Quantum Chemical Study of Hydrogen Bonded Guanine-Water Complexes

Brijesh Kumar Sharma[1], Achchhe Lal[2] and [*]Devendra Kumar Singh[1]

[1]*Department of Physics, Udai Pratap (Autonomous) College, Varanasi-221002, India*

[2]*Department of Physics, Harishchndra P G College, Varanasi-221002, India*

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Abstract: - The Optimized geometries of all the four isomers of Guanine-water complexes have been obtained at B3LYP/6-311++G(d,p), X3LYP/6-311++G(d,p), B3PW91/6-311++G(d,p) levels. Structural parameters of the optimized geometries, total energies and the APT charges of guanine-water complex have been computed. Frequency calculations are carried out on each optimized structure and their IR and Raman spectra have been discussed. The calculated frequencies of the guanine are found to be in good agreement with the experimental values in the most of the cases.

Key words: MP2, DFT, B3LYP, Optimized geometry.

I. Introduction

Guanine is one of the five main nucleobases found in the nucleic acids DNA and RNA. Guanine is a derivative of purine, consisting of a fused pyrimidine-imidazole ring system with conjugated double bonds. Being unsaturated, the bicyclic molecule is planar. The guanine nucleoside is called guanosine.The first isolation of guanine was reported in 1844 by the German chemist Julius Bodo Unger (1819–1885), who obtained it as a mineral formed from the excreta of sea birds, which is known as guano and which was used as a source of fertilizer; guanine was named in 1846. In both DNA and RNA, guanine is one of the most important nucleic acid bases. In addition to being the largest nucleic acid bases, it has also the most complex tautomeric equilibria [1-3]. The property of amino tautomers of guanine has been discussed in several recent works [4–8]. The interaction between guanine and one water molecules [9] or two [10] can influence the NH2-nonplanarity phenomena and this has been discussed for the cyclic complex where water acts as a proton donor towards the carbonyl bond while accepting a proton from the vicinal NH bond of guanine. In a recent work [11], the optimized geometries, harmonic vibrational frequencies and energies of four cyclic structures of monohydrated guanine have been computed using density functional theory (DFT) combined with the 6-311G(d,p) basis set. In these calculations, only the amino group hydrogen atoms were considered as having a nonplanar structure. In the present work, the same parameters are calculated with geometry optimization and vibrational assignment using density functional theory (DFT) B3LYP, X3LYP and B3PW91 method employing 6-311++G (d,p) as the basis set.

II. Computational methods

The ground state geometries and vibrational spectra for free guanine and its hydrogen-bonded complexes with molecules of water have been optimized. The total energies, structural parameters of the optimized geometries parameters (bond length and bond angles) the APT charges, IR intensity, Raman activity and ring breathing vibration of have been computed using density functional theory (DFT) B3LYP, X3LYP and B3PW91 method employing 6-311++G (d,p) as the basis set. For theoretical study, we have used GAUSSIAN 09 [12] package of programs. The geometries were optimized by minimizing the energies without imposing any constraint on the geometry. It has well known that this level of theory is sufficient to reliably predict molecular geometries hydrogen bonded systems. The geometry of the free guanine and guanine -water complex have been fully optimized by the density functional theory (DFT) B3LYP, X3LYP and B3PW91 method employing 6-311++G (d,p) as the basis set for the first time. The optimized geometrical parameters (bond length and bond angles), total energies [13], ring breathing vibration $\upsilon 1$, IR intensity, Raman activity and dipole moment have been calculated for guanine and guanine -water complexes and compared. The optimized structure of free guanine and guanine -water isomers at B3LYP/6-311++ G (d,p) along with atomic numbering have been shown in Figure 1and Figure 2 (I-IV) respectively.

