



Boron Nitride Sheet as a Novel Surface for Medical Adsorption and Drug Synthesis

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<http://dx.doi.org/10.13005/ojc/310103>

(Received: December 01, 2014; Accepted: January 10, 2015)

ABSTRACT

In this study we investigate Adenine, Guanine, Cytosine and Thymine molecules adsorption on Boron Nitride by Density-functional theory (DFT). For this purpose we calculate adsorption energy (DE_{ad}), HOMO- LUMO energy gap (DE_g), voltage difference (DV) and (Dq) of Adenine, Guanine, Cytosine and Thymine molecules on different adsorption distances on Boron Nitride layer and compare them.

Key words: Boron Nitride, Adsorption, DFT studies.

INTRODUCTION

Boron nitride is a synthetic material, which although discovered in the early 19th century was not developed as a commercial material until the latter half of the 20th century. Boron and nitrogen are neighbors of carbon in the periodic table - in combination boron and nitrogen have the same number of outer shell electrons - the atomic radii of boron and nitrogen are similar to that of carbon. It is not surprising therefore that boron nitride and carbon exhibit similarity in their crystal structure (1-5). In the same way that carbon exists as graphite and diamond, boron nitride can be synthesized in hexagonal and cubic forms. Hexagonal boron nitride (h-BN) is the equivalent in structure of graphite. Like graphite its plate like microstructure

and layered lattice structure give it good lubricating properties. h-BN is resistant to sintering and is usually formed by hot pressing (6-10). BN is a very good electrical insulator. It offers very high thermal conductivity and good thermal shock resistance.

Unlike graphene, a h-BN sheet is a wide gap insulator, as is bulk h-BN, and is a promising material for opto-electronic technologies, tunnel devices and field-effect transistors. Using a combination of mechanical exfoliation and reactive ion etching, monolayer and multilayer suspended h-BN sheets can be prepared. The band gap of boron nitride nanoribbons can be altered by edge passivation with different types of atoms. A combination of an odd number of h-BN layers is a non-centrosymmetric ionic crystal which is

piezoelectric due to $D3h$ symmetry. The corrugations on the h-BN sheet results in a strong polarization in the plane of the sheet which depends non-analytically on the wave vector of the corrugations. h-BN sheet has a non-linear elastic deformation up to an ultimate strength followed by a strain softening to failure. Moreover, the band gap of boron nitride nanotubes can be reduced by a transverse electric field due to a mixing of states within the highest occupied molecular orbital and the lowest unoccupied molecular orbital. The reduction in the band gap due to uniaxial strain results in tunneling magnetoresistance ratio which increases linearly with applied strain¹¹⁻¹⁵.

Boron nitride (BN) is a modern man made compound that perfectly parallels the crystalline structure and properties of naturally occurring elementary carbon. Actually hexagonal boron nitride hBN (or white graphite) is a high performance lubricant similar to natural graphite, while cubic boron nitride cBN (or borazone) is second in hardness after diamond, both substances being classified as the best superabrasives. Even more, a perfect crystallographic analogy exists between the boron nitride polymorphs and the carbon allotropes: hBN (hexagonal boron nitride) has the same crystal lattice as graphite, rBN (rhombohedral boron nitride) has the same crystal lattice as rhombohedral graphite, cBN (cubic boron nitride) has the same crystal lattice as diamond, wBN (wurtzitic boron nitride) has the same crystal lattice as lonsdaleite (a wurtzitic variety of diamond). For boron nitride as well as for carbon the same distinction can be made between the low density –low hardness polymorphs and high density – high hardness polymorphs¹⁶.

Boron nitride has a great potential in nanotechnology. The studies show that BN may be particularly suitable for biological applications. The objective of the present work was to investigate the adsorption potential of Boron Nitride¹⁷⁻²⁴.

