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B-Deoxyribonucleic Acid Energy Band Gap Semi-empirical Computer Simulation: Progress Report

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Abstract

DNA-the carrier of genetic information in all living species and the building block of life, is often heralded as the cornerstone of a new generation of electronic devices because of its electronic properties. Its biological properties are largely becoming irrelevant because it is used as a basic material for nanostructures. The unique assembly properties of DNA together with its unparalleled recognition, optical characteristics, stability and adaptability suggest that DNA may become one of the most important species in the general area of molecular electronics. One existing medical application of DNA is the assembled microfabricated DNA chips which can be used to probe whether certain genetic codes are in a given specimen of DNA.

The DNA structure is ideal for electron transfer since some of the electron orbitals belonging to the bases overlap quite well with each other along the axis of the DNA. Due to the variety of DNA sequences, layouts, and conditions, physical mechanism responsible for conduction remains unclear. In this study, the energy band gaps and relative energies of the CG and AT base pairs of a double helix structure of B-DNA with 2'-endo sugar form and four CG and AT B-DNA sequences are being calculated using semi-empirical geometry optimization/Polak-Ribiere algorithm, to investigate whether DNA behaves as an insulator, semiconductor, or a superconductor, basing on the electron transfer theory. The calcu-

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lated HOMO-LUMO difference signifies the energy band gap of the molecule. DNA consisting only of C and G bases is expected to conduct somewhat better than DNA with A and T bases or a poly (dG)-poly (dC) DNA is a large-gap semiconductor (i.e. an insulator). The calculations are being performed using HyperChem suite of programs and utilizing Parametric Method Number 3 (PM3). The computations are being carried out on a Windows 2000 workstation in a Pentium III PC.

Introduction

The electronic structure of DNA strands has received recently considerable attention due to the suggestion of the possibility that DNA may act as a molecular wire. Furthermore, increasing use is being made in nanotechnology of DNA strands as connectors and in the biochip world. If DNA strands could be made with a switch to turn the current flowing through them on and off, they could be used to build extremely tiny electrical devices. DNA strands might even be able to wire themselves together. Molecules at the end of DNA strands will link themselves to certain other molecules, .so it might be possible to create a wiring grid by laying down these target molecules as terminals and letting the DNA strands attach themselves [1].

A lot of experiments have been made to investigate the electronic properties of DNA. Conductivity measurement were performed by Rakitin et. al. on 15μm long B-DNA bundled of ~10^2 molecules each in standard buffer at pH 7.5 doped across the electron gap. A semiconductor plateau (conductor gap) of about 200meV was observed for B-DNA of this type [2], exhibiting a narrow-band-gap semiconductor behavior. The experiment involved substitution of imino proton of each base pair with a metal ion to alter the electronic properties of the DNA.

However, experimental setups often proved to be hard to control for such sensitive compounds. A small variation in parameters might alter the whole experiment. A change in humidity for example, can change the crystallographic structure of B-DNA to the A form [3], if very high enough.

In this study, a computer simulation where parameters are more controlled is being carried out partially for double helix B-DNA. Energy band gaps and related energies are being calculated to investigate the electronic properties of the said DNA conformer.

Computational Details

The semi-empirical calculations were performed using HyperChem™ [4] and Spartan Pro [9] suites of quantum chemistry programs and utilizing Parametric Method Number 3 (PM3) and Austin Model 1 (AM1) respectively. The computations are being carried out on a Windows 2000 workstation in a Pentium III PC.

The energy band gap of B-DNA with 2'-endo sugar form and relative energies of four different CG and AT base pair sequences are being calculated using semi-empirical geometry optimization via Polak Ribiere algorithm. B-DNA has been considered as a standard structure of DNA and its space-filling model as the most common form of DNA in cells [6]. It is characterized as a right-handed antiparallel double helix held together by *Watson-Crick* base pairs [5].