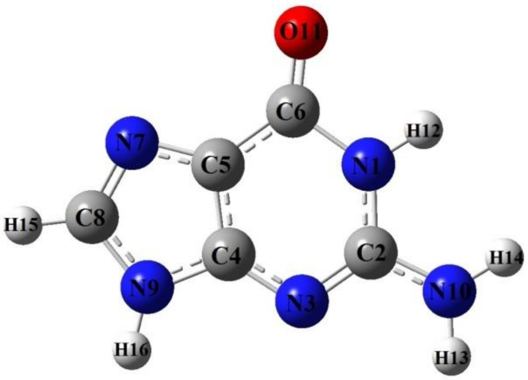
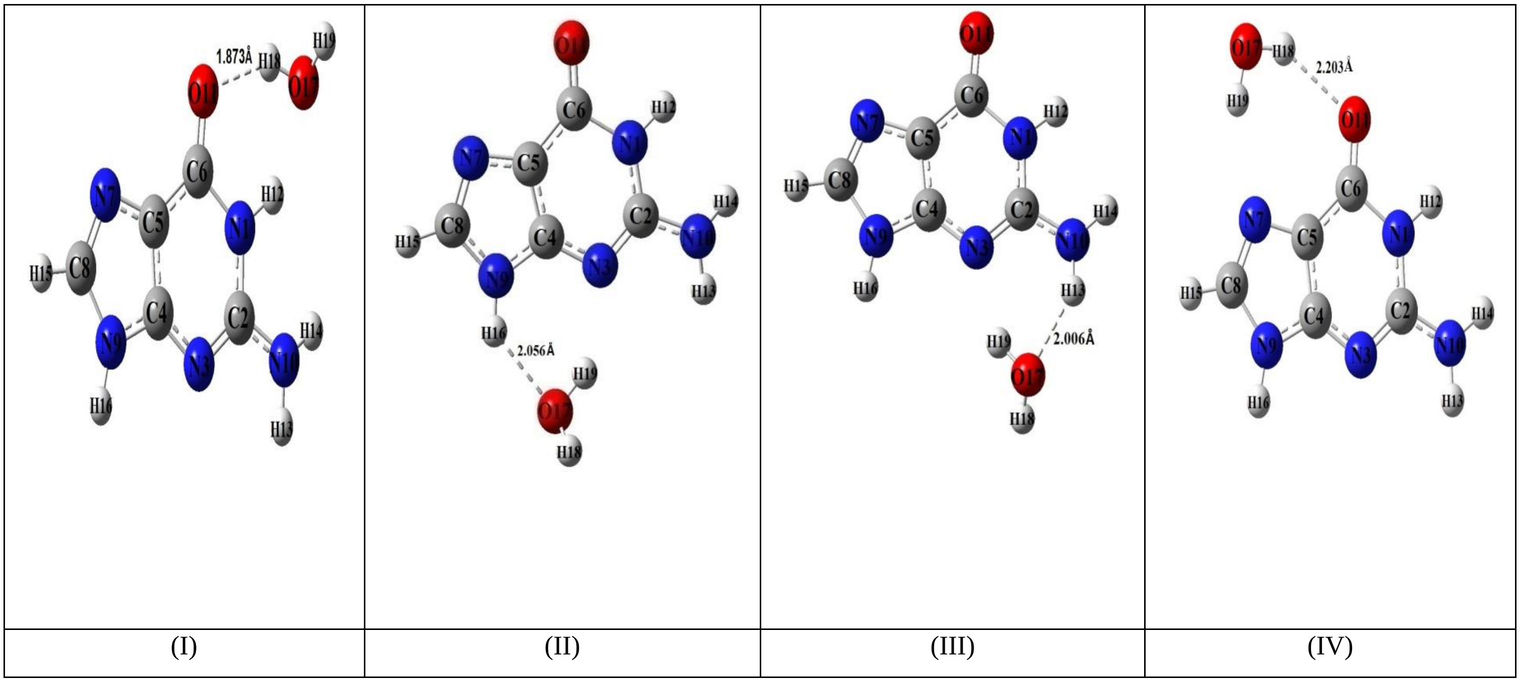


Figure 1: Optimized structure of guanine at B3LYP/6-311++G (d,p)



(I) (II) (III) (IV)

Figure 2: (I-IV): Optimized structure of four stable isomers of guanine -water complexes obtained at B3LYP/6-311++G (d,p) level.

