

Study of the Hydrogen Bond in Different Orientations of Adenine-Thymine

Base Pair: Ab initio Study

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Abstract

Theoretical *ab initio* calculations have been performed to determine the properties of hydrogen bonds in adenine and thymine base pairs in gas phase in nine (9) different orientations. In order to gain deeper insight into structure, charge distribution and energies of A-T base pairs, we have performed quantum chemical *ab initio* and density functional calculations at the HF and B3LYP levels with 3-21G*, 6-31G*, 6-31G** and 6-31++G** basis sets. (Table 3)

The calculated donor acceptor atom distance Watson – Crick A-T base pairs are in good agreement with the experimental mean values obtained from an analysis of 21 high resolution DNA structures.

In addition for further correction about interaction energies between adenine and thymine, the basis set super position error (BSSE), associated with the hydrogen bond energy has been computed via the counterpoise method, using the individual bases as fragments.

In Watson-Crick A-T base pair there is a good agreement between theory and experimental results. The distances for (N₂...H₂₃-N₁₉), (N₈-H₁₃...O₂₄) and (C₁...O₁₈) are 2.84, 2.94 and 3.63 respectively in B3LYP/6-31G** level in good agreement with experimental results (2.82, 2.98 and 3.52 Å).

Interaction energy of Watson Crick A-T base pair is -13.90 and -10.24 kcal/mol in B3LYP/6-31G** and HF/6-31G** levels. The interaction energy of model (9) A-T base pair is larger than

others, – 18.28 and –17.26 kcalmol⁻¹, and for model (2) is the smallest value, –13.53 and –13.03 kcalmol⁻¹ in B3LYP/6-31G** and B3LYP/6-31++G** levels respectively. The computed B3LYP/6-31G** bond enthalpies for Watson–Crick AT pairs of –14.4 kcalmol⁻¹ agree well with the experimental results of –12.1 kcalmol⁻¹ [11], deviating by as little as –2.3 kcalmol⁻¹. The basis set super position error (BSSE) of some cases is large (9.85 kcalmol⁻¹), and some is quite small (0.6 kcalmol⁻¹)

Introduction

The interaction between nucleotide bases is an important element in structure of DNA consequently. These interactions act with hydrogen bonding between base pairs [2]. Apart from providing water with physical properties that make it the ideal medium for many processes of life to take place in, it is responsible for various types of self-organization and molecular recognition, such as the folding of proteins. In 1953, Watson and Crick [24] using data from other people labs build a model of DNA. This model involve pairing the nucleic base adenine with thymine and cytosine with guanine. They showed that the fundamental unite of DNA involves the helical intertwining of two chains held together by hydrogen bonds through the pairings of A-T and C-G (Scheme1). The adenine and guanine are purine and thymine and cytosine are pyrimidine. In the past decade, *ab initio* and DFT quantum chemical studies [3] have appeared on the geometry, energy and other aspects of the hydrogen bonds that hold together AT and GC pairs. The adequacy of DFT for hydrogen-bonded systems has received much attention lately [4]. It is known from the investigations of sim et al [4a]. They found that the DFT results are of comparable quality to those from correlated *ab initio* methods. Others [3c,j-l] have shown that this is also true for the corresponding structures minor but signification deviations from experimental values were obtained with both DFT and *ab initio* methods. C. F. Guerra and others [5,6] have shown that these structural deviations are a result of intermolecular interactions of the base pairs with the environment in the crystal.

J. Maranon and co-workers^[7] obtained the geometry of the adenine–thymine DNA base pair (A-T) molecule, (Scheme 1) in molecular dynamic simulations using Gaussian 94 package^[8]. The geometry of A-T base pair was optimized with the restriction that both molecules can only move over the same plane. The *ab initio* calculations were carried out by using HF/3-21G* level. As results of this calculate it is obtained that the lengths of hydrogen were $d(N_2...H_{23}-N_{19}) = 0.2796\text{nm}$ and $d(N_8-H_{13}-O_{24}) = 0.2988\text{nm}$ ^[7]. J. Maranon and co-workers^[7] studied a MD simulation of the double hydrogen bonds of the adenine-thymine in water and simulate each hydrogen bond of the base pair by two covalent bonds and use an adequate value of the van der Waals parameters in order to give a good simulation of the hydrogen bond. Also structural geometries and energies of A-T carried out by HF/6-31G** and B3LYP/6-31G** base by Meyer and Sohnel^[3].

In this work we try to calculate geometries, energies and atomic charges of the hydrogen bonds in the Watson – Crick DNA base pairs and other different orientations of A-T base pairs, (see Figure 1) with *ab initio* and DFT quantum chemical studies.