The *Austing Model* 1 (AM1) [8] was developed to modify the core-core function which had resulted to large activation energies. The Modified Neglect of Diatomic Overlap (MNDO) was then reparameterized. The core-core repulsion of AM1 has the form:

$$V_{nn}(A,B) = V_{nn}^{MINDO}(A,B) + \frac{Z'_A Z'_B}{R_{AB}}\left(\sum_k a_{kA} e^{-b_{kA}(R_{AB}-c_{kA})2} + \sum_k a_{kB} e^{-b_{kB}(R_{AB}-c_{kB})2}\right)$$

where k is between 2 and 4 depending on the atom. It should be noted that the Gaussian functions more or less were added as patches onto the underlying parameters, which explains why different number of Gaussians are used for each atom. As with the MNDO, the G_{ss}, G_{sp}, G_{pp}, G_{p2}, H_{sp} parameters are taken from atomic spectra, while the rest, including the a_k, b_k, and c_k constants, are fitted to molecular data.

The parametrization of AM1 [8] by taking the G_{ss}, G_{sp}, G_{pp}, G_{p2}, H_{sp} parameters from atomic data and varying the rest until a satisfactory fit had been obtained. The AM1 expression for the core-core repulsion (equation 1) was kept, except that only 2 Gaussians were assigned to each atom. These Gaussian parameters were included as an integral part of the model, and allowed to vary freely. The resulting method was denoted *Modified Neglect of Diatomic Overlap, Parametric Method Number 3* (MNDO-PM3 or PM3 for short), and is essentially AM1 with all the parameters fully optimized.

The electronic energy [8] (including the core-core repulsion) calculated by AM1 and PM3 is, in analogy with that calculated by *ab initio* methods, the total energy relative to a situation where the nuclei (with their core electrons) and their valence electrons are infinitely separated. The electronic energy is normally converted to a heat of formation by subtracting the electronic energy of the isolated atoms which make up the system, and adding the experimental atomic heat of formation. The heat of formation is given by

$$\Delta H_f(molecule) = E_{elec}(molecule) - \sum^{atoms} E_{elec}(atoms) + \sum^{atoms} \Delta H_f(atoms)$$

Since the two-electron integrals are optimized to give a better fit to the given molecular data set, the average errors of heat of formation and bond distances of PM3 are lesser than AM1. However, the electrostatic potential generated by a PM3 wave function is of lower quality than one generated by the AM1 method.

Calculation of the energy band gap requires the energy of the *Frontier Orbitals*: HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), which are largely responsible for the chemical and spectroscopic properties of the molecules [7]. Basing from the Molecular Orbital Theory, calculation of the overall wavefunction ψ of the molecule can be approximated using the sum of the atomic orbitals known as the Linear Combination of Atomic Orbitals (LCAO) [7]. The LCAO-MO provides the linear combination of all the HOMO's and LUMO's of all the atoms comprising the phosphates, sugars, and nucleobases of the B-DNA. The HOMO-LUMO [10] energy difference provides the energy band gaps which serves as the basis for conduction.

Results and Discussions

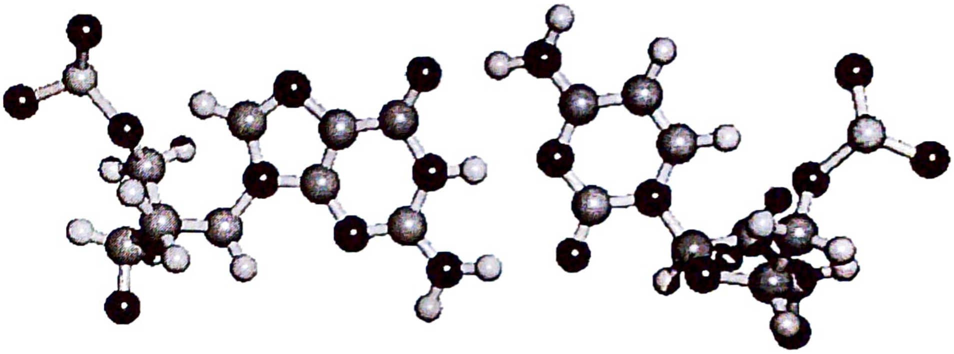


Figure 1. *Cytosine-Guanine Molecular Structure*

Figure 1 shows the molecular structure of Cytosine-Guanine component of a double strand DNA.