The two pairs of nucleobases, adenine (A) with thymine (T) and cytosine (C) with guanine (G), have long been considered the key to DNA's stability, replication, and capacity for information storage, with the hydrogen bonds between them playing an integral role. Adenine and guanine belong to the double-ringed class of molecules

called purines. Cytosine, thymine, and uracil are all pyrimidines. Uracil replaces thymine in RNA. Adenine, guanine, thymine, cytosine and uracil are bases because of the presence of one or more of the following groups: - NH₂, - NH - and = N - groups. Importantly, - NH₂ and - NH - groups can react with carboxylic acids and phosphoric acid to form amides. They are usually simply called bases in genetics. Because A, G, C, and T appear in the DNA, these molecules are called DNA-bases; A, G, C, and U are called RNA-bases. Formation of hydrogen-bonded pairs composed of one purine and one pyrimidine, such as guanine-cytosine and adenine-thymine.

These nucleotides are important for a number of reasons. Most of them, not just ATP, are the sources of energy that drive most of our reactions. ATP is the most commonly used source but GTP is used in protein synthesis as well as a few other reactions. UTP is the source of energy for activating glucose and galactose. CTP is an energy source in lipid metabolism. AMP is part of the structure of some of the coenzymes like NAD and Coenzyme A. And, of course, the nucleotides are part of nucleic acids. Neither the bases nor the nucleotides are required dietary components.

Knowledge of the interaction between biologically active molecules, such as proteins or nucleic acid, and solid surfaces is relevant to the preparation of biocompatible materials and biosensors. The adsorption of small organic molecules, in particular, amino acids or nucleic acid bases, on surfaces is thereby studied to help in the understanding of complex intermolecular processes, e.g., in the origin of life research²⁵.

Self-organisation of organic molecules appears as one of the most promising approaches to the further miniaturisation of electronic devices. Due to their Watson–Crick complementarity, DNA bases are promising candidates for the design of functional self-organized structures. Two-dimensional structures of self-assembled DNA bases on various substrates, like especially highly oriented graphite or Au (111) surfaces, have been investigated both experimentally and theoretically to a great extent. The thorough understanding of the molecule–substrate interaction is essential for

the understanding and successful prediction of the intermolecular interaction of surface adsorbed molecules. In this context, we investigate here computationally the adsorption mechanism of single adenine, guanine, cytosine and thymine molecules on the surface of Boron Nitride²⁶.

It is of fundamental importance for understanding the function of DNA purine and Pyrimidine bases to understand their spontaneous adsorption on surfaces. For this reason, the theoretical study of nucleic acids and their adsorption on different types of electrode materials has recently been of great interest²⁷.

Adsorption of small biomolecules on inert surfaces acts as a laboratory of molecular interactions and is an excellent starting point for addressing molecular recognition and self-organization processes. By studying these systems we gain insight into the delicate balance between intermolecular forces that contribute to supramolecular binding, for example, the unique identification of antigens and their binding sites in our biochemistry. It is natural to begin an investigation of molecular interactions and organization by focusing on key building blocks, like the nucleic acids or the amino acids. Three-dimensional biopolymer systems, like the DNA double helix or proteins, permit folding of an extreme complexity that limits direct access to most of the structure, and direct experimental probing of the atomic-scale organization is difficult. Theoretical modeling must therefore map out interactions and organization not only between primary but also secondary and higher order structure in the absence of any calibration with experiments. In contrast, trapping nuclei bases on inert surfaces not only simplifies the possibilities for structural reorganizations but also makes the molecular interactions accessible to direct characterization through advanced atomic-scale experiments²⁵⁻²⁷.

The determination of the structure of adsorbed Adenine, Guanine, Cytosine and Thymine on BN surfaces is important for understanding its bonding and reactivity in catalysis and other surface phenomena and adsorption of these molecules on BN may be able to yield changes in the interactions

between the BN layer and foreign atoms or molecules²⁸⁻³¹.

In nanostructure research, molecular interaction with the nanostructure surface is a subfield of considerable interest because of potential applications such as storage, chemical sensors, and electronic devices. Doping or functionalizing nanostructures through chemical binding of atoms, molecules, or molecular groups is viewed as a viable approach to tailoring their properties.