In the present paper we address a different point. Whereas both density functional and *ab initio* methods satisfactorily reproduce experimental A-T hydrogen bond distance and interaction energies in different states of A-T base pairs. We try to calculate geometries, energies enthalpies and atomic charges of the hydrogen bonds in the Watson-Crick DNA base pair and other different orientations of A-T base pairs, (see Figure 1) with *ab initio* and DFT quantum chemical studies.

Density functional quantum chemical calculations have recently provided a relatively consistent picture on base pair interaction energies and geometries, we have performed calculations of this type for the A-T base pairs. This can lead more detailed information on structure, charge distribution and energetic of the base pair as compared to the simple iso-sterism concept.

The enthalpies of A-T base pair in nine different orientations calculated in B3LYP/6-31G* and B3LYP/6-31G** and HF/6-31G** levels with frequency calculations in these levels.

Methods

Ab initio calculation at the HF/3-21G*, HF/6-31G*, HF/6-31G** and density functional theory (DFT) studies at the B3LYP/3-21G*, B3LYP/6-31G*, B3LYP/6-31G** and B3LYP/6-31++G** levels were carried out to determine the complex structures with the Gaussian 98 program [9].

The interaction energies were corrected for the basis set super position error (BSSE) by the standard counterpoise method approach [10].

Ab initio interaction energies were evaluate using HF/3-21G*, HF/6-31G*, HF/6-31G** optimized geometries and density functional theory B3LYP/3-21G*, B3LYP/6-31G*, B3LYP/6-31G** and B3LYP/6-31++G** levels. The counterpoise correction method (CP) calculated according to equation (1).

$$\Delta E_{BSSE} = E(AB, r_c)^{AB} - E(A, r_e) - E(B, r_e) + E^{DEF} \quad (1)$$

$$\text{With} \quad E^{DEF} = [E(A, r_e) - E(A, r_c)^{AB}] + [E(B, r_e) - E(B, r_c)^{AB}]$$

The deformation energy E^{DEF} is defined as the energy difference between the geometry optimized monomers and the structures of the monomers adopted in the complex.

The label r_c is used here to indicate the geometry of the product complex AB while r_e indicate the geometry of the separate reactants.

Adenine-Thymine (A-T) complex was studied both in the Watson – Crick and eight different orientations (Figure1).

Mean values of intermolecular donor acceptor atom distance of A-T pairs in the Watson –Crick have been determined from 21 DNA structures with a resolution better than 1.5 Å using the program HB explore^[1] for comparison between experiment and calculated data .

The frequencies of A-T in the Watson –Crick and eight different orientations was calculated in B3LYP/6-31G**, B3LYP/6-31G* and HF/6-31G** levels.

Bond enthalpies (ΔH_{298}) were obtained from frequency calculations at 298K and 1atm assuming an ideal gas with equation (2) :

$$\Delta H_{298} = \sum (E_0 + H_{Corr})_{Product} - \sum (E_0 + H_{Corr})_{reactants} \quad (2)$$

With $H_{Corr} = E_{total} + k_B T$

and $E_{total} = E_{trans} + E_{rot} + E_{vib} + E_{elec}$

Here E_0 is total electronic energy of monomers and dimer and H_{Corr} is thermal correction for enthalpy .And also E_{trans} , E_{rot} , E_{vib} and E_{elec} are the translational, rotational , zero point vibrational energy and electronic energies based on our frequency calculations. The basis set super position error (BSSE), associated with the hydrogen bond energy, has been computed by the counterpoise method ^[10], by using the individual bases as fragments.

Results and discussions

The results obtained give a clearly picture of the differences between different orientations of A-T base pairs. Nevertheless we discuss briefly a methodological aspect of the calculations first and then proceed with a discussion of the basic results without reiterating statements on the finer details of approximations and methods. The results of our B₃LYP and HF study on the formation of the adenine-thymine complexes are summarized and compared with literature in Table 1 (geometries), and 2(energies). Scheme1 defines the proton donor acceptor distance used throughout this work.

The computed B3LYP/6-31G** bond enthalpies for Watson –Crick AT pairs of -14.4 kcal mol⁻¹ agree well with the experimental results of -12.1 kcalmol⁻¹ ^[11], deviating by as little as -2.3 kcalmol⁻¹ (see Table 2). The basis set super position error (BSSE) of some cases is large

(9.85 kcalmol⁻¹), and some is quite small (0.6 kcalmol⁻¹). Comparison of the hydrogen bond enthalpies (ΔH_{298}) from *ab initio* and DFT calculations are shown in figure 4.

The distance for (N₂...H₂₃-N₁₉), (N₈-H₁₃...O₂₄) and (C₁...O₁₈) for A-T Watson –Crick base pair are 2.84, 2.94 and 3.63Å respectively in B3LYP/6-31G** level, in good agreement with experimental results (2.82, 2.98 and 3.52 Å)^[1].

