and show a deshilding of the H2 proton.

Table 4. HF/6-31g** calculation of the σ_{iso} and relative (to TMS) shifts in ppm for ^{13}C-NMR and ^{1}H-NMRof nucleotides using GIAO method.The chemical shift($\delta=\sigma_{iso}^{TMS}-\sigma_{iso}^{sample}$)

Atom		CMP HF/6-31g**	UMP HF/6-31g**	Dtmp HF/6-31g**	AMP HF/6-31g**	GMP UHF/6-31g**	IMP HF/6-31g**
C5'	**σ iso**	145.7379	145.7585	144.6637	144.4321	143.9664	143.0432
	δ	57.4169	57.3963	58.4911	58.7227	59.1884	60.1116
C4'	**σ iso**	125.0030	124.2624	116.5172	119.0297	120.4998	119.6716
	δ	78.1518	78.8924	86.6376	84.1251	82.655	83.4832
C3'	**σ iso**	138.5291	138.7352	139.4666	136.2105	136.4825	137.2991
	δ	64.6257	64.4196	63.6882	66.9443	66.6723	65.8557
C2'	**σ iso**	136.5700	135.2260	168.1820	129.7849	130.5617	133.0502
	δ	66.5848	67.9288	34.9728	73.3699	72.5931	70.1046
C1'	**σ iso**	114.3494	115.4666	125.1421	121.3473	122.4062	122.6759
	δ	88.8054	87.6882	78.0127	81.8075	80.7486	80.4789
C6	**σ iso**	17.7335	22.5274	-2.8103	48.3429	48.1187	43.8521
	δ	185.4213	180.6274	205.9651	154.8119	155.0361	159.3027
C5	**σ iso**	105.0896	90.2017	58.1032	76.4490	90.7034	77.3226
	δ	98.0652	112.9531	145.0516	126.7058	112.4514	125.8322
C4	**σ iso**	20.8724	35.1250	46.5828	52.4248	54.9622	53.3777
	δ	182.2824	168.0298	198.5720	150.7300	148.1926	149.7771
C2	**σ iso**	46.5906	52.6562	58.2824	38.1050	54.5839	32.5896
	δ	156.5642	150.4986	144.8724	165.0498	148.5709	170.5652
C8	**σ iso**				36.0893	49.3810	59.9410
	δ				167.0655	153.7738	143.2138
H6	**σ iso**	22.8798	23.0883	22.0930			
	δ	9.4562	9.2477	10.2430			
H5	**σ iso**	26.6215	26.4179				
	δ	5.7145	5.9181				
H1'	**σ iso**	28.5188	29.0910	28.6257	27.0261	28.6363	27.5669
	δ	3.8172	3.2450	3.7103	5.3099	3.6997	4.7691
H8	**σ iso**				16.5496	18.3740	23.4879
	δ				15.7864	13.9620	8.8481
H5'	**σ iso**	28.8930	28.8735	29.7987	29.7432	28.4663	28.3321
	δ	3.443	3.4625	2.5373	2.5928	3.8697	4.0039
H5''	**σ iso**	28.3595	28.3058	28.6257	28.6482	29.8138	29.3953
	δ	3.9765	4.0302	3.7103	3.6828	2.5222	2.9407
H2	**σ iso**				23.5399		23.3880
	δ				8.7961		8.9480

Charge, multipilicity -2,1.Standard; TMS: Isotropic carbon shielding tensor=203.1548 and isotropic hydrogen shielding tensor=32.3360 at HF/6-31g** and GIAO method.

