Quantum Mechanical Investigations of Programmable Artificial Photosynthetic Systems Based on Assemblies of Modified Peptide Nucleic Acids and Lipid Molecules

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Having in mind the actuality of PNA role in the prebiotic chemistry and construction of the artificial cells, we have decided to perform geometry optimization of the fragments of PNA using quantum mechanical Hartree-Fock method with 6-31G basis set implemented in the Gaussian98 program package[1]. The results of optimization of Adenine, Thymine, Guanine and Cytosine PNA fragments are presented in the Figures 1-4.

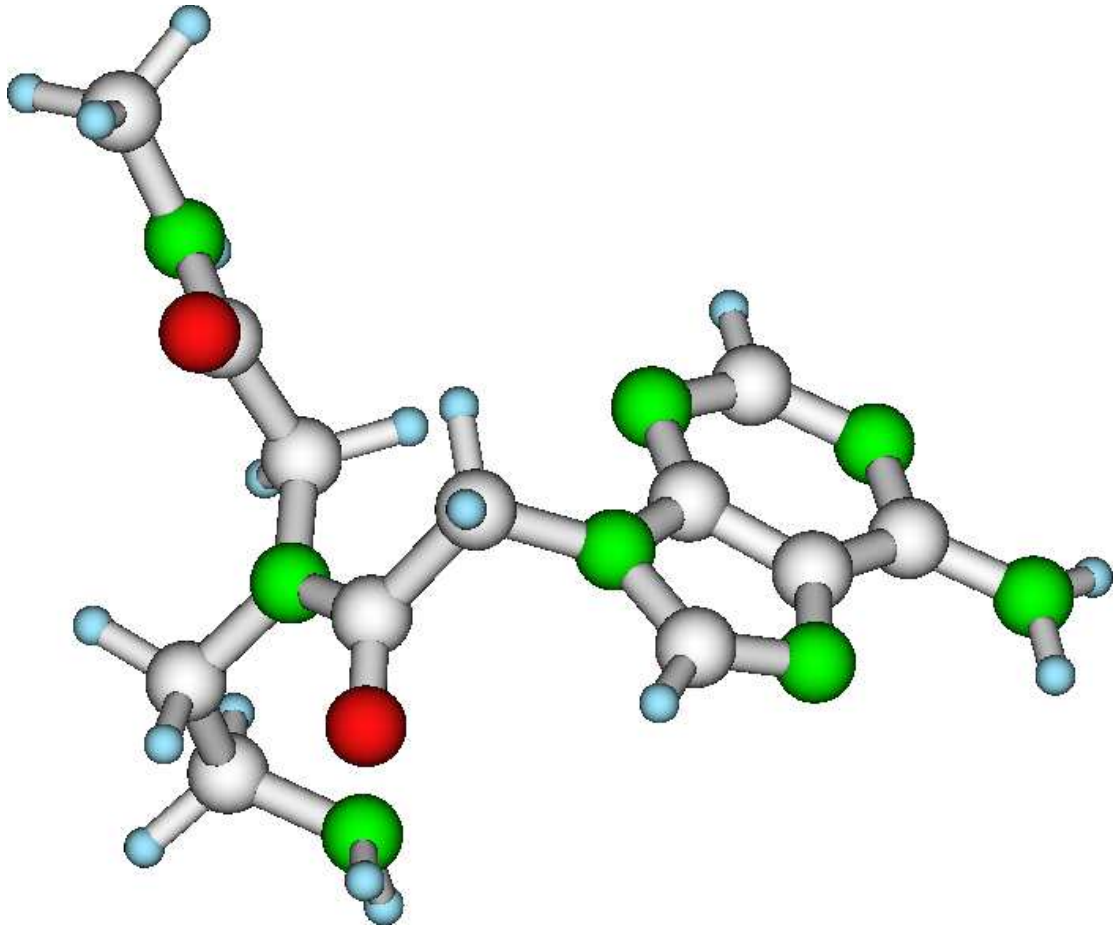

Figure 1. Adenine PNA fragment optimized by HF 6-31G.