It turns out that the DFT (B3LYP/6-31G**) distances are in excellent agreement with the experimental data, whereas HF distances are somewhat too long (Table1). For other models of A-T base pair result in different levels summarize in Table (1). Therefore we have to conclude that, at least for the hydrogen bonded systems studied in this work, density functional calculations give similar or even better results than the conventional *ab initio* studies.

The interaction energy of model (9) A-T base pair is larger than others, - 18.28 and -17.26 kcalmol⁻¹, and for model (2) is the smallest value, -13.53 and -13.03 kcalmol⁻¹ B3LYP/6-31G** and B3LYP/6-31++G** levels respectively. Comparison of the hydrogen bond energies, ΔE_{BSE} and ΔE from *ab initio* and DFT calculations are shown in figure 5,6

The Hartree Fock approach (HF) yields distances that are up to 0.15 Å longer than DFT values. In general the intermolecular distances determined with density functional theory are somewhat shorter as compared to HF optimizations.

The deformation of the bases (changes in bond lengths larger than 0.003 Å) caused by the formation of the hydrogen bonds is shown in Figure 2. All the N-H bonds that participate in hydrogen bonding expand by 0.011-0.036 Å .the largest elongations are found for the N₁₉-H₂₃ of thymine in A-T (2) orientation and the smallest are found for N₈-H₁₂ of adenine. The C=O distances of oxygen atoms involved in hydrogen bonding increase by some 0.018 Å .

Atomic charges of A-T base pairs are shown in Figure 3. The small interaction energy between A and T is also reflected in the electron distribution at the atoms involved in hydrogen bonding and the corresponding charges (Figure 3). It turns out to be the case, as can be seen from Figure 3, which display the atomic charges for the separate, noninteracting bases: All proton acceptor atoms have a negative charge whereas the corresponding proton they face are all positively charged.

The results obtained give the intermolecular ($H_{14}...O_{18}$) distance in A-T (9) 1.811 Å in B3LYP/6-31G** level, and show that with reduced interaction energies in different models of A-T increase the intermolecular ($H...O$) distance (Table 2 and 3).

Conclusions

We have unraveled a hitherto unresolved discrepancy between theoretical and experimental hydrogen bond lengths and energies in Watson-Crick and other different orientations. Our results clearly show that A-T base pairs select different geometries that vary in energy and structures. This difference is a reason of various hydrogen bonds between O, N and H atoms. In general the results obtained in B3LYP/6-31G** are in well agreement with experimental values. It turns out that the B3LYP/6-31G** distances are in excellent agreement with the experimental data, whereas HF distances are somewhat too long.