We studied the adsorption of Adenine, Guanine, Cytosine and Thymine molecules on the BN sheet by means of density functional theory (DFT) calculations. Adsorption energy ΔE_{ad} (kcal/mol), HOMO- LUMO energy gap ΔE_g (eV), voltage difference ΔV (a.u) and Δq (e) were studied³²⁻³⁵.

Computational methods

The quantum chemical computations in the present work were carried out with Gaussian 2009 software package. The adsorption of the Adenine, Guanine, Cytosine and Thymine molecules was investigated on pristine Boron Nitride using density functional theory calculations.

The geometry of the Boron Nitrid and Adenine, Guanine, Cytosine and Thymine molecules have been optimized by Becke's hybrid three-parameter exchange functional and the non-local correlation functional of Lee, Yang, and Parr (B3LYP) method with 6-31g* basis set of Barone using ab initio GAUSSIAN quantum chemical package³⁶⁻³⁸. The B3LYP density functional has been previously shown to reproduce experimental properties and has been commonly used for nanostructures.

The optimization was done along with a frequency calculation to verify that the geometry was a real minimum without any imaginary frequency. In the current study, we have performed systematic first principle calculations on the atomic and electronic nanostructures. The description of the intra-molecular energy of individual molecules, Boron Nitride and Adenine, Guanine, Cytosine, Thymine is wanted within the nano system as compared with the calculations performed for the

free separate molecules. In this approach, we can determine the interaction energy by computing the energy of the free BN and Adenine, Guanine, Cytosine, Thymine individually for every geometrical arrangement of the system. Adsorption energy, energy gap, voltage difference and Δq have been calculated at the level of Cndo pop=chelp theory.

RESULTE AND DISCUSSION

In this study, we report adsorption energy (kcal/mol), HOMO energies, LUMO energies and HOMO- LUMO energy gap (eV), voltage difference ΔV , and Δq calculations for the Boron Nitride layer which are doped by Adenine, Guanine, Cytosine and Thymine molecules in various distances.

The adsorption energy E_{ad} of the Adenine attached BN was calculated as follows:

$$E_{ad} = E(\text{Adenine}/\text{BN}) - [E(\text{BN}) + E(\text{Adenine})]$$

Where $E(\text{Adenine}/\text{BN})$ corresponds to the energy of the Boron Nitride, in which Adenine has been adsorbed on the surface, $E(\text{BN})$ is the energy of the isolated sheet, and $E(\text{Adenine})$ is the energy of a single Adenine molecule. We calculate other values of adsorption energy for Guanine, Cytosine and Thymine attached BN the same way.

The HOMO-LUMO band gap is a gap between the HOMO (the highest occupied

molecular orbital) and LUMO (the lowest unoccupied molecular orbital) (32). In order to check the validity of this description about the structural stability of the Adenine-BN, Guanine-BN, Cytosine-BN and Thymine-BN systems, the HOMO–LUMO frontier orbitals have been calculated. Recently, the HOMO–LUMO band gap has been suggested is a measure of the structural stability and semi-conducting properties of. The band gap of these systems as the relative differences in the energy of the HOMO and the LUMO is reported in Tables 1-4. In Figure1 we show the models for adsorption state for molecules on the Boron Nitride.