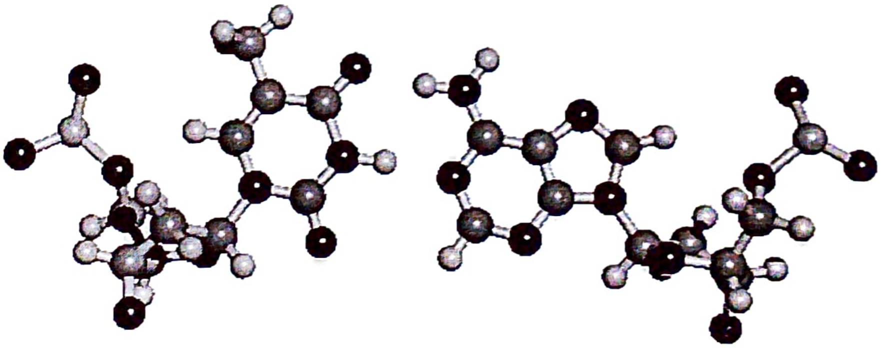


Figure 2. *Adenine-Thymine Molecular Structure*

Figure 2 shows the molecular structure Adenine-Thymine component of a double strand DNA.

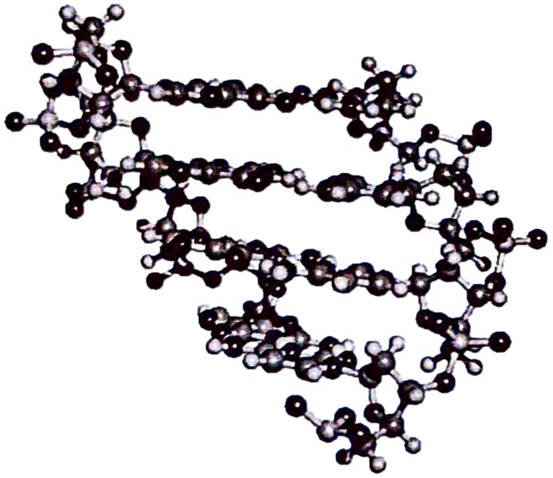


Figure 3. *Poly[4] (dG)-poly[4] (dC) B-DNA*

Figure 3 shows the helical structure of a poly(dG)-poly(dC) B-DNA connected in four sequences.

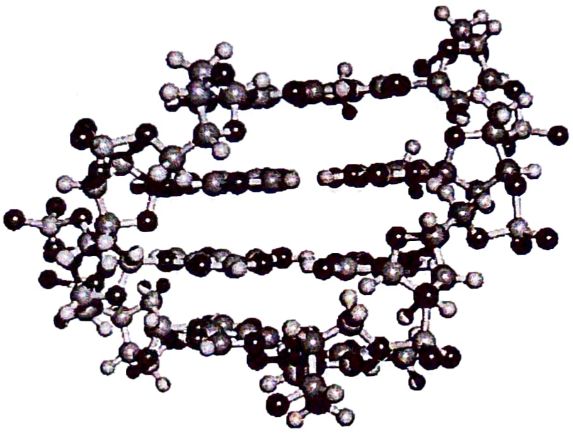


Figure 4. *Poly[4] (dT)-poly[4] (dA) B-DNA*

Figure 4 shows the helical structure of a Poly- (dT)-poly-(dA) B-DNA connected in four sequences.

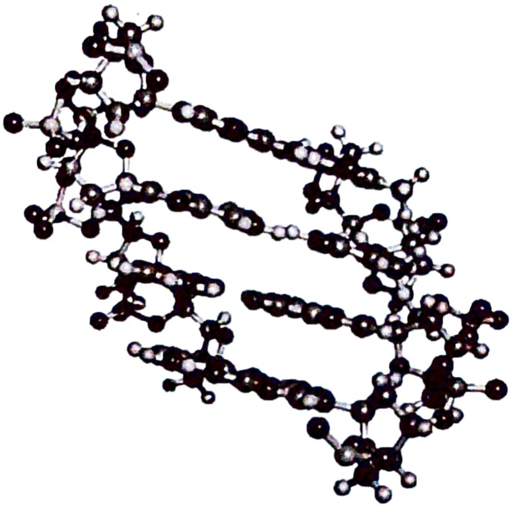
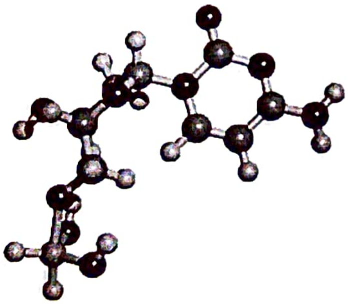
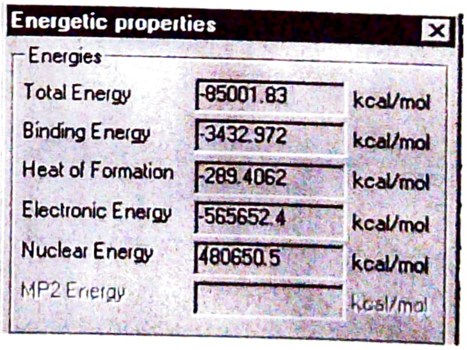