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Base pairs	HF/3-21G*	HF/6-31G*	HF/6-31G**	B3LYP/3-21G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-31++G**
A-T (1)							
Exp. ^[1]							
r(H ₁₃ ...O ₂₄)	1.971	2.075	2.087	1.822	1.928	1.921	1.920
r(N ₂ ...H ₂₂)	1.747	1.979	1.976	1.611	1.831	1.799	1.828
r(H ₄ ...O ₁₈)	2.574	2.981	2.963	2.497	2.849	2.804	2.863
r(N ₈ ...O ₂₄) (2.98)	2.973	3.071	3.081	2.856	2.948	2.940	2.939
r(N ₂ ...N ₁₉) (2.82)	2.779	2.994	2.990	2.690	2.876	2.848	2.875
r(C ₁ ...O ₁₈) (3.52)	3.419	3.787	3.775	3.363	3.672	3.633	3.684
∠(N ₈ H ₁₃ O ₂₄)	172.1	172.9	172.9	174.2	174.5	174.6	174.1
∠(H ₁₃ O ₂₄ C ₂₀)	124.3	126.4	126.3	122.8	124.5	124.5	125.8
∠(N ₂ H ₂₂ N ₁₉)	178.1	178.0	178.8	178.1	179.7	179.7	179.4
∠(H ₂₃ N ₂ C ₁)	115.2	117.0	116.6	116.3	117.8	117.5	117.3
A-T (2)							
r(H ₁₃ ...O ₁₈)	1.972	2.087	2.092	1.839	1.949	1.944	1.943
r(N ₂ ...H ₂₂)	1.745	1.985	1.978	1.606	1.834	1.796	1.818
r(H ₄ ...O ₂₄)	2.571	2.981	2.964	2.473	2.833	2.776	2.825
r(N ₈ ...O ₁₈)	2.973	3.082	3.086	2.870	2.967	2.961	2.960
r(N ₂ ...N ₁₉)	2.778	2.998	2.991	2.686	2.878	2.844	2.866
r(C ₁ ...O ₂₄)	3.419	3.970	3.777	3.346	3.660	3.610	3.651
∠(N ₈ H ₁₃ O ₁₈)	171.7	172.7	172.7	173.4	174.2	174.1	173.9
∠(H ₁₃ O ₁₈ C ₁₆)	123.1	124.8	124.7	121.3	122.4	122.1	122.0
∠(N ₂ H ₂₂ N ₁₉)	178.0	177.8	177.0	178.7	178.8	179.1	178.8
∠(H ₂₃ N ₂ C ₁)	114.3	116.1	115.9	115.3	116.8	116.5	116.5
A-T (3)							
r(H ₁₃ ...O ₁₈)	1.846	2.001	2.011	1.727	1.877	1.869	1.876
r(N ₂ ...H ₂₂)	1.881	2.039	2.047	1.732	1.896	1.875	1.887
r(N ₈ ...O ₁₈)	2.855	3.001	3.009	2.766	2.900	2.891	2.898
r(N ₂ ...N ₁₉)	2.904	3.048	3.054	2.795	2.934	2.914	2.926
∠(N ₈ H ₁₃ O ₁₈)	175.6	175.8	176.4	176.7	176.9	177.1	176.6
∠(H ₁₃ O ₁₈ C ₁₆)	123.8	123.9	123.5	122.2	122.1	121.0	122.7
∠(N ₂ H ₂₂ N ₁₉)	177.2	177.5	177.8	178.0	178.6	178.7	178.6
∠(H ₂₃ N ₂ C ₁)	119.5	120.4	120.6	120.6	121.2	121.1	120.6
A-T (4)							
r(H ₁₂ ...O ₂₄)	2.018	2.148	2.148	1.871	1.959	1.964	1.965
r(N ₁₁ ...H ₂₂)	1.726	1.954	1.950	1.599	1.804	1.779	1.791
r(N ₈ ...O ₂₄)	3.01	3.136	3.135	2.895	2.970	2.973	2.974
r(N ₁₁ ...N ₁₉)	2.751	2.964	2.959	2.668	2.844	2.821	2.836
r(H ₁₅ ...O ₁₈)	2.518	2.915	2.907	2.432	2.802	2.756	2.791
r(C ₁₀ ...O ₁₈)	3.245	3.594	3.588	3.185	3.492	3.453	3.483
∠(N ₈ H ₁₃ O ₂₄)	172.6	170.0	170.0	171.8	170.3	170.1	170.1
∠(H ₁₅ O ₂₄ C ₂₀)	130.8	132.0	132.0	129.9	131.7	131.2	131.9
∠(N ₁₁ H ₂₂ N ₁₉)	172.6	175.1	175.2	172.7	174.1	174.6	174.9
∠(H ₂₃ N ₁₁ C ₁₀)	117.7	118.6	118.5	118.3	119.7	119.5	119.5
A-T (5)							
r(H ₁₂ ...O ₁₈)	2.008	2.155	2.155	1.882	1.987	1.988	1.985
r(N ₁₁ ...H ₂₂)	1.720	1.951	1.946	1.595	1.804	1.767	1.801
r(N ₈ ...O ₁₈)	3.008	3.144	3.143	2.907	2.996	2.996	2.993

Table
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Table (I). (Continued.)