The expectation values of the adsorption energy ΔE_{ad} (kcal/mol), HOMO- LUMO energy gap ΔE_g (eV), voltage difference ΔV (a.u), and Δq (e) of Adenine-BN, Guanine-BN, Cytosine-BN and Thymine-BN systems are displayed in Figures 2-5 and also these calculated values are compared in Tables 1

The Lennard-Jones function is a very famous empirical function in molecular dynamics. The Lennard—Jones potential is an effective potential that describes the interaction between two uncharged molecules or atoms. The Lennard—Jones potential is mildly attractive as two uncharged molecules or atoms approach one another from a distance, but strongly repulsive when they approach too close. As such it is a model for all interatomic

Table 1: Calculated adsorption energy (kcal/mol), HOMO energies, LUMO energies, HOMO-LUMO energy gap (eV), voltage difference (a.u) and Δq (e) for Adenine-BN system in various distances

Distance	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	Δq	ΔV
10	-943.267	4.913	3.817	1.0952	0	2947.18
9	-943.21	4.923	3.827	1.0955	0	2942.47
8	-943.14	4.935	3.838	1.0963	0	2937.15
7	-943.07	4.949	3.852	1.0971	0	2930.92
6	-942.98	4.965	3.867	1.0979	0	2923.79
5	-942.94	5.168	3.886	1.0985	0	2915.49
4	-944.502	5.006	3.906	1.0998	0.0047	2905.79
3	-974.938	5.002	3.902	1.0998	0.0984	2895.19
2	-1099.158	4.746	3.659	1.0868	0.7853	2890.51
1.6	-813.63	6.022	4.892	1.1300	1.0650	2894.77
1.55	-742.50	5.148	3.943	1.2054	2.0121	2895.71
1.4	-395.42	4.631	1.763	2.8670	1.6824	2901.67
1.3	50.258	4.652	2.099	2.5532	0.8400	2903.79

pair potentials. Its simplicity and accuracy make it highly suitable for molecular dynamics simulations. The form of the function ($V(r)$) is given by:

$$V(r) = 4\epsilon \left\{ \left[\frac{\sigma}{r} \right]^{12} - \left[\frac{\sigma}{r} \right]^6 \right\}$$

In which r is the interatomic separation, ϵ is the energy constant (or well depth) and σ is effectively the diameter of one of the atoms.

At short range (small r) the potential energy is large and positive, revealing that this is a very unfavourable arrangement of the atoms (it indicates

Table 2: Calculated adsorption energy (kcal/mol), HOMO energies , LUMO energies, HOMO-LUMO energy gap (eV), voltage difference (a.u) and Δq (e) for Guanine-BN system in various distances

Distance	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	Δq	ΔV
10	-938.89	4.912	3.817	1.094	0	2927.05
9	-938.80	4.926	3.830	1.095	0	2921.89
8	-938.70	4.943	3.847	1.096	0	2916.06
7	-940.99	4.964	3.867	1.097	0	2909.22
6	-938.39	4.989	3.891	1.098	0	2901.36
5	-938.27	5.018	3.918	1.099	0.0002	2892.18
4	-940.68	5.043	3.942	1.009	0.0070	2881.46
3	-981.44	5.009	3.909	1.099	0.1327	2869.98
2	-1061.79	4.693	3.610	1.083	0.9869	2866.02
1.8	-929.69	4.462	3.397	1.065	1.1779	2868.68
1.7	-760.05	4.404	3.342	1.062	1.1845	2870.09
1.65	-715.74	4.358	3.292	1.065	1.1525	2872.04
1.55	-546.15	4.486	2.719	1.767	2.0344	2873.44
1.5	424.11	4.495	2.239	2.256	1.0908	2876.01
1.4	-395.32	4.496	2.281	2.214	1.8457	2876.55
1.3	535.41	4.525	1.612	2.913	0.7546	2888.65
1.2	1523.90	4.528	1.619	2.908	0.8472	2897.70

Table 3: Calculated adsorption energy (kcal/mol), HOMO energies , LUMO energies, HOMO-LUMO energy gap (eV), voltage difference (a.u) and Δq (e) for Cytosine-BN system in various distances