Figure 5. CG-CG-AT-AT B-DNA Oligomers

Figure 5 shows the helical structure of two CG and two AT B-DNA molecular structure.

Optimized Geometry for deoxycytosine (dC)

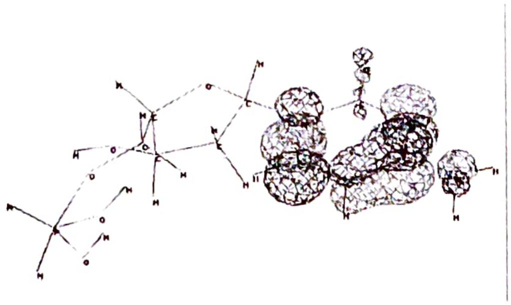


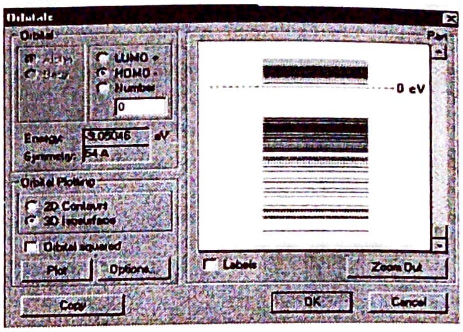


Total Energy	-85001.83	kcal/mol
Binding Energy	-3432.972	kcal/mol
Heat of Formation	-289.4062	kcal/mol
Electronic Energy	-565652.4	kcal/mol
Nuclear Energy	480650.5	kcal/mol
MP2 Energy		kcal/mol

Energetic properties of deoxycytosine

dC Energy Band Gap: -8.72 eV





Orbitals

Orbital

● Alpha
○ Beta

○ LUMO+
● HOMO-
○ Number
0

Energy: -9.05046 eV
Symmetry: 54 A

Orbital Plotting

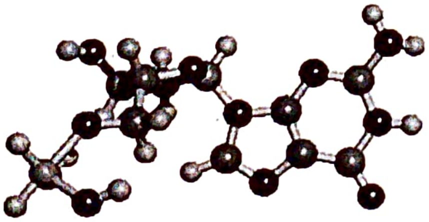
○ 2D Contours
● 3D Isosurface

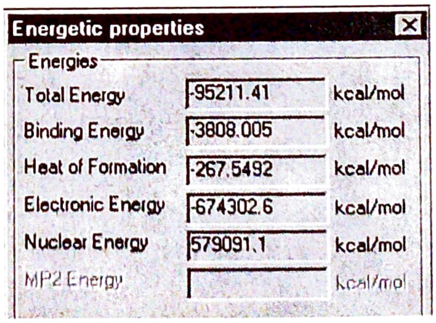
☐ Orbital squared

☐ Labels

The region in green corresponds to the HOMO; the region in violet corresponds to the LUMO.