Base pairs	HF/3- 21G*	HF/6- 31G*	HF/6- 31G**	B3LYP/3- 21G*	B3LYP/6- 31G	B3LYP/6- 31G*	B3LYP/6- 31++G**
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r(N ₁₁ ...N ₁₉)	2.747	2.961	2.956	2.665	2.844	2.811	2.845
r(H ₁₅ ...O ₂₄)	2.522	2.906	2.900	2.413	2.777	2.716	2.798
r(C ₁₀ ...O ₂₄)	3.247	3.590	3.586	3.171	3.473	3.421	3.492
∠(N ₈ H ₁₂ O ₁₈)	172.9	170.4	170.4	172.3	170.2	170.2	170.4
∠(H ₁₂ O ₁₈ C ₁₆)	129.5	130.6	130.5	128.1	129.0	128.5	129.9
∠(N ₁₁ H ₂₃ N ₁₉)	173.3	176.5	176.5	173.3	175.9	175.3	176.3
∠(H ₂₃ N ₁₁ C ₁₀)	117.3	117.6	117.6	117.7	118.7	118.6	118.4
A-T (6)							
r(H ₁₂ ...O ₁₈)	1.850	2.023	2.025	1.740	1.888	1.883	1.888
r(N ₁₁ ...H ₂₃)	1.888	2.072	2.070	1.737	1.906	1.891	1.989
r(N ₈ ...O ₁₈)	2.849	3.007	3.006	2.765	2.895	2.888	2.894
r(N ₁₁ ...N ₁₇)	2.908	3.079	3.076	2.796	2.940	2.925	2.933
∠(N ₈ H ₁₂ O ₁₈)	170.8	167.4	167.2	170.2	168.5	168.1	168.2
∠(H ₁₂ O ₁₈ C ₁₆)	132.2	130.9	130.8	130.3	129.9	129.6	129.0
∠(N ₁₁ H ₂₃ N ₁₇)	177.8	178.1	177.0	176.9	176.5	176.4	176.5
∠(H ₂₃ N ₁₁ C ₁₀)	122.3	122.8	122.9	122.0	123.5	123.5	123.3
A-T (7)							
r(H ₂₃ ...N ₁)	1.800	2.021	2.011	1.661	1.864	1.827	1.865
r(O ₂₄ ...H ₁₄)	1.822	1.995	1.996	1.712	1.854	1.838	1.850
r(N ₉ ...O ₂₄)	2.798	2.955	2.953	2.733	2.852	2.834	2.841
r(N ₁₉ ...N ₁)	2.829	3.032	3.020	2.733	2.905	2.871	2.908
r(O ₁₈ ...H ₄)	3.288	3.594	3.756	3.162	3.439	3.391	3.464
r(C ₁ ...O ₁₈)	3.917	4.197	4.184	3.813	4.056	4.014	4.084
∠(N ₉ H ₁₄ O ₂₄)	160.6	159.3	158.9	164.5	163.2	162.5	161.2
∠(N ₁₉ H ₂₃ N ₁)	176.1	175.1	174.9	177.2	176.8	176.7	175.8
∠(H ₁₄ O ₂₄ C ₂₀)	133.1	134.8	135.0	129.2	131.1	131.6	133.9
∠(H ₂₃ N ₁ C ₁)	128.1	129.6	129.2	129.2	130.9	130.4	129.6
A-T (8)							
r(H ₂₃ ...N ₃)	1.797	2.019	2.016	1.654	1.871	1.837	1.860
r(O ₁₈ ...H ₁₄)	1.829	2.002	2.002	1.730	1.879	1.864	1.872
r(N ₉ ...O ₁₈)	2.805	2.958	2.956	2.745	2.874	2.857	2.858
r(N ₁₉ ...N ₃)	2.826	3.027	3.024	2.725	2.911	2.879	2.902
r(O ₂₄ ...H ₄)	3.276	3.586	3.581	3.128	3.429	3.386	3.437
r(C ₁ ...O ₂₄)	3.903	4.196	4.192	3.788	4.049	4.012	4.064
∠(N ₉ H ₁₄ O ₁₈)	160.9	158.4	158.4	163.5	162.4	161.9	160.9
∠(N ₁₉ H ₂₃ N ₃)	175.9	173.7	173.8	176.4	175.7	175.7	174.5
∠(H ₁₄ O ₁₈ C ₁₆)	130.8	133.7	133.7	127.8	129.2	129.4	131.6
∠(H ₂₃ N ₃ C ₁)	127.0	128.3	128.2	128.1	129.9	129.5	128.4
A-T (9)							
r(H ₂₃ ...N ₃)	1.878	2.056	2.048	1.731	1.901	1.870	1.880
r(O ₁₈ ...H ₁₄)	1.773	1.950	1.948	1.668	1.822	1.803	1.811
r(N ₉ ...O ₁₈)	2.763	2.925	2.921	2.695	2.830	2.810	2.817
r(N ₁₇ ...N ₃)	2.900	3.063	3.055	2.793	2.937	2.908	2.918
∠(N ₉ H ₁₄ O ₁₈)	164.1	162.0	162.7	166.0	165.7	165.1	164.6
∠(N ₁₇ H ₂₃ N ₃)	175.9	176.7	176.6	175.0	177.3	177.4	177.3
∠(H ₁₄ O ₁₈ C ₁₆)	129.7	130.1	130.3	127.7	127.5	127.8	128.5
∠(H ₂₃ N ₃ C ₁)	131.7	133.5	133.3	131.9	133.9	133.7	133.4

Table (2). Calculated binding energy of A-T base pairs in various levels (in kcal mol⁻¹)