Distance	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	Δq	ΔV
10	-0.32	4.821	3.731	1.090	0	3007.41
9	-0.39	4.813	3.723	1.089	0	3003.58
8	-0.49	4.802	3.713	1.088	0	2999.14
2.5	-71.37	4.629	3.554	1.075	0.225	2961.92
2	-81.63	4.632	3.554	1.077	0.559	2961.68
1.8	-18.60	4.947	3.848	1.099	0.562	2963.88
1.7	36.41	5.181	4.072	1.109	0.481	2966.04
1.6	131.96	5.290	4.178	1.112	0.465	2969.15
1.5	227.74	4.986	2.556	2.430	0.995	2969.92
1.4	383.37	5.041	1.977	3.064	0.724	2977.20
1.3	798.99	5.056	2.003	3.053	0.741	2984.65
1.2	1503.66	5.059	2.115	2.943	0.829	2993.59
1.1	2758.23	5.051	2.261	2.790	0.923	3028.38

Table 4: Calculated adsorption energy (kcal/mol), HOMO energies , LUMO energies, HOMO-LUMO energy gap (eV), voltage difference (a.u) and Δq (e) for Thymine-BN system in various distances

Distance	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	Δq	ΔV
10	-41.217	4.936	3.839	1.096	0	2974.69
9	-41.13	4.951	3.854	1.097	0	2970.04
8	-41.03	4.969	3.871	1.098	0	2964.77
7	-40.91	4.991	3.892	1.099	0	2958.62
6	-40.78	5.017	3.917	1.100	0	2951.56
5	-40.71	5.047	3.946	1.101	0	2943.34
4	-42.53	5.081	3.978	1.125	0.005	2933.76
3	-72.77	5.103	3.999	1.104	0.089	2923.55
2	-117.04	5.162	4.055	1.106	0.691	2919.81
1.9	-121.32	5.165	4.058	1.107	0.723	2920.70
1.7	142.44	5.202	4.093	1.108	0.858	6924.15
1.6	343.61	5.157	4.050	1.107	0.819	2926.56
1.5	641.83	5.022	3.92	1.102	0.737	2929.73
1.4	1072.42	5.439	4.36	1.103	1.593	2931.37
1.3	1638.09	4.594	1.993	2.600	1.392	2935.88

that the two atoms are strongly overlapping). At long range the potential energy is small and negative. This indicates that at this range the pair of atoms experiences a stabilising influence. (In fact this corresponds to the London dispersion energy, caused by a subtle form of electrical attraction known as the instantaneous dipole-dipole interaction). At a separation slightly greater than sigma, the energy is at a minimum. This where the atom pair is stable, and will be content to remain in this position until some external influence disturbs them. The basic shape of this curve is common to almost all empirical potentials and captures the essentials of interatomic (nonbonding) forces.

We can use the potential energy function to calculate the force between the atoms. Mathematically this is given by the negative of the first derivative of the function - in other words the negative of the slope of the graph at all points. Such a derivation shows that when the atoms are close the force is repulsive, at long range it is attractive, and at the energy minimum, the force is zero - as expected! The mathematical form of the force is as follows:

$$\vec{F}(\vec{r}) = \frac{24\epsilon}{r^2} \left\{ 2 \left[\frac{\sigma}{r} \right]^{12} - \left[\frac{\sigma}{r} \right]^6 \right\} \vec{r}$$

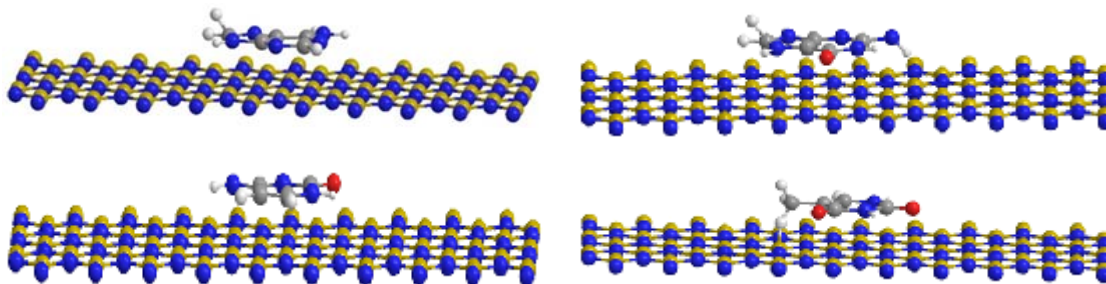


Fig. 1: The views of the molecules attached BN. Adenine-BN (a), Guanine-BN (b), Cytosine-BN (c) and Thymine-BN (d) systems