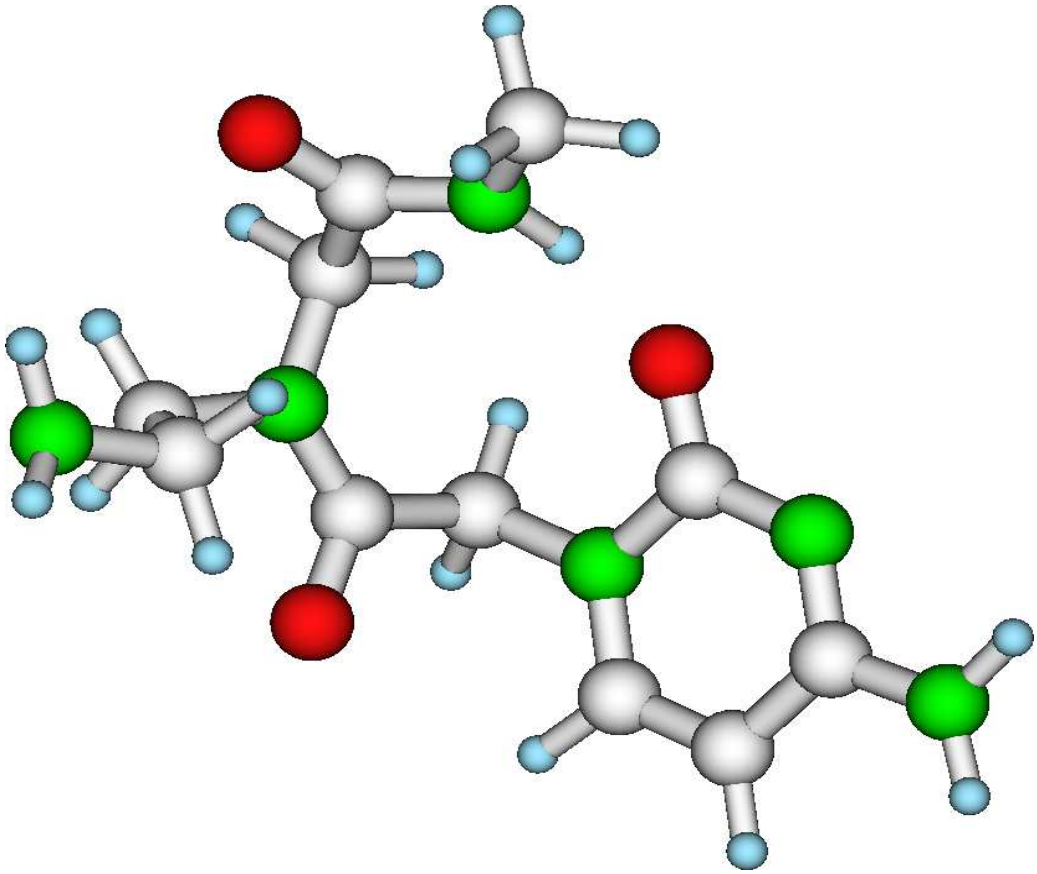

Figure 2. Cytosine PNA fragment optimized by HF 6-31G.