III. Result and Discussions

Molecular Geometry:

The calculated optimized molecular energies, zero point vibrational energies, dipole moments and thermodynamic functions usingB3LYP, X3LYP and B3PW91 methods with 6-311++G(d,p) basis sets for all the four conformers of free guanine and guanine-water complexes are shown in Table 1. As the total optimized energy is lowest for Isomer I, it will be the most stable conformer. The optimized structures of all the four conformers using B3LYP with 6-311++G(d, p) are shown inFigure 2.The dipole moment of Isomer I is found to be smallest and that of Isomer IV is largest, therefore Isomer IV is more polar than any other conformer.

The calculated bond lengths and bond angles Isomer I using DFT method with B3LYP, X3LYP and B3PW91functionals in conjunction with 6-311++G(d,p) basis set are reported along with the corresponding experimental values [14] in Table 2. We see that thecalculated bond lengths are very close to experimental values while calculated using B3PW91/6-311++G(d,p) andbond angles are very close to experimental values while calculated using B3LYP/6-311++G(d,p). The APT (atomicpolarizability tensor) charges at various atomic sites of Isomer IcalculatedusingDFT functionalsB3LYP, X3LYP, B3PW91 along with 6-311++G(d,p) basis set are shown in Table 3.

Table 1: Calculated energies, zero-point vibrational energy, dipole moment and thermodynamic functions of the guanine and guanine-water conformers at DFT methods.

S.No.	Species	Total energies E(hartree)	Zero-point Vibrational energy(J/mol)	Dipole moment (Debye)	Constant volume molar heat capacity (Cv) (cal/mol K)	Entropy (cal/mol K)
	B3LYP/6-311++G(d,p)					
1.	**Guanine**	-542.70946850	301335.5	7.0617	31.695	93.389
	Guanine-Water					
2.	**Isomer I**	-619.19024690	370987.4	5.2659	42.194	102.923
3.	**Isomer II**	-619.18594430	370370.4	7.4220	42.515	103.892
4.	**Isomer III**	-619.18552542	370179.2	6.0582	42.478	103.948
5.	**Isomer IV**	-619.18414727	367405.9	10.4876	41.808	105.923
	X3LYP/6-311++G (d,p)					
1.	**Guanine**	-542.48940914	303421.1	6.9744	31.656	88.191
	Guanine-Water					
2.	**Isomer I**	-618.93883312	371900.4	5.2617	42.085	102.751
3.	**Isomer II**	-618.93448025	371294.5	7.4553	42.409	103.698
4.	**Isomer III**	-618.93404060	371099.1	6.0859	42.371	103.772
5.	**Isomer IV**	-618.93261141	368422.4	10.5122	41.669	105.571
	B3PW91/6-311++G (d,p)					
1.	**Guanine**	-542.50130360	304765.2	6.9946	31.570	88.149
	Guanine-Water					
2.	**Isomer I**	-618.94824072	373493.9	5.3322	41.892	102.361
3.	**Isomer II**	-618.94356678	372555.6	7.6722	42.365	103.817
4.	**Isomer III**	-618.94336777	372807.2	5.9785	42.151	103.498
5.	**Isomer IV**	-618.94239055	372199.5	10.2058	42.926	106.867

Total energies (Hartree) for free Guanine and Guanine-Water complexes:

Table 1 shows energies of free guanine and guanine -water complexes. From Table 1 we see that stability of guanine molecule increases when we use DFT method B3LYP than the DFT method X3LYP and B3PW91 and 6-311++G(d,p) basis set. Also in four isomers of guanine-water complexes, the isomer 1 is most stable having least optimized energy while isomers 2 and 3 are always higher in energies and very similar energies. Isomer 4 has highest energy among all isomers as weak hydrogen bond is involved in this isomer. We also see that asguanine-water complex is more stable than the free guanine molecule.