A-T (1)	Δ E	Δ E _{BSEF}	Δ H ₂₉₈
---------	-----	---------------------	--------------------

HF/3-21G*	-22.0	-14.05		
HF/6-31G*	-11.73	-10.02		
HF/6-31G**	-11.81	-10.24	-10.08	
B3LYP/3-21G*	-28.89	-19.32		$\Delta H_{\text{exp}}^* = -12.1^{[11]}$
B3LYP/6-31G*	-16.20	-13.47	-14.7	$\Delta \bar{H}_{298} = -12.75$
B3LYP/6-31G**	-16.44	-13.90	-14.4	
B3LYP/6-31++G**	-12.79	-13.35		
BP86/TZ2P ^[12]	-13.0	-12.3	-11.8	
A-T (2)	ΔE	ΔE_{BSSE}	ΔH_{298}	
HF/3-21G*	-21.98	-14.02		
HF/6-31G*	-11.65	-9.96		
HF/6-31G**	-11.73	-10.19	-10.03	$\Delta H_{\text{exp}}^{**}$
B3LYP/3-21G*	-28.46	-18.86		$\Delta \bar{H}_{298} = -12.78$
B3LYP/6-31G*	-15.76	-13.06	-14.3	
B3LYP/6-31G**	-15.98	-13.54	-14.0	
B3LYP/6-31++G**	-12.45	-13.03		
A-T (3)	ΔE	ΔE_{BSSE}	ΔH_{298}	
HF/3-21G*	-21.60	-15.86		
HF/6-31G*	-12.69	-11.69		
HF/6-31G**	-12.70	-11.86	-10.90	$\Delta H_{\text{exp}}^{**}$
B3LYP/3-21G*	-28.08	-21.04		$\Delta \bar{H}_{298} = -13.97$
B3LYP/6-31G*	-17.01	-15.33	-16.0	
B3LYP/6-31G**	-17.13	-15.64	-15.0	
B3LYP/6-31++G**	-14.11	-14.80		
A-T (4)	ΔE	ΔE_{BSSE}	ΔH_{298}	
HF/3-21G*	-23.06	-15.10		
HF/6-31G*	-12.36	-10.66		
HF/6-31G**	-12.41	-10.90	-10.69	$\Delta H_{\text{exp}}^{**}$
B3LYP/3-21G*	-29.99	-20.14		$\Delta \bar{H}_{298} = -13.60$
B3LYP/6-31G*	-16.76	-14.14	-15.2	
B3LYP/6-31G**	-16.97	-14.46	-14.9	
B3LYP/6-31++G**	-13.54	-14.19		
A-T (5)	ΔE	ΔE_{BSSE}	ΔH_{298}	
HF/3-21G*	-23.11	-15.18		
HF/6-31G*	-12.33	-10.64		
HF/6-31G**	-12.39	-10.88	-10.67	$\Delta H_{\text{exp}}^{**}$
B3LYP/3-21G*	-29.89	-20.02		$\Delta \bar{H}_{298} = -13.46$
B3LYP/6-31G*	-16.52	-13.88	-15.0	
B3LYP/6-31G**	-16.76	-14.28	-14.7	
B3LYP/6-31++G**	-13.35	-13.92		
A-T (6)	ΔE	ΔE_{BSSE}	ΔH_{298}	
HF/3-21G*	-20.51	-15.08		
HF/6-31G*	-11.51	-10.66		
HF/6-31G**	-11.49	-10.83	-9.72	$\Delta H_{\text{exp}}^{**}$
B3LYP/3-21G*	-27.29	-20.33		$\Delta \bar{H}_{298} = -12.81$
B3LYP/6-31G*	-15.92	-14.36	-14.9	
B3LYP/6-31G**	-15.97	-14.50	-13.8	
B3LYP/6-31++G**	-13.04	-13.82		

Table (2). (Continued.)

A-T (7)	ΔE	ΔE_{BSSE}	ΔH_{298}	
HF/3-21G*	-23.05	-16.85		
HF/6-31G*	-13.19	-11.90		
HF/6-31G**	-13.31	-12.11	-11.69	$\Delta H_{\text{exp}} = **$
B3LYP/3-21G*	-29.16	-21.72		$\Delta \bar{H}_{298} = -14.80$
B3LYP/6-31G*	-17.27	-15.25	-16.5	
B3LYP/6-31G**	-17.52	-15.65	-16.2	
B3LYP/6-31++G**	-14.48	-15.15		
A-T (8)	ΔE	ΔE_{BSSE}	ΔH_{298}	
HF/3-21G*	-23.0	-16.75		
HF/6-31G*	-13.08	-11.79		
HF/6-31G**	-13.20	-12.04	-11.59	$\Delta H_{\text{exp}} = **$
B3LYP/3-21G*	-28.57	-21.11		$\Delta \bar{H}_{298} = -14.43$
B3LYP/6-31G*	-16.78	-14.77	-16.0	
B3LYP/6-31G**	-17.00	-15.10	-15.7	
B3LYP/6-31++G**	-14.08	-14.71		
A-T (9)	ΔE	ΔE_{BSSE}	ΔH_{298}	
HF/3-21G*	-25.20	-19.40		
HF/6-31G*	-15.34	-14.32		
HF/6-31G**	-15.41	-14.54	-13.67	$\Delta H_{\text{exp}} = **$
B3LYP/3-21G*	-31.10	-24.38		$\Delta \bar{H}_{298} = -16.79$
B3LYP/6-31G*	-19.39	-17.91	-18.5	
B3LYP/6-31G**	-19.59	-18.29	-18.2	
B3LYP/6-31++G**	-16.79	-17.26		

ΔE and ΔE_{BSSE} are the bond energy at zero K without and with correction for the BSSE, respectively. ΔH_{298} is the bond enthalpy at 298 K. ΔH_{exp} , experimental ΔH from spectrometry data^[11] with corrections for AT according to Brameld et al.^[9]

* ΔH_{exp} has been found only for A-T (1) model.^[11]

** We guess that the ΔH_{exp} of the other forms of A-T (n), $n \neq 1$ is near the $\Delta \bar{H}_{298}$ (average of theoretical ΔH_{298}) values that obtained from theoretical calculations.