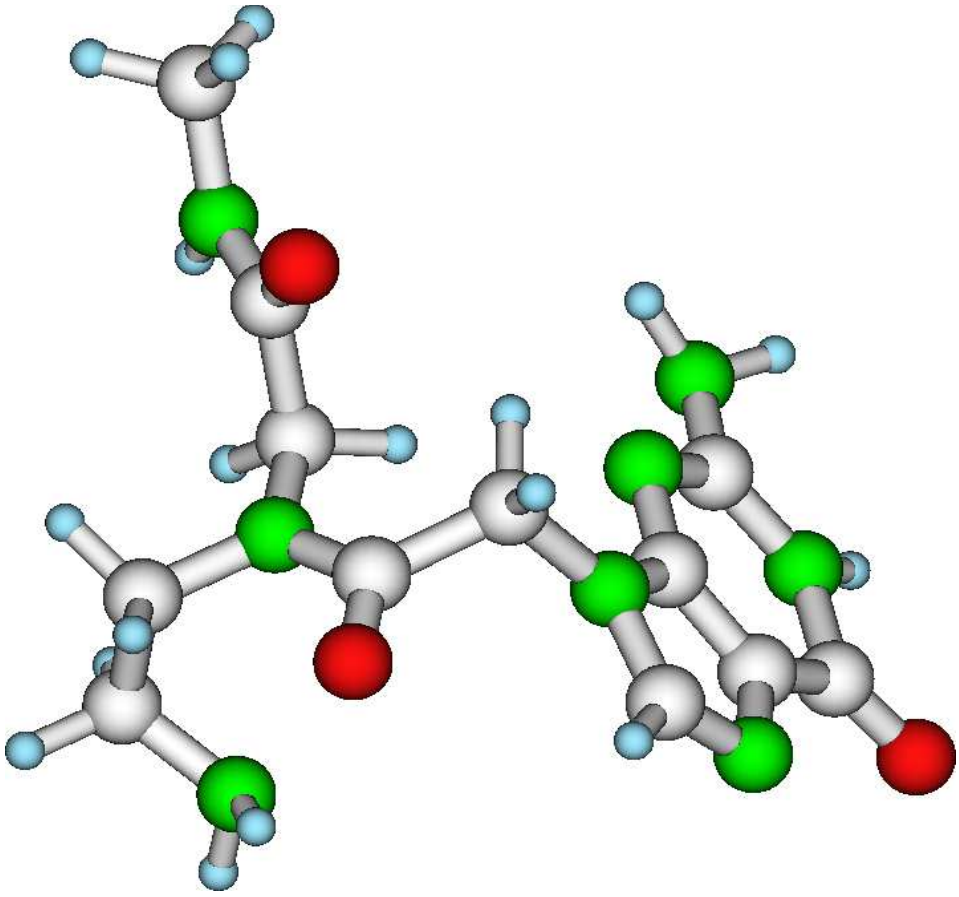

Figure 3. Guanine PNA fragment optimized by HF 6-31G

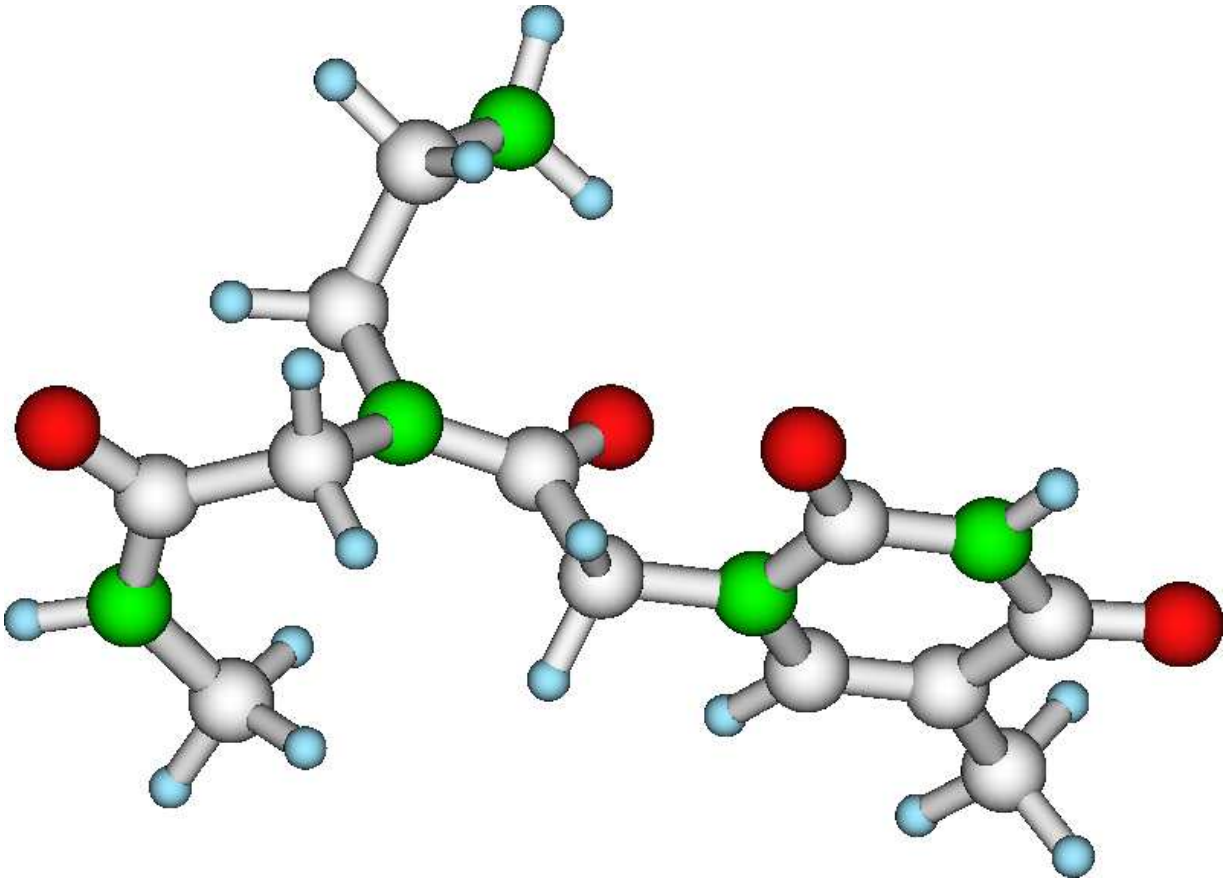

Figure 4. Thymine PNA fragment optimized by HF 6-31G

Total energies of PNA base fragments obtained after HF 6-31G geometry optimization are:

Total energy(AdeninePNA) = -1049.76682048 atomic units (a.u.)
Total energy(ThyminePNA) = -1036.75538574 a.u.
Total energy(CytosinePNA) = -977.916085909 a.u.
Total energy(GuaninePNA)= -1124.60517780A a.u.