Table 2: Theoretical bond lengths (angstroms) and bond angles (degrees) of guanine and guanine- water complexes compared with experimental data [Ref.] of guanine.

Parameters[a]	Exptl.[b]	Theoretical					
		B3LYP/6-311++G (d,p)		X3LYP/6-311++ G (d,p)		B3PW91/6-311++ G (d,p)	
		Guanine	Isomer I	Guanine	Isomer I	Guanine	Isomer I
			Bond lengths (Å)				
N1-C2	1.371	1.367	1.367	1.370	1.367	1.367	1.363
C2-N3	1.315	1.304	1.312	1.310	1.311	1.309	1.310
N3-C4	1.364	1.359	1.352	1.354	1.351	1.351	1.349
C4-C5	1.392	1.374	1.394	1.393	1.394	1.392	1.393
C5-C6	1.405	1.425	1.432	1.436	1.431	1.435	1.429
C5-N7	1.405	1.387	1.381	1.380	1.380	1.376	1.376
N7-C8	1.319	1.292	1.303	1.303	1.302	1.302	1.302
C8-N9	1.369	1.387	1.385	1.385	1.385	1.380	1.380
N9-C4	1.364	1.354	1.368	1.368	1.368	1.365	1.365
C2N10	1.333	1.348	1.371	1.361	1.369	1.358	1.367
C6-O11	1.239	1.221	1.227	1.213	1.226	1.212	1.226
N1-H12	-	0.995	1.023	1.012	1.023	1.011	1.025
N10-H13	-	0.990	1.008	1.005	1.008	1.005	1.008
N10-H14	-	0.989	1.008	1.004	1.008	1.003	1.007
C8-H15	-	1.063	1.079	1.079	1.079	1.081	1.081
N9-H16	-	0.990	1.008	1.008	1.008	1.008	1.008
O17-H12	-	-	1.934	-	1.924	-	1.904
O11-H18	-	-	1.873	-	1.865	-	1.852
			Bond angles (Degree)				
N1-C2-N3	124.6	122.7	123.7	123.3	123.7	123.4	123.8
C2-N3-C4	111.9	114.0	112.6	112.8	112.6	112.6	112.4
N3-C4-C5	127.6	127.4	128.8	129.2	128.8	129.4	129.1
C4-C5-C6	119.2	119.3	118.3	118.7	118.3	118.5	118.1
C5-C6-N1	111.9	110.5	110.5	109.5	110.6	109.5	110.6
C6-N1-C2	124.6	125.8	125.7	126.5	125.8	126.7	125.9
N1-C2-N10	115.3	117.5	116.6	117.4	116.6	117.4	116.7
N10-C2-N3	120.0	119.6	119.5	119.3	119.5	119.2	119.4
N1-C6-011	120.4	118.7	119.5	119.0	119.6	119.0	119.5

011-C6-C5	127.7	130.6	129.8	131.4	129.8	131.5	129.8
C6-C5-N7	131.2	130.8	130.8	130.5	130.8	130.5	130.9
N7-C5-C4	109.6	109.8	110.8	110.8	110.8	110.9	110.9
C5-C4-N9	106.1	105.9	104.9	104.9	104.9	104.8	104.8
C4-N9-C8	107.0	106.2	106.7	106.8	106.7	106.8	106.8
N9-C8-N7	113.0	111.5	112.7	112.6	112.7	112.8	112.8
C8-N7-C5	104.2	105.7	104.7	104.8	104.7	104.7	104.6
N3-C4-N9	126.2	126.6	126.1	125.9	126.2	125.8	126.1

[a] See Fig. 1 for atom numbering.

[b] Ref. [14]

Structural parameters:

The calculated optimized geometrical parameters namely bond lengths(in Å) and bond angles (in Degree) of the guanine and guanine-water complexes Isomer I using DFT method B3LYP, X3LYP and B3PW91 and 6-311++G(d,p) basis set are reported along with the corresponding experimental values [14] in Table 2. We see that thecalculated bond lengths are very close to experimental values while calculated using B3LYP/6-311++G(d,p) and bond angles are very close to experimental values while calculated using B3PW91/6-311++G(d,p). The APT (atomic polarizability tensor) charges at various atomic sites of Isomer I using DFT method B3LYP, X3LYP, B3PW91and 6-311++G(d,p) basis set are shown in Table 3.