Table (3). Abbreviations of some various quantum chemical methods

Method	
DFT	Density Functional Theory
HF	Hartree Fock
B3LYP	Beck3-LYP (one of methods at Density Functional Theory)
BP86	(one of methods at Density Functional Theory)

Figure Caption

Scheme 1. Adenine-thymine base pair in Watson-Crick structure

Fig1. Watson -Crick geometry of adenine-thymine base pair and other Different orientations of A-T.

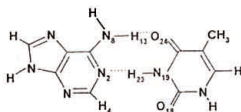
Fig 2. Deformation [\AA] of the individual bases caused by hydrogen bonding in the base pairs, from B3LYP/6-31G (d, p) optimizations without any symmetry constraint (only changes in bond length $\geq 0.003 \text{ \AA}$ are given).

Fig 3. Selected atomic charges of monomers and different orientation A-T base pairs from a Mulliken population analysis (B3LYP/6-31G (d, p))

Fig 4. Comparison of the hydrogen bond enthalpies (ΔH_{298}) in kcal mol^{-1} of the different orientations of adenine-thymine base pair, obtained from ab initio and DFT calculations.

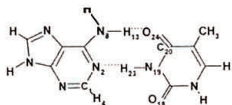
Fig 5. Comparison of the hydrogen bond energies (ΔE_{BSSE}) in kcal mol^{-1} for different orientations of adenine-thymine base pair, obtained from ab initio and DFT calculations.

Fig 6. Comparison of the hydrogen bond energies (ΔE) in kcal mol^{-1} for different orientations of adenine-thymine base pair, obtained from ab initio and DFT calculations.

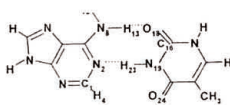


A-T(1) Watson-Crick

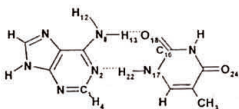
Scheme 1.



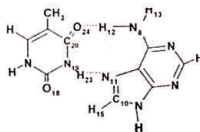
A-T(1) Watson-Crick



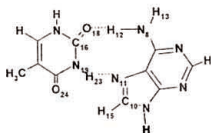
A-T(2)



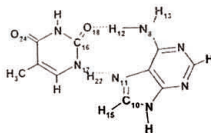
A-T(3)



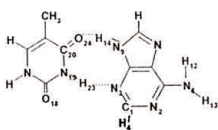
A-T(4)



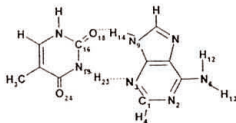
A-T(5)



A-T(6)



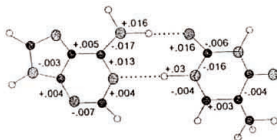
AT(7)



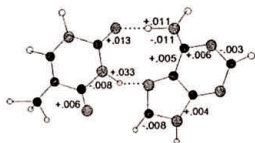
AT(8)



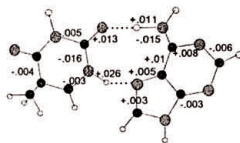
A-T(2)



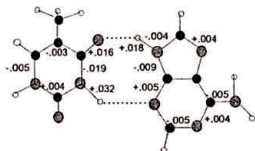
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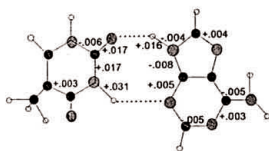
A-T(5)



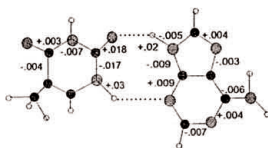
A-T(6)



A-T(7)



A-T(8)

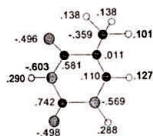


A-T(9)

Fig2.