Total energies of PNA base pair fragments (see Figures 5 and 6) fragments obtained after HF 6-31G geometry optimization are:
Total energy(AdeninePNA :: ThyminePNA) = -2086.56672010 a.u.
Total energy(GuaninePNA :: CytosinePNA) = -2102.56740649 a.u.

The interaction energies between base pairs: GuaninePNA :: CytosinePNA and AdeninePNA :: ThyminePNA are calculated as the differences between total energies of these base pairs and sum of total energies of not interacting base pairs:
Interaction energy1 = Total energy(AdeninePNA :: ThyminePNA) - (Total energy AdeninePNA + Total energy ThyminePNA) = 1.21129 eV = 27.9329 kcal/mol
Interacting energy2 = Total energy(GuaninePNA :: CytosinePNA) - (Total energy GuaninePNA + Total energy CytosinePNA) = 1.25565 eV = 28.9557 kcal/mol

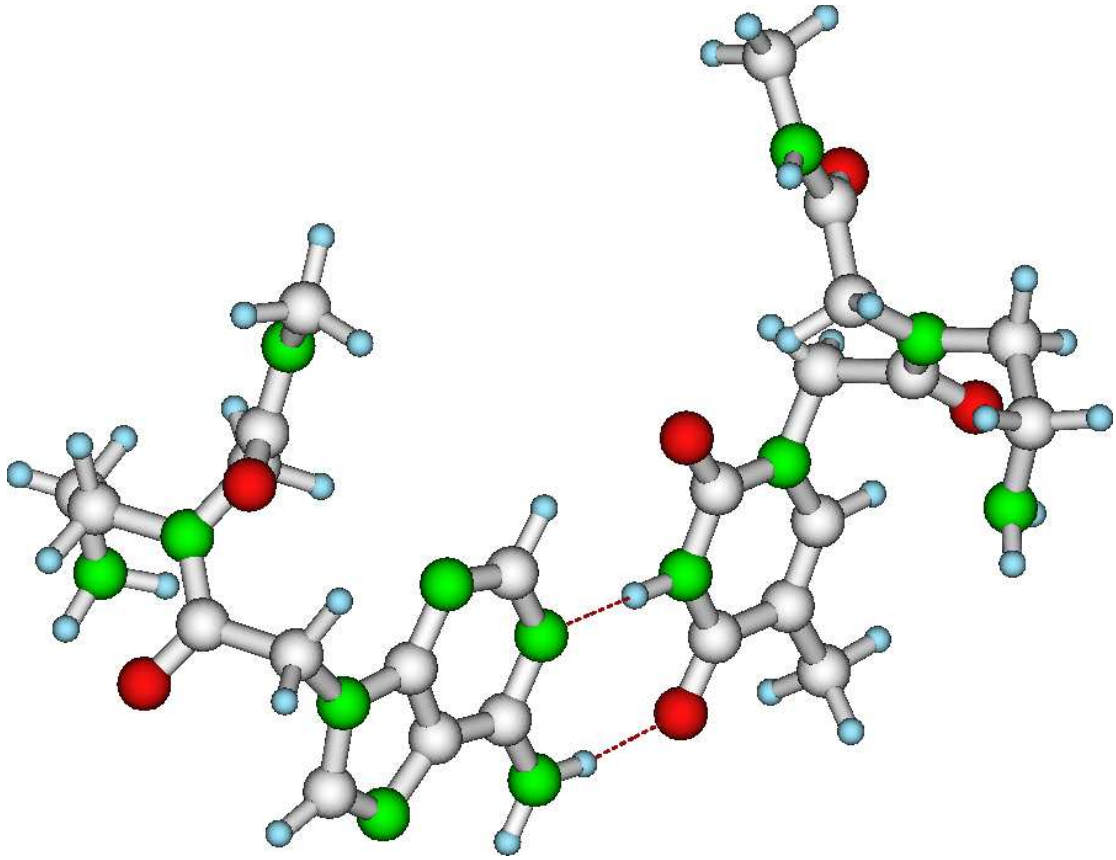

Figure 5. Optimized geometry of two PNA base pairs: AdeninePNA :: ThyminePNA (used HF 6-31G)