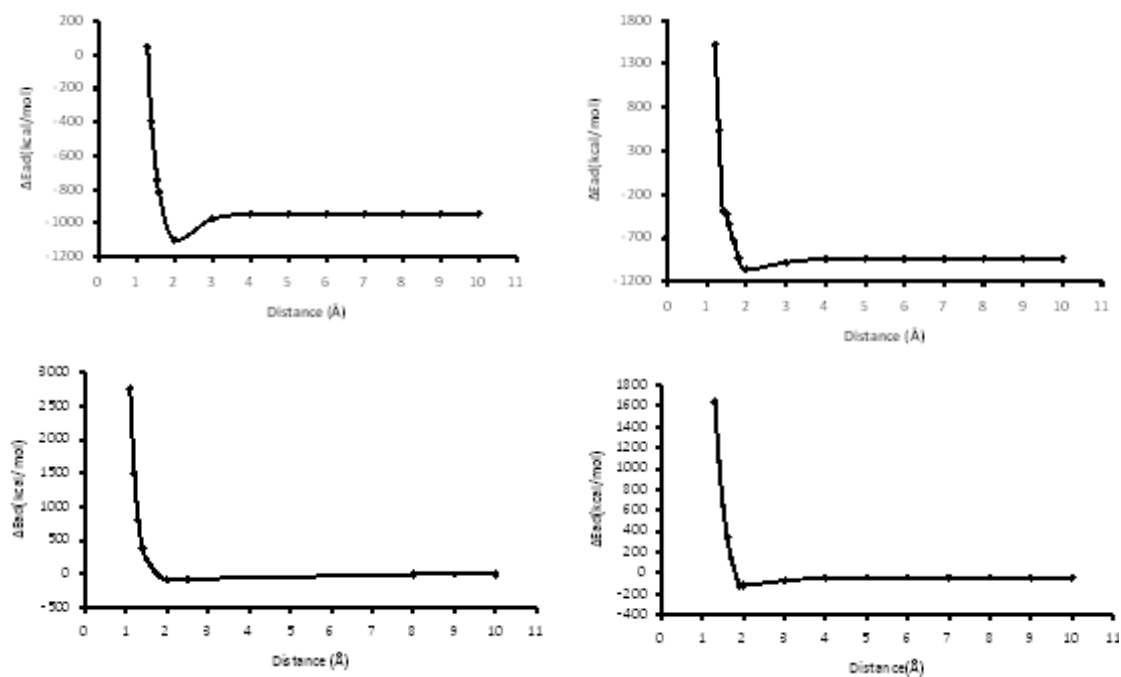


Fig. 2: The graphs of the calculated adsorption energy(kcal/mol) for Adenine-BN (a), Guanine-BN (b), Cytosine-BN (c) and Thymine-BN (d) systems