Table 5. HF/6-31g** calculation of the σ_{iso} and relative (to TMS) shifts in ppm for ^{13}C-NMR and ^{1}H-NMR of nucleotides using GIAO method .The chemical shift ($\delta=\sigma_{iso}^{TMS}-\sigma_{iso}^{sample}$)

Atom		CMP HF/6-31g**	UMP HF/6-31g**	dTMP HF/6-31g**	AMP HF/6-31g**	IMP HF/6-31g**
C5'	**σ iso**	144.4316	144.7378	144.5127	144.5747	143.0697
	δ	58.7232	58.417	58.6421	58.5801	60.0851
C4'	**σ iso**	128.5971	127.9280	116.7535	119.2291	119.6237
	δ	74.5577	75.2268	86.4013	83.9257	83.5311
C3'	**σ iso**	139.7201	139.7256	140.1737	136.5302	137.5016
	δ	63.4347	63.4292	62.9811	66.6246	65.6532
C2'	**σ iso**	135.1847	135.1323	167.8796	130.2058	133.3556
	δ	67.9701	68.0225	35.2752	72.949	69.7992
C1'	**σ iso**	114.3049	115.1538	122.0994	122.3760	123.1952
	δ	88.8499	88.001	81.0554	80.7788	79.9596
C6	**σ iso**	116.4636	117.8828	110.8992	73.4423	45.8608
	δ	86.6912	85.272	92.2556	129.7125	157.294
C5	**σ iso**	125.1888	136.3046	97.3654	77.9742	84.0715
	δ	77.9660	66.8502	105.7894	125.1806	119.0833
C4	**σ iso**	59.5013	152.1461	39.9990	41.0316	38.8281
	δ	143.6535	51.0087	163.1558	162.1232	164.3267
C2	**σ iso**	47.0160	49.9364	54.4262	100.7886	113.6832
	δ	156.1388	153.2184	148.7286	102.3662	89.4716
C8	**σ iso**				45.0491	54.2788
	δ				158.1057	148.876
H6	**σ iso**	28.07510	28.3370	25.8110		
	δ	4.2609	3.999	6.525		
H5	**σ iso**	28.7797	29.5580			
	δ	3.5563	2.778			
H1'	**σ iso**	29.0722	28.9963	28.2572	27.7218	27.8366
	δ	3.2638	3.3397	4.0788	4.6142	4.4994
H8	**σ iso**				17.5058	23.7885
	δ				14.8302	8.5475
H5'	**σ iso**	30.2715	28.1786	29.7758	29.8267	28.3611
	δ	2.0645	4.1574	2.5602	2.5093	3.9749
H5''	**σ iso**	28.2296	30.2478	28.6540	28.8172	29.4726
	δ	4.1064	2.0882	3.682	3.5188	2.8634
H2	**σ iso**				27.2772	26.8111
	δ				5.0588	5.5249

Charge and multipilicity -2,3.

Table 6. HF/6-31g** calculation of the σ_{iso} and relative (to TMS) shifts in ppm for ^{13}C-NMR and ^{1}H-NMR of nucleotides using CSGT method .The chemical shift($\delta=\sigma_{iso}^{TMS}-\sigma_{iso}^{sample}$) (Charge and multipilicity -2,3 but in the UMP ,GMP Charge and multipilicity -2,1).