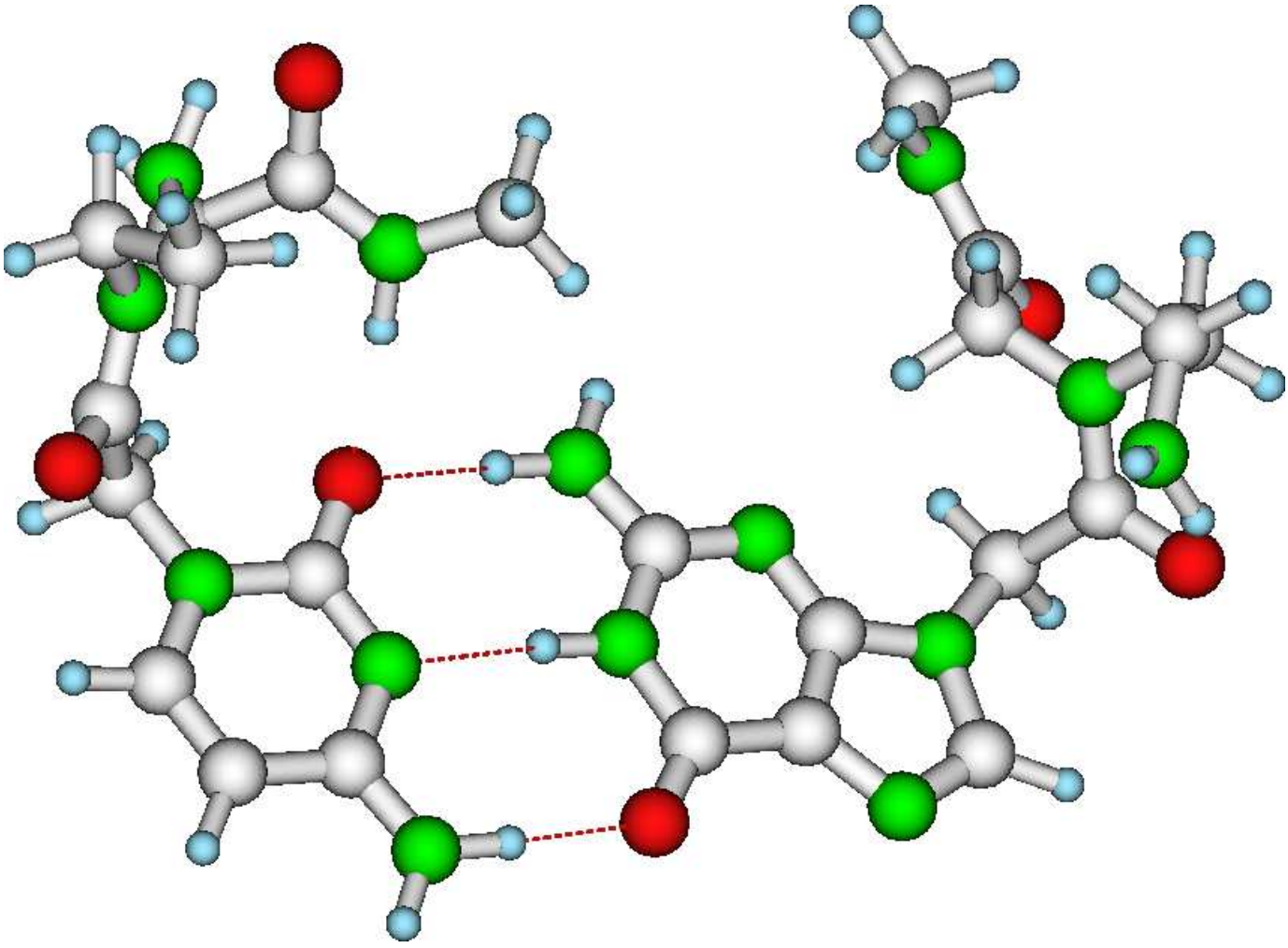

Figure 6. Otimized geometry of two PNA base pairs: GuaninePNA :: CytosinePNA (used HF 6-31G)

Interesting result was obtained using HF 6-311G optimization of geometry of PNA triade Adenine-Thymine-Cytosine (see Figure 6). It was found that during geometry optimization appears the additional Hydrogen-bonding between two peptide groups. That might explain why PNA is more stable in comparison with DNA. The distance of this H-bond is 2.5 Angstroms and exist positive value of overlapping population that indicates to the weak intramolecular chemical bonding in this place.