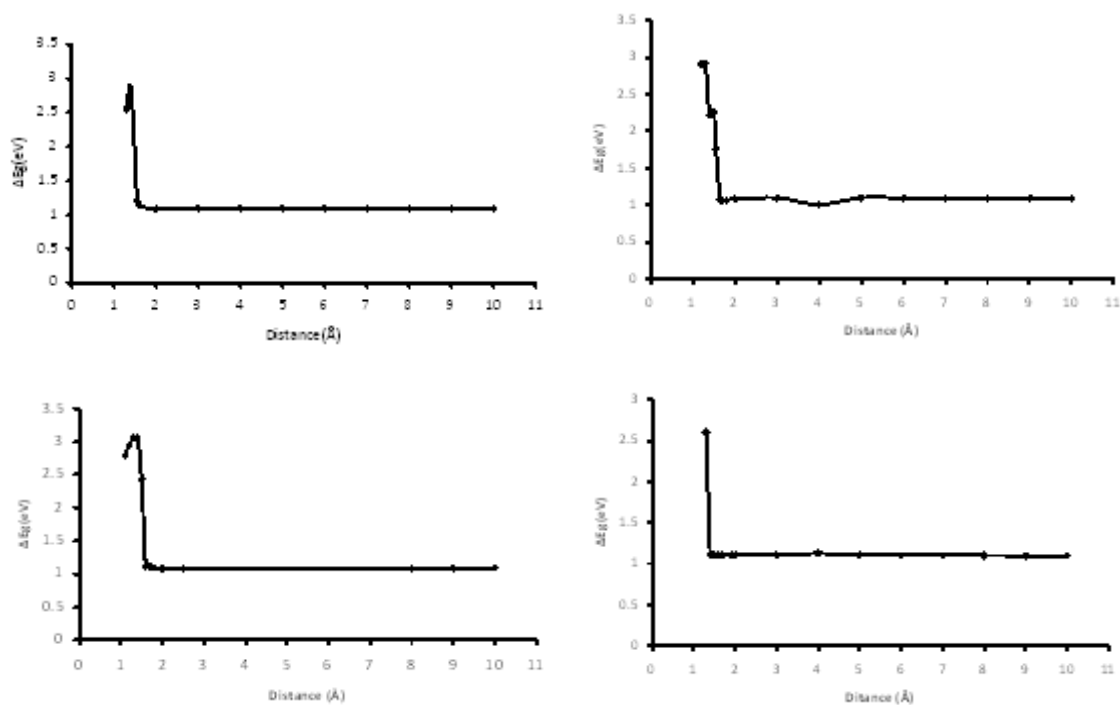


Fig. 3: The graphs of HOMO-LUMO energy gap (eV) for Adenine-BN (a), Guanine-BN (b), Cytosine-BN (c) and Thymine-BN (d) systems