Atom		CMP HF/6-31g**	UMP HF/6-31g**	dTMP HF/6-31g**	AMP HF/6-31g**	GMP HF/6-31g**	IMP HF/6-31g**
C5'	**σ_{iso}**	143.5865	144.4550	143.1603	142.5842	141.7915	141.4108
	δ	58.8838	58.0153	59.31	59.8861	60.6788	61.0595
C4'	**σ_{iso}**	129.0800	123.8851	117.5519	119.0347	120.1933	118.7217
	δ	73.3903	78.5852	84.9184	83.4356	82.2770	83.7486
C3'	**σ_{iso}**	137.7569	136.4916	139.3018	135.0234	134.7652	135.6780
	δ	64.7134	65.9787	63.1685	67.4469	67.7051	66.7923
C2'	**σ_{iso}**	132.9524	133.1553	169.1122	128.0299	128.0103	131.6512
	δ	69.5179	69.315	33.3581	74.4404	74.4600	70.8191
C1'	**σ_{iso}**	112.8441	113.7610	121.2065	120.4178	120.3920	121.7782
	δ	89.6262	88.7093	81.2638	82.0525	82.0783	80.6921
C6	**σ_{iso}**	110.9464	17.6067	108.2275	65.4386	40.7526	37.7798
	δ	91.5239	184.8636	94.2428	137.0317	161.7177	164.6905
C5	**σ_{iso}**	117.9032	82.7890	93.9393	68.7544	80.8440	76.2858
	δ	84.5671	119.6813	108.531	133.7159	121.6263	126.1845
C4	**σ_{iso}**	53.7061	27.8423	32.1656	33.2339	47.2220	30.1681
	δ	148.7642	174.6280	170.3047	169.2364	155.2483	172.3022
C2	**σ_{iso}**	39.6321	43.9663	45.9880	95.5502	45.4833	108.8609
	δ	162.8382	158.5040	156.4823	106.9201	156.9870	93.6094
C8	**σ_{iso}**				38.8129	43.4451	47.4506
	δ				163.6574	159.0252	155.0197
H6	**σ_{iso}**	28.0169	23.1122	26.5468			
	δ	1.8629	6.7676	3.3330			
H5	**σ_{iso}**	28.7529	26.2918				
	δ	1.1269	3.588				
H1'	**σ_{iso}**	29.1494	28.6338	27.7399	27.5243	28.1543	27.2920
	δ	0.7304	1.2460	2.1394	2.3555	1.7255	2.5878
H8	**σ_{iso}**				19.9906	20.6753	24.3382
	δ				9.8892	9.2045	5.5416
H5'	**σ_{iso}**	29.7627	28.3989	29.3079	29.5676	29.5700	28.5723
	δ	0.1171	1.4809	0.5719	0.3122	0.3098	1.3075
H5''	**σ_{iso}**	28.1346	28.5557	28.4023	28.8386	28.6063	29.1470
	δ	1.7452	1.3241	1.4775	1.0412	1.2735	0.7328
H2	**σ_{iso}**				27.7386		26.8239
	δ				2.1412		3.0559

Standard; TMS: Isotropic carbon shielding tensor=202.4703 and isotropic hydrogen shielding tensor=29.8798 at HF/6-31g** and CSGT method.

Table 7. B3LYP/6-31g** calculation of the σ_{iso} and relative (to TMS) shifts in ppm for ^{13}C-NMR and ^{1}H-NMR of nucleotides using GIAO method .The chemical shift($\delta=\sigma_{iso}^{TMS}-\sigma_{iso}^{sample}$) (Charge and multipilicity -2,3)

Atom		CMP	UMP	Dtmp	AMP	GMP
C5'	σ_{iso}	125.1186	125.0175	125.8444	123.7966	124.8869
	δ	66.7458	66.8469	71.0200	73.0678	66.9775
C4'	σ_{iso}	100.5310	100.3551	132.8034	104.7505	100.7997
	δ	91.3334	91.5093	64.0610	92.1139	91.0647
C3'	σ_{iso}	121.1567	120.5738	117.1316	118.4242	118.0159
	δ	70.7077	71.2906	79.7328	78.4402	73.8485
C2'	σ_{iso}	121.6867	119.7113	152.4803	5.7177	114.2909
	δ	70.1777	72.1531	44.3841	81.1467	77.5735
C1'	σ_{iso}	95.1572	97.5965	99.9643	104.6410	101.1458
	δ	96.7072	94.2679	96.9001	92.2234	90.7186
C6	σ_{iso}	94.6250	98.9236	99.1797	58.3578	39.5631
	δ	97.2394	92.9408	97.6847	138.5066	152.303
C5	σ_{iso}	109.6685	110.6851	09.0991	62.5382	79.9156
	δ	82.1959	81.1793	87.7653	134.3262	11609488
C4	σ_{iso}	48.8156	45.0549	49.0805	34.7782	44.1841
	δ	143.0488	146.8095	147.7839	162.0862	147.6803
C2	σ_{iso}	39.9668	45.6711	45.8944	58.2037	79.8451
	δ	151.8976	146.1933	145.9700	133.6607	112.0193
C8	σ_{iso}				83.17749	71.0496
	δ				108.6869	120.8148
H6	σ_{iso}	27.6159	27.8787	27.7230		
	δ	4.1373	3.8745	4.0302		
H5	σ_{iso}	28.0004	28.5408			
	δ	3.7528	3.2124			
H1'	σ_{iso}	28.0928	27.9649	27.4090	27.0993	28.3448
	δ	3.6604	3.7883	4.3442	4.6539	3.4084
H8	σ_{iso}				25.8246	25.1968
	δ				5.9286	6.5564
H5'	σ_{iso}	28.192	28.1991	28.2480	28.2296	28.3068
	δ	3.5612	3.5541	3.5052	3.5236	3.4464
H5''	σ_{iso}	28.187	28.1867	28060	28.3688	28.1400
	δ	3.5662	3.5665	3.7272	3.3844	3.6132
H2	σ_{iso}				25.1473	
	δ				6.6059	