We are doing now more exact calculations of PNA base pairs and triade using Density Functional Theory with PerdewWang1991, Becke3-parametersPerdewWang91 and PerdewBurkeErnzerhof potentials and 6-31diffusionGaussianpolarized** basis set [1].

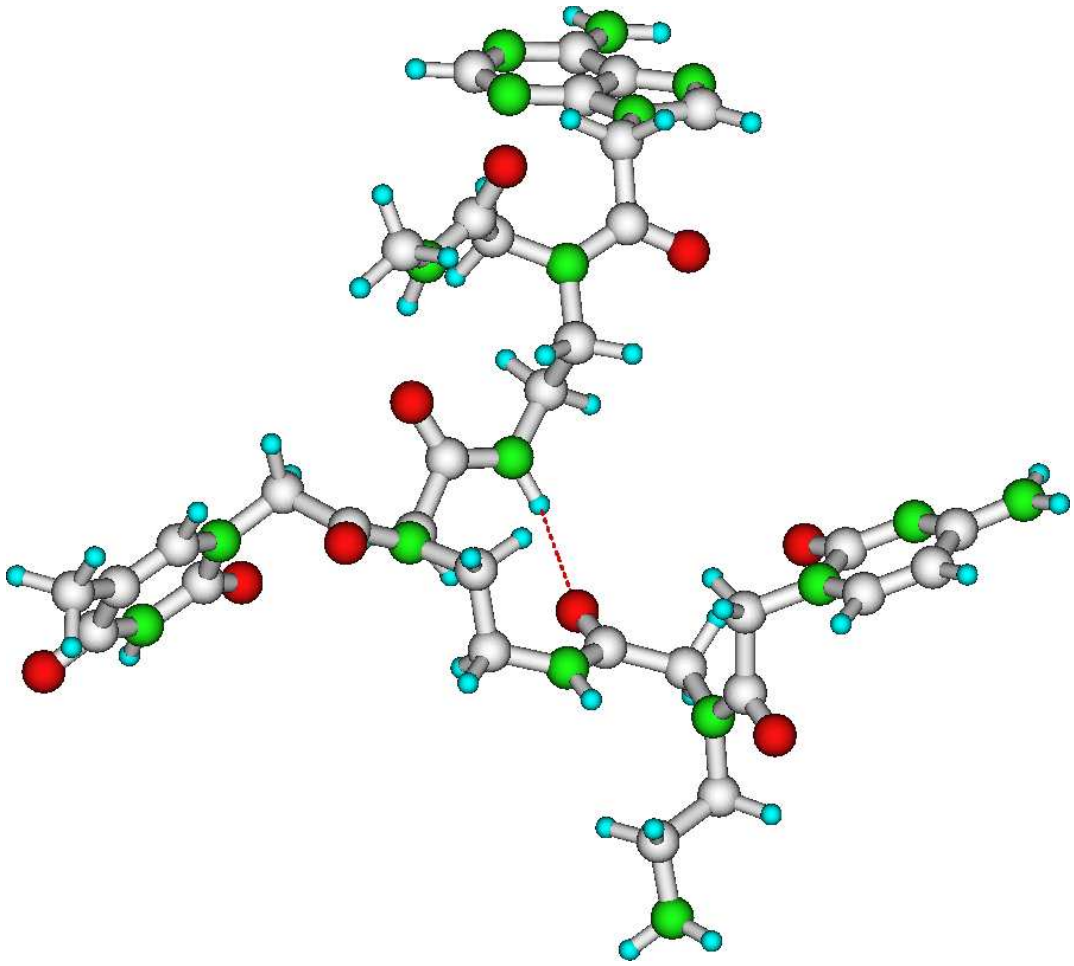

Figure 7. Optimized geometry of PNA triade: Adenine-Thymine-Cytosine PNA (used HF 6-31G)

In order to investigate the electron charge transfer in the artificial photosynthetic system it was performed quantum mechanical HF/6-31G optimization of the geometry of supramolecular system composed from modified peptide nucleic acid with implemented light harvesting sensibilizator N,N,N',N'-tetramethyl-naphthalene-1,4-diamine (photo-electron donor), phenancyl ester lipid and sulfite (electron donor) molecules (see Figure 8). We are using time-dependent Sroedinger equation method in density functional theory for the investigations of all electron relay chains starting from the excited states of sensibilizator N,N,N',N'-tetramethyl-naphthalene-1,4-diamine and electron hopping to lipid molecule, and then electron relaxation and migration from sulfite to guanine, adenine and back to sensibilizator.