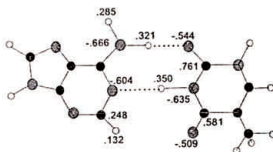
Adenine



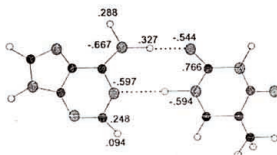
Thymine



A-T(1)(Watson-Crick)



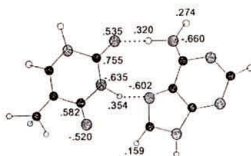
A-T(2)



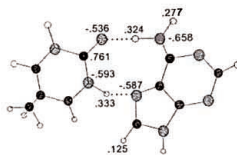
A-T(3)



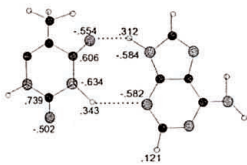
A-T(4)



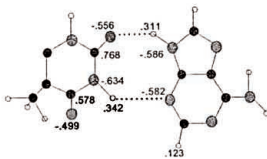
A-T(5)



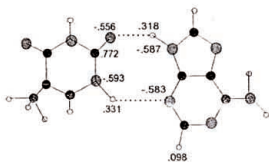
A-T(6)



A-T(7)



A-T(8)



A-T(9)

Fig3.

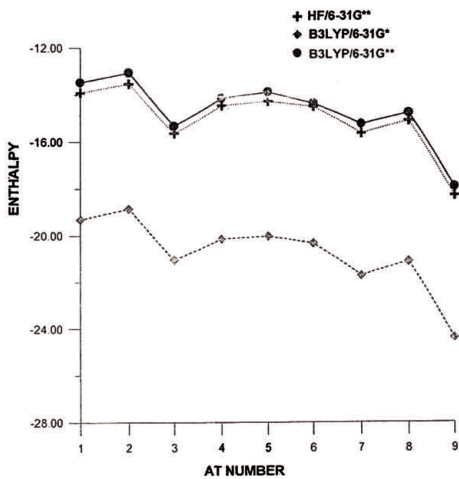


Fig4.

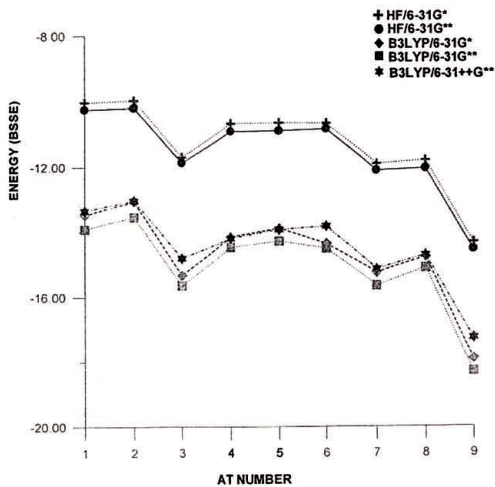


Fig 5.

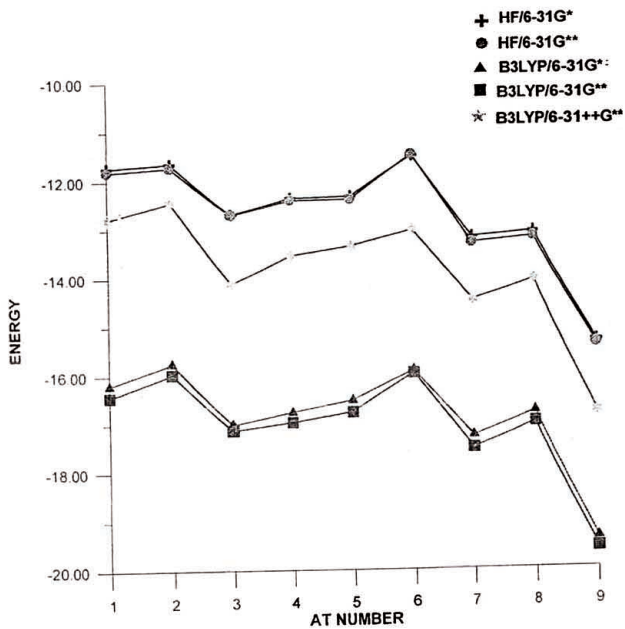


Fig 6.

Title: Study of the hydrogen bond in different orientations of adenine-thymine pair. An abdominitio study

Author(s): M. Monajjem, B. Chahkandi, K. Zare

Received: May 15, 04

July 7, 04

Dear Dr. Monajjem,

First of all I'd like to apologize for a long reviewing of your and co-authors manuscript with the above title.

It has been sent to me as the Editor to process and I have sent it to the referees who are experts in this field. After reviewing the Editorial Board concluded that the manuscript is acceptable for publication after a minor amendment (see comments below) and it will be published to one of the nearest issue of the journal.

Sincerely yours,

Rada D. Ozhina
Executive Editor-in-Chief
Biochemistry (Moscow)

1. Editorial conclusion

- ☐ **1.1.** Acceptable without any revision
- ☒ **1.2.** Acceptable after a minor amendment (see comments below)
- ☐ **1.3.** Not acceptable before a major revision and clarification (see comments below)
- ☐ **1.4.** Not acceptable and rejected:
 - ☐ **1.4.1.** Conclusions and statements are not supported by experimental data;