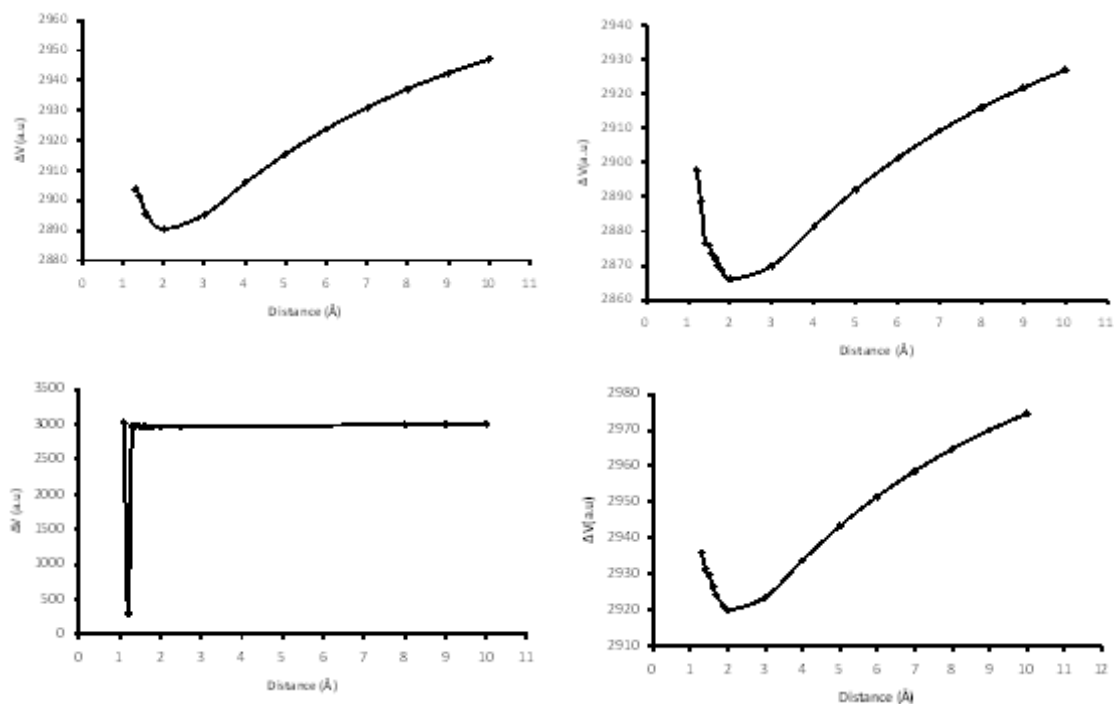


Fig. 4: The graphs of voltage differences (a.u) for Adenine-BN (a), Guanine-BN (b), Cytosine-BN (c) and Thymine-BN (d) systems

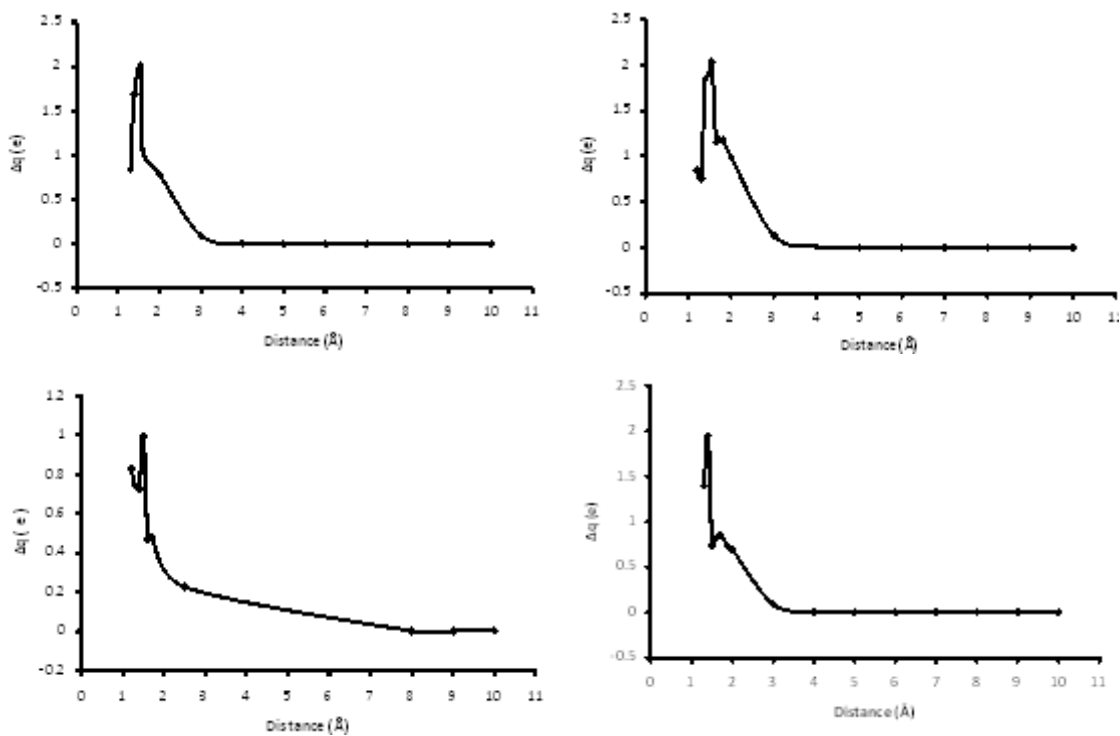


Fig. 5: The graphs of Δq (e) for Adenine-BN (a), Guanine-BN (b), Cytosine-BN (c) and Thymine-BN (d) systems

Note that the force F is a vector, with components in three directions: X,Y,Z. This is quite different from the potential function, which is a scalar

and has only one value for each distance r . This is one reason why it is more convenient to work with potential functions rather than force laws.

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