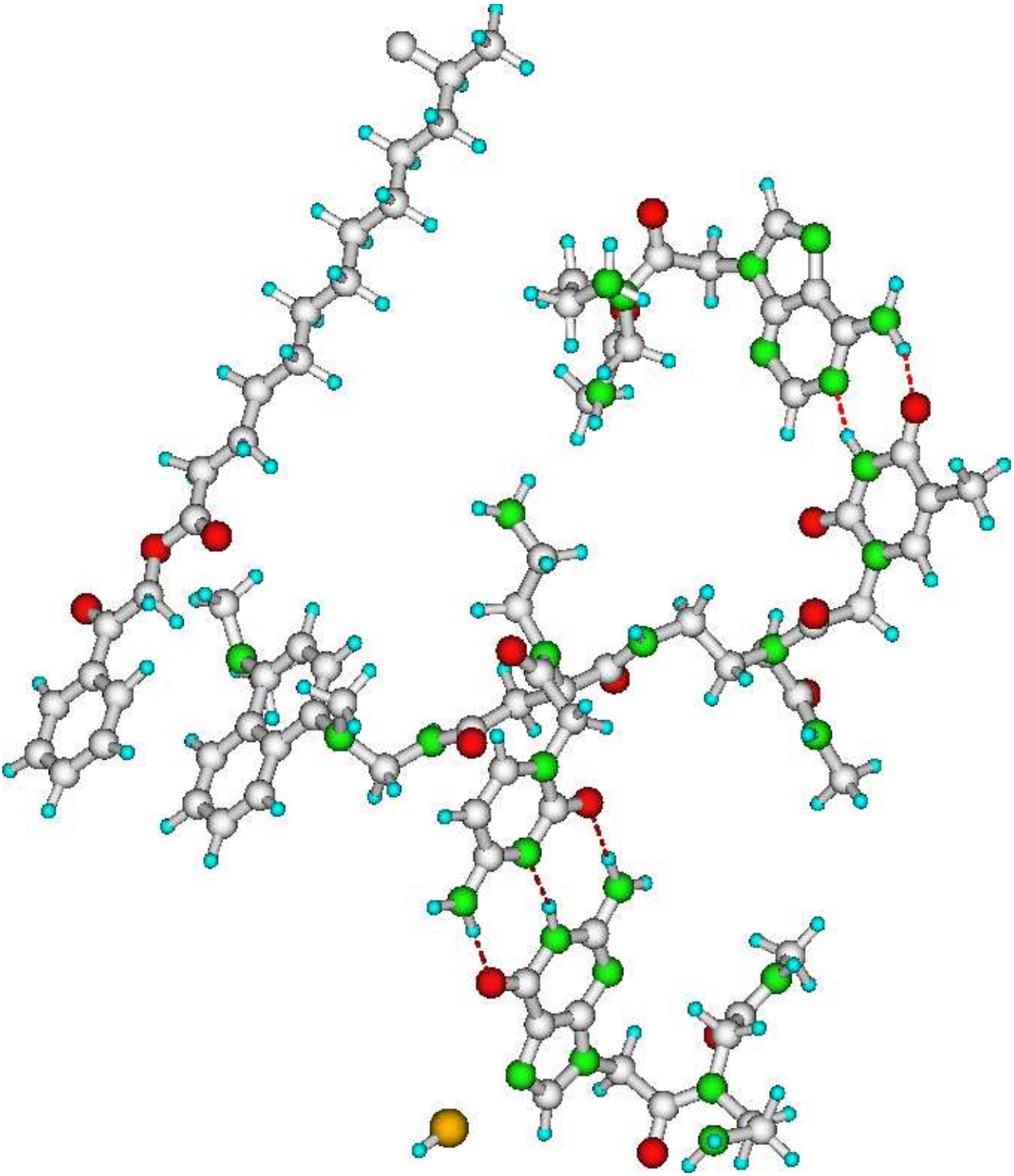

Figure 8. Optimized geometry of artificial photosynthetic system based on self-assembly of modified peptide nucleic acid and lipid molecule (used HF 6-31G)

For the reasons to control artificial photosynthetic systems and make them programmable it was implemented set of logically controlled gates in the modified peptide nucleic acid. Geometry of these supermolecules were optimized by HF/6-31G and now we are applying time dependent Sroedinger equation method in density functional theory for the electron charge transfer investigations. Two variable logic function AND implementation in the artificial photosynthetic system based on modified peptide nucleic acid is shown in the Figure 9.