Atomic Polar Tensor (APT) charges:

The atomic polar tensor (APT) charges for the free guanine and guanine-water complexes computed at DFT method B3LYP, X3LYP and B3PW91 and 6-311++G(d,p) basis set are collected in Table (3.1-3.3).Also the APT charges for free guanine and Isomer 1 (most stable isomer) of guanine-water complexes at B3LYP /6-311++ G (d,p) level are collected in Table 3.1. For atomic numbering scheme, see Figures 1 and 2(a-d) respectively**.** In term of the electron charge 1e =1.602188x10^{-19}C. From Tables 3.1, we see that due to high negative charges on respective atoms compared to the other atoms results enhancement of the bond length. In free guanine we see that the bond length of the magnitudes of the bond lengths between the pairs (C6=O11) and (C2=N10) are found to be differed due as O11 is more negative than the N10. Thus N10 attracts more to C atom than O11 which gives difference in their bond lengths. Hence the bond length of (C6=O11) is shorter than the bond length of (C2=N10). Similarly, with the help of APT charges we can explain the difference in the bond length of others pairs e.g. C2N1& C6N1; C4C5 & C5C6.

Table 3.1: APT Charges at various atomic sites of guanine and guanine -water complexes at B3LYP /6-311++G (d,p) Level

Atoms	**Guanine**	**Guanine-Water**			
		Isomer I	**Isomer II**	**Isomer III**	**Isomer IV**
N1	-0.658	-0.723	-0.669	-0.673	-0.662
C2	1.222	1.165	1.144	1.179	1.211
N3	-0.864	-0.840	-0.851	-0.908	-0.861
C4	0.694	0.672	0.603	0.674	0.698
C5	-0.294	-0.285	-0.250	-0.276	-0.282
C6	1.227	1.253	1.252	1.258	1.253
N7	-0.349	-0.359	-0.385	-0.357	-0.394
C8	0.184	0.189	0.207	0.179	0.201

N9	-0.412	-0.412	-0.446	-0.394	-0.412
N10	-0.880	-0.811	-0.794	-0.879	-0.882
O11	-0.889	-0.998	-0.896	-0.895	-0.929
H12	0.204	0.357	0.206	0.204	0.208
H13	0.246	0.231	0.223	0.339	0.249
H14	0.245	0.230	0.224	0.225	0.246
H15	0.076	0.073	0.074	0.074	0.083
H16	0.249	0.252	0.359	0.246	0.256

Table 3.2: APT Charges at various atomic sites of guanine and guanine-water complexes at X3LYP/6-311++G (d,p) Level

Atoms	Guanine	Guanine-Water			
		Isomer I	Isomer II	Isomer III	Isomer IV
N1	-0.662	-0.727	-0.674	-0.677	-0.666
C2	1.215	1.172	1.152	1.187	1.217
N3	-0.864	-0.846	-0.856	-0.914	-0.866
C4	0.684	0.676	0.606	0.678	0.702
C5	-0.281	-0.288	-0.253	-0.280	-0.285
C6	1.250	1.260	1.259	1.264	1.259
N7	-0.357	-0.360	-0.387	-0.358	-0.396
C8	0.180	0.191	0.208	0.180	0.202
N9	-0.403	-0.415	-0.449	-0.397	-0.415
N10	-0.882	-0.816	-0.798	-0.885	-0.886
O11	-0.898	-1.004	-0.900	-0.899	-0.934
H12	0.203	0.360	0.208	0.205	0.210
H13	0.246	0.233	0.224	0.342	0.251
H14	0.243	0.231	0.225	0.226	0.248
H15	0.074	0.074	0.074	0.075	0.084
H16	0.252	0.254	0.361	0.248	0.258
O17	-	-0.731	-0.694	-0.712	-0.669
H18	-	0.461	0.276	0.273	0.333
H19	-	0.276	0.418	0.441	0.353