Standard; TMS: Isotropic carbon shielding tensor=191.8644 and isotropic hydrogen shielding tensor=31.7532 at B3LYP/6-31g** and GIAO method

Table 8. B3LYP/6-31g** calculation of the σ_{iso} and relative (to TMS) shifts in ppm for ^{13}C-NMR and ^{1}H-NMR of nucleotides using CSGT method .The chemical shift ($\delta=\sigma_{iso}^{TMS}-\sigma_{iso}^{sample}$) (Charge and multipilicity -2,3)

Atom		CMP	UMP	dTMP	AMP	GMP
C5'	**σ iso**	125.0595	124.9494	125.8703	123.9715	124.9160
	δ	68.0156	68.1257	67.2048	69.1036	68.1591
C4'	**σ iso**	102.2623	102.0066	108.0079	105.9576	101.9721
	δ	90.8128	91.0685	85.0672	87.1175	91.1030
C3'	**σ iso**	120.227	119.7958	116.3437	117.7040	117.5142
	δ	72.8481	73.2793	76.7314	75.3711	75.5609
C2'	**σ iso**	119.1631	117.3912	154.0507	114.4254	112.8987
	δ	73.912	75.6839	39.0244	78.6497	80.1764
C1'	**σ iso**	94.8540	97.3514	100.2233	103.6580	100.9656
	δ	98.2211	95.7237	92.8518	89.4171	92.1095
C6	**σ iso**	92.0962	96.4334	93.7506	51.9503	33.6294
	δ	100.9789	96.6417	99.3245	141.1248	159.4457
C5	**σ iso**	104.8438	105.6880	105.4772	56.2713	73.0739
	δ	88.2313	87.3871	87.5979	136.8038	120.0012
C4	**σ iso**	44.0677	39.2908	42.6477	28.8969	38.3183
	δ	149.0074	153.7843	150.4274	164.1782	154.7568
C2	**σ iso**	34.8292	39.1514	39.9325	54.8565	73.7037
	δ	158.2459	153.9237	153.1426	138.2186	119.3714
C8	**σ iso**				81.0588	65.9616
	δ				112.0163	127.1135
H6	**σ iso**	27.4817	27.5233	27.4850		
	δ	1.9140	1.8724	1.9107		
H5	**σ iso**	28.0327	28.5885			
	δ	1.363	0.8072			
H1'	**σ iso**	28.0928	27.4041	27.2944	27.0993	28.3448
	δ	1.3029	1.9916	2.1013	2.2964	1.0509
H8	**σ iso**				25.8246	25.1968
	δ				3.5711	4.1989
H5'	**σ iso**	28.1635	28.2112	27.6311	28.2296	28.3068
	δ	1.2322	1.1845	1.7646	1.1661	1.0889
H5''	**σ iso**	28.187	27.7599	27.5160	28.3688	28.1400
	δ	1.2087	1.6358	1.8797	1.0269	1.2557
H2	**σ iso**				25.1473	
	δ				4.2484	

Standard; TMS: Isotropic carbon shielding tensor=193.0751 and isotropic hydrogen shielding tensor=29.3957 at B3LYP/6-31g** and CSGT method

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