Optimized Geometry for deoxyguanosine (dG)





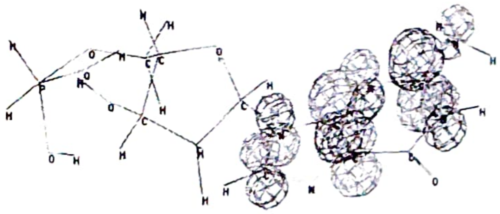
Energetic properties

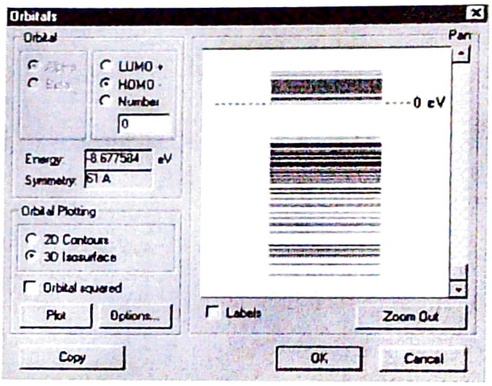
Energies

Total Energy	-95211.41	kcal/mol
Binding Energy	-3808.005	kcal/mol
Heat of Formation	-267.5492	kcal/mol
Electronic Energy	-674302.6	kcal/mol
Nuclear Energy	579091.1	kcal/mol
MP2 Energy		kcal/mol

Energetic properties of deoxyguanosine (dG)

dG Energy Band Gap: -8.28 eV





Orbitals

Orbital

○ LUMO +
● HOMO -
○ Number 0

Energy: -8.677584 eV
Symmetry: 61 A

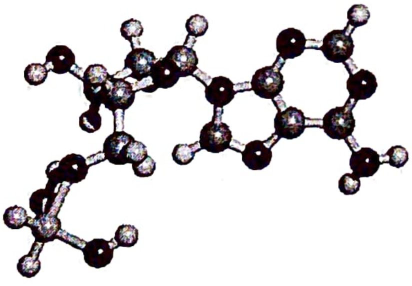
Orbital Plotting

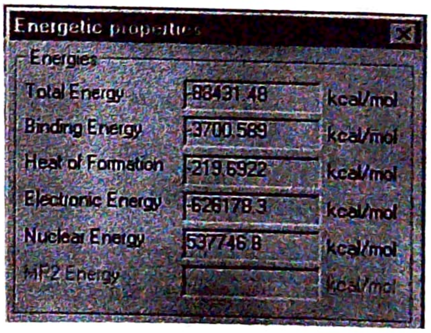
○ 2D Contours
● 3D Isosurface

☐ Orbital squared

The region in green corresponds to the HOMO; the region in violet corresponds to the LUMO.

Optimized Geometry for deoxyadenosine (dA),





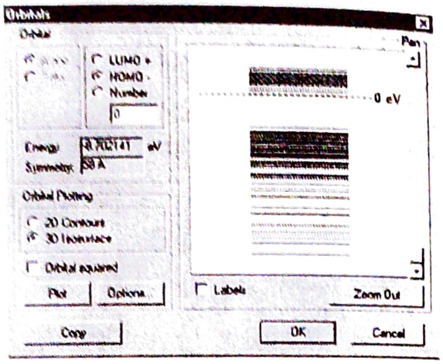
Energetic properties

Energies

Total Energy	-88431.48	kcal/mol
Binding Energy	-3700.589	kcal/mol
Heat of Formation	-219.6922	kcal/mol
Electronic Energy	-626178.3	kcal/mol
Nuclear Energy	537746.8	kcal/mol
MP2 Energy		kcal/mol

Energetic properties of deoxyguanosine (dA)

dA Energy Band Gap: -8.40 eV



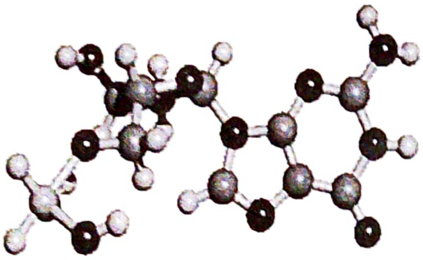
Number: 0

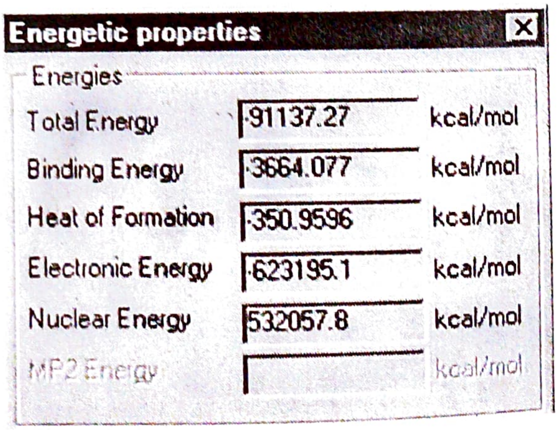
Energy: -8.702141 eV

Symmetry: 58 A

The region in green corresponds to the HOMO; the region in violet corresponds to the LUMO.