Table 3.3: APT Charges at various atomic sites of guanine and guanine-water complexes at B3pw91/6-311++G (d,p) Level

Atoms	Guanine	Guanine-Water			
		Isomer I	Isomer II	Isomer III	Isomer IV
N1	-0.656	-0.730	-0.669	-0.672	-0.655
C2	1.203	1.159	1.141	1.175	1.146
N3	-0.854	-0.836	-0.851	-0.909	-0.831
C4	0.673	0.665	0.595	0.666	0.665
C5	-0.275	-0.281	-0.247	-0.275	-0.260
C6	1.235	1.244	1.245	1.253	1.232
N7	-0.356	-0.360	-0.386	-0.357	-0.404
C8	0.175	0.185	0.203	0.177	0.199
N9	-0.398	-0.410	-0.446	-0.392	-0.405
N10	-0.882	-0.813	-0.797	-0.885	-0.816
O11	-0.889	-0.998	-0.891	-0.898	-0.915
H12	0.204	0.372	0.209	0.206	0.214
H13	0.248	0.234	0.225	0.348	0.236
H14	0.245	0.233	0.227	0.228	0.231
H15	0.074	0.074	0.075	0.075	0.085
H16	0.253	0.255	0.367	0.250	0.260
O17	-	-0.735	-0.694	-0.718	-0.664
H18	-	0.275	0.274	0.272	0.325
H19	-	0.465	0.421	0.450	0.358

Table 4: Infrared Intensities and Raman Scattering Activities of guanine and guanine - water at B3LYP /6-311++G (d,p) Level

Calculated Wave numbers (cm^{-1})						Approximate description of vibration
Guanine			Guanine water (Isomer I)			
Wavenumbers	IR Int.	Raman Activity	Wavenumbers	IR Int.	Raman Activity	
3757	64	51	3889	85	118	ν (NH)
3646	77	148	3697	50	55	ν (NH)
3628	122	186	3645	79	147	ν (NH)
3590	36	77	3585	86	191	ν (NH)
3242	642	34	3528	0	131	δ(NH)
1609	348	87	1761	756	38	δ(NH)

1553	68	18	1630	201	7	Ring breathing
1065	16	8	1309	0	22	r(NH)
525	0	3	680	49	0	ω(NH)
489	1	5	658	0	0	ω(NH)
320	2	1	502	160	3	τ (NH)

Abbreviations used: ν-stretching, δ-In-plane-deformation, γ–Out-of-plane-bending, r-rocking , ω-wagging, τ-Twisting

IV. Conclusions

Our DFT Calculations show that the energy of the free guanine is obtained and energies of four guanine -water complexes is obtained as and .from this result, isomer I is most stable than other isomers. The hydrogen bond formed between O17-H12,O11-H18 in isomer I is 1.934 and 1.873,O17-H16 in isomer II is 2.056,O17-H13 in isomer III is 2,006 and O11-H19 in isomer IV is 2.202 respectively. The hydrogen bond obtained in each Isomer indicates that isomer I is more stable than other isomers. The APT charges at various atomic sites of guanine -water complexes at B3LYP /6-311++G (d,p) level shows that APT charges of isomer I is decreases in some atoms and increases in some atoms but in case of N9 it is same.

Zero-point Vibrational energy, Dipole moment, Constant volume molar heat capacity and Entropy also calculated for guanine and guanine -water complexes(Listed in Table1) for isomer I, isomer II and isomer III almost same but significant changes will occurred in case of isomer IV. Our vibrational assignments are in good agreement with experimental data. Comparison of some modes of vibrational frequency of guanine and guanine -water complexes listed in table 4, significant changes will be occurred in stretching, rocking, wagging, twisting, in plane deformation and ring breathing mode frequencies.

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