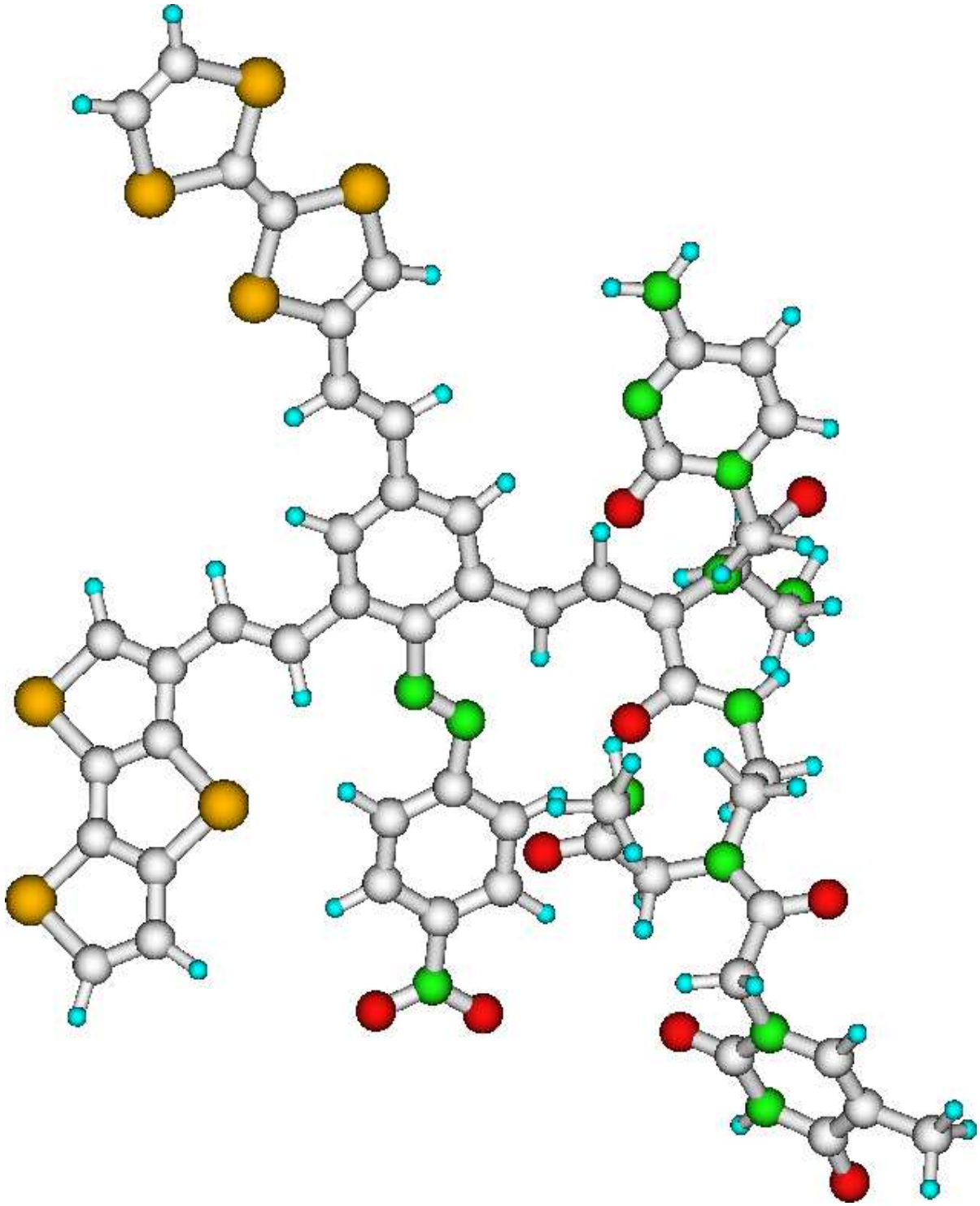

Figure 9. Optimized geometry of logically AND controlled artificial photosynthetic system based on modified peptide nucleic acid (used HF 6-31G)

References :

1. M.J.Frisch, G. W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M. W. Gill, B. Johnson, W. Chen, M.W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople,Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh PA, USA (2000).