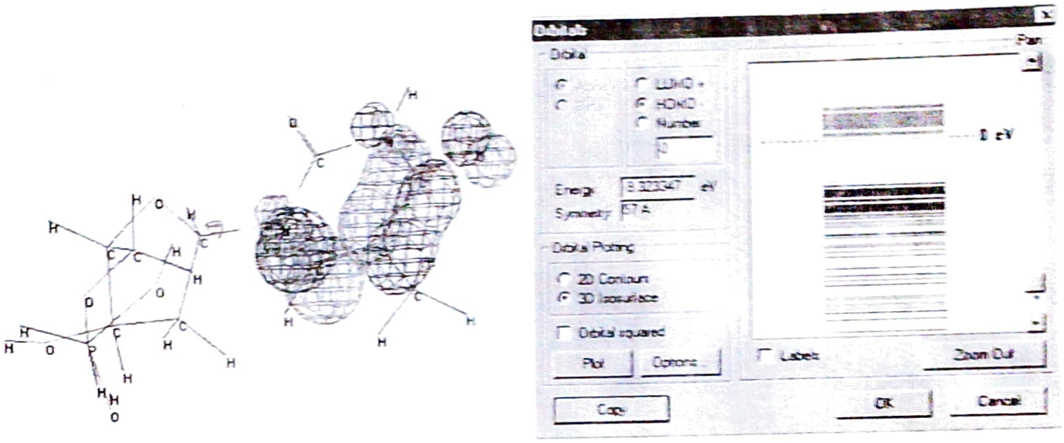
Optimized Geometry for (deoxy)thymidine (dT)





Total Energy	-91137.27	kcal/mol
Binding Energy	-3664.077	kcal/mol
Heat of Formation	-350.9596	kcal/mol
Electronic Energy	-623195.1	kcal/mol
Nuclear Energy	532057.8	kcal/mol
MP2 Energy		kcal/mol

dT Energy Band Gap: -9.02 eV



The region in green corresponds to the HOMO; the region in violet corresponds to the LUMO.

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References

[1] *http://www.waveguide.org/archives/emfl/Mar1999/DNAelectricalelectronicproperties.html*

[2] A. Rakitin, P. Aich, C. Papadopoulos, Y. Kobzar, A.S. Vedeneev, J. S. Lee, J.M. Xu, "Metallic Conduction Through Engineered DNA: DNA Nanoelectronic Building Blocks,:" *Physical Review Letters,* Vol. 86, No. 16, 16 April 2001, © The American Physical Society.

[3] D.P. Snustad, M. J. Simmons, *Principles of Genetics*, Copyright © 2000 John Wiley & Sons, Inc.

[4] HyperChem ™Release^3. *Windows Molecular Modelling System,* © 1993, HyperCube, Inc. and Autodesk, Inc.Developed by HyperCube, Inc.

[5] K.E. van Holde, W. Curtis Johnson, P. Shing Ho, *Principles of Biochemistry*, Copyright © 1998 Printice Hall Inc., Simon & Schuster/ A Viacom Company, Upper Saddle River, New Jersey 07458.

[6] H. Lodish, A. Berk, S. L. Zipursky, P. Matsudaira, D. Baltimore, J. Darnell, *Molecular Cell Biology,* Copyright © 2000 W. H. Freeman & Co.

[7] P. W. Atkins, *Physical Chemistry*, 5th ed. © 1994 Oxford University Press, Walton Street, Oxfort OX2 6DP.

[8] F. Jensen, *Introduction to Computational Chemistry*, Copyright © 1999 John Wiley & Sons Ltd., Baffins Lane, Chichester, West Sussex PO19 IUD, England.

[9] SPARTAN Pro version 7.0; Wavefunction, Inc.